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Revisting the synthesis and applications of graphene oxide†

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Over the last two decades, graphene and its derivatives have attracted lots of attention because of its peculiar properties. In this review, a general introduction, history, synthesis and applications of graphene and graphene oxide have been provided. However, we have emphasized the different synthetic routes adopted for synthesizing graphene oxide (GO). Till now, several methods have been developed for the synthesis of graphene oxide such as micro-mechanical, exfoliation of pyrolytic graphite; CVD, epitaxial growth, etc. Here in this review paper, we have discussed four methods for the synthesis of graphene oxide, namely Brodie's method, Staudenmaier method, Hofmann method, and Hummer's method. Mostly, graphene oxide has been synthesized by graphite oxidation. Because of excellent properties, chemical functionalization and ease of production graphene and its derivatives have made their way to various applications. Few of the applications of graphene oxide like in electronic devices, energy storage devices, biosensors, coating technology, and graphene oxide composites and paper-like materials have also been incorporated into this paper.

Keywords: Graphite oxide, graphene oxide, graphene.

1. Introduction

Graphene is a name given to the flat monolayer of carbon atoms tightly packed into two-dimensional (2D) honeycomb lattice and is a basic building block for graphitic materials of all other dimensionalities. Graphene is the origin compound of some carbon allotropes, along with graphite, carbon nanotubes and fullerenes[1,2]. In Graphite, each carbon is sp^2 hybridized and the atomic layers of carbon are stacked over each other by van der Waal's interactions and its one-atom-thick layer of carbon is known as "Graphene". For the first time in 1994, Boehm[3] introduced the name Graphene. Graphene is known as a wonder material because of its amazing properties. Owing to the special two-dimensional structure, graphene possessed many unique properties different than other carbon materials, including a high specific surface area[4], extraordinary electronic properties, and electron transport capabilities[5], and high thermal conductivity[6]. Graphene grasp a great compact for use in energy storage materials[7,8], drug delivery systems[9,10], biosensors[11,12], polymercomposites[13,14], liquid crystal devices[15], supercapacitors[16–18], nanoelectronics[19–21] and other areas, whereas, Graphene oxide shows potential in various industrial applications like capacitors, sensors, photovoltaic cells, and transparent electrodes[22,23].

In graphite, perpendicularly aligned graphene layers prove it to be a poor conductor due to weak van der Waals forces of attraction between them whereas shows good conductivity within the plane (i.e. a direction parallel to graphene layers) due to in-plane metallic character[24]. Graphene is an expensive material which is difficult to synthesis and various cost-effective methods have been tried to synthesize derivatives of Graphene.

Graphene oxide is one such material formed by the strong oxidation of Graphite in acidic medium due to its ability to disperse in water and other solvents. On one side, Graphene can be synthesized by the methods like micro-mechanical exfoliation of pyrolytic graphite[25], Chemical Vapour Deposition (CVD)[26,27] and epitaxial growth[28–30]. On the other side, Staudenmaier, Hofmann, Brodie, and Hummers method have been used for the synthesis of graphene oxide[31]. Various functional groups like epoxy, carbonyl, hydroxyl, and carboxyl are attached to graphene oxide. The oxygen-containing functional groups like epoxy and hydroxyl are present on the upper and lower surface of graphene layers or a plane and other

†**Review.**

functional groups like carbonyl and carboxyl on the edges of sheets of graphene oxide[32–34]. To synthesis graphene, firstly we need to synthesis graphite oxide via different oxidative chemical processes which is then converted into single layer (graphene oxide). Further, graphene is fabricated on reduction of graphene oxide using reduction processes like chemical, thermal or microwave reduction processes.

1.1. History

Graphene has attracted a lot of attention in past decade in the field of science and technology. Before knowing its history, few terms like graphite, graphite oxide, graphene, graphene oxide, and intercalation graphite compounds are needed to be discussed.

Earlier graphene oxide was synthesized by the oxidation of graphite using H_2SO_4 and HNO_3. In 1859, Brodie[35] a British scientist modified the Schafhaeutl method by introducing oxidants like $KClO_3$ along with H_2SO_4 and HNO_3. He observed the intercalation of graphite and chemical oxidation of the graphite forming graphene oxide surface. Now the graphene is being surrounded by oxygen atoms in its oxidized form. This results to the decrease in inter-planar forces and hence these graphene oxide layers can be easily exfoliated by the application of thermal, ultrasonic and other energetic conditions. It's important to prepare graphene oxide for the synthesis of graphene. In 1858, Hummer and Offman[36] proposed different methods for graphene oxide oxidation by reacting to the graphite with potassium permanganate ($KMnO_4$) and concentrated H_2SO_4. Modified Hummer's method is the most commonly used method for the synthesis of graphene oxide. In 1962, Boehm[37] was the first who reported about graphene-like structures. They had synthesized graphene or reduced graphene oxide by dispersing graphene oxide in reducing alkaline solution. They concluded that this method produces flakes of reduced graphene oxide having low oxygen and hydrogen content. The "Graphite oxide soot" is derived from the combustion of graphene oxide at high temperature. Through electron microscopy, it was revealed that this soot contains thin carbon multilayer hexagonal sheets (nearly 12.6 Å equal to 2–3 layers) known as graphene nanoplatelets.

Meantime, graphite and its intercalated products were gaining attention because of their astonishing properties like they opened up the route for ion storage. Hence, Boehm[3] was the first one to introduce the name graphene (an intercalated compound of graphite) in 1994. In 1970, Blakely[38] found that graphene can be produced from graphite by isolating carbon on a nickel surface. At high temperature, carbon layers get dissolved and get separated into single or multilayers on the metal surface. Till 1995, several terms like graphite layers, carbon layers or carbon sheets were used for graphene. After that IUPAC decided one definition for graphene i.e. "A single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi-infinite size".

Earlier it was known to scientists that a 2-D crystal of carbon atoms i.e. graphene exist but no one worked on extracting it from graphite. Until 2004, two researchers' Prof. Andre Geim and Prof. Kostya Novoselov isolated, discovered, and characterized graphene at the University of Manchester. The method they had used for the extraction of graphene layers was the Scotch tape method. For this work, they won the Nobel Prize in Physics in 2010 "for groundbreaking experiments regarding the 2-D material graphene".

2. Synthesis of graphene oxide

From the past years, several theoretical and experimental efforts had been made to understand the structure of graphite oxide. Graphene oxide structure is studied through the analysis of graphite oxide itself. Graphene oxide is known as the most common precursor of graphene. Graphene oxide is graphite that has been intercalated and oxidized. Few methods were used for the synthesis of graphite oxide so that graphene oxide can be synthesized from it in bulk amount; the methods are reported here in this review. For the first time in 1840, Schafhaeutl synthesized graphene oxide by intercalation of graphite sheets and then it was synthesized by Brodie in 1859[39]. Methods used for the synthesis of graphene oxide are Brodie method[40], Staudenmaier method[41], Hofmann method[42] and Hummer's method[43]. In all these methods, graphite powder is chemically reacted with acids (HCl, H_2SO_4, and HNO_3) and then graphite layers were intercalated by compound of alkali metals ($KClO_3$, $KMnO_4$, $NaNO_3$, etc.) that helps in the further break down of graphitic layers into smaller pieces.

2.1. Brodie's method

In 1859, B.C. Brodie developed this method; in this method oxidation of graphite was done in the presence of potassium chlorate ($KClO_3$) and fuming nitric acid (HNO_3)

that results in the formation of a new compound consisting of C, H, and O showing an increased mass of graphite flakes. The interfacial angles of crystal lattice isolated from the above material were difficult to measure via reflective goniometry. Further oxidative treatments result in increased oxygen content. The ratio determined for C: H: O percentage composition was 61.04: 1.85: 37.11. According to his elemental analysis, $C_{11}H_4O_5$ was the molecular formula for his final product. He discovered that this synthesized material was dispersible in pure water and in basic media but not in acidic medium. So, he termed the resulted material as graphic acid. After heating the material, the C: H: O composition changed to 80.13: 0.58: 19.29 due to loss incarbonic acid and carbonic oxide. Though this method had some drawbacks such as release of toxic gases during the reaction and time consuming still several researchers had used this method for the synthesis of graphene oxide[44–46].

2.2. Staudenmaier method

Staudenmaier improvised Brodie's work in 1898 by using an excess of oxidizing agent ($KClO_3$) and concentrated H_2SO_4 for increasing the acidity of the mixture as an extra additives[42]. The graphite oxide formed from this process was in highly oxidized form and in turn, simplified the process for the synthesis of graphene oxide.

The drawbacks of this method are: (i) again like Brodie's method of synthesis, it is time-consuming and hazardous, and (ii) $KClO_3$ added in this process lasted for a week, chlorine released during this process has to be removed by an inert gas. This method has also been used by researchers and other groups for the production of graphite oxide[47–52]. Hofmann further modified this method.

2.3. Hofmann method

In 1937, Hofmann[42] came up with a new method for the oxidation of graphite to synthesize graphite oxide. He used concentrated HNO_3 acid, concentrated H_2SO_4 acid and $KClO_3$ in this process. $KClO_3$ being a strong oxidizing agent acts as an *in situ* source of dioxygen that oxidizes graphite powder in the presence of acid solution. Many research groups used this method for the synthesis of graphene oxide for numerous applications[53,54].

2.4. Hummer's method

In 1958, Hummer and Offman showed an alternative approach to fabricate graphite oxide on oxidizing graphite powder by reacting it with the mixture of concentrated H_2SO_4, $KMnO_4$, and $NaNO_3$[43].

Graphene oxide can be easily dissolved in polar solvents due to presence of hydroxyl (-OH), epoxide, and carboxyl (-COOH) functional groups. However, it has been noticed that in the synthesis of graphite oxide stirring time duration, and temperature variance affects oxygen-containing functional group composition.

3. Applications of graphene oxide (GO)

In several electronic devices, GO has been used as a starting material as one of the components. An example of one such device is Field-effect transistor (FET)[55,56], being

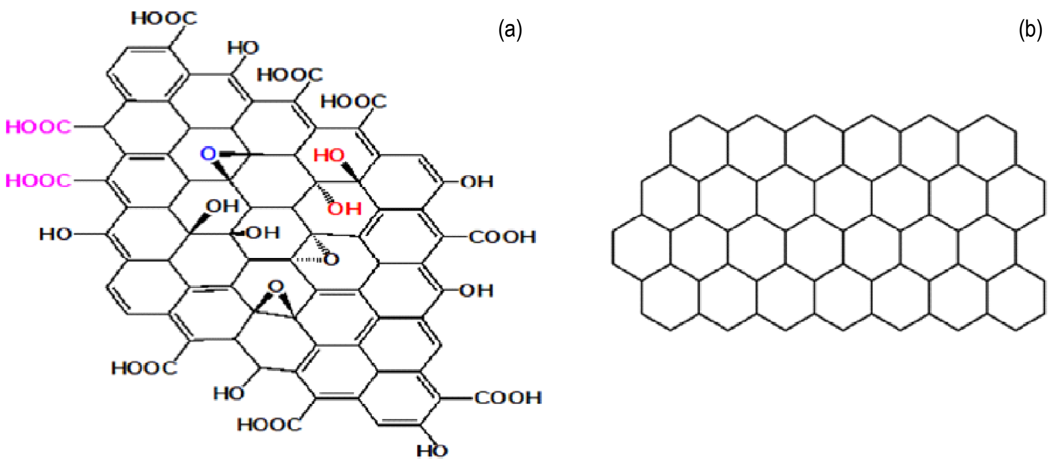

Fig. 1. Structure of (a) Graphene oxide and (b) Graphene respectively.

used as chemical sensors[57,58], and as biosensors for detecting hormonal catecholamine molecules[59], DNA[60], and avidin[61]. Liu[62] studied the electrochemical glucose sensor where GO was functionalized with glucose oxidase after being deposited on an electrode. GO can be used in several major areas, one of them is in the transparent conductive film production after being deposited on any substrate. Such films or coatings can be used in solar cells, chemical sensors, flexible electronics, and touch screen devices. Cai[60], Becerril[63], and Matyba[64] used GO in the light-emitting diodes (LEDs) and solar cell devices as a transparent electrode. Saha[65] and Li[66] also used GO transparent electrodes as a whole transport layer in LEDs and Polymer solar cells.

3.1. Energy storage devices

Because of the high surface area of GO, these are considered to be used as electrode materials in double-layer capacitors and batteries as well as in solar cells, and fuel cells[67–72]. In comparison to other graphene materials, GO can be synthesized easily and therefore it can soon be used for energy-related objectives. In the future, due to hydrogen storage capacity of GO, it will prove to be useful in hybrid cars as storage of hydrogen fuel. GO nanocomposites can be used in lithium-ion batteries as high-capacity energy storage material.

3.2. Biosensors

Being a fluorescent material GO can be used for biosensing applications like early disease detection, and for finding cure for cancer, and detection of biologically relevant molecules. GO has been successfully used for the detection of DNA, and proteins in fluorescent-based biosensors along with better diagnostics promise for HIV.

3.3. Coating technology

Multilayer GO films are impermeable (under dry conditions), and optically transparent. On exposure to water or water vapor, only certain sized molecules are allowed to cross the film. Millions of randomly stacked flakes of GO converted to GO films leaving nano-sized capillaries in between them. These nano-sized capillaries are reduced by chemical reduction method along with hydro-iodic acid that creates film of rGO, completely impermeable to liquids, gases, and strong chemicals (>100 nm thick). Covering of copper plates or glasswares were conducted by using such graphene "paint" could be used as corrosive acid containers. Graphene-coated plastic films can also be used in medical packaging to improve their shelf life.

3.4. Composites and paper-like materials

GO gets easily mixed with many polymers and form nanocomposites that greatly enhances original polymer properties, like tensile strength, thermal stability, elastic modulus, and electrical conductivity. GO flakes tend to attach in solid form and forms thin, extremely stable paper-like structures which can be stretched, folded, and wrinkled. And such kind of free-standing GO films is considered for other applications like hydrogen storage, nano filtration membranes, and ion conductors.

3.5. Water purification

GO serves as good material for water purification as water simply "pops throughthe very small holes in GO and leaves the salt behind." Permeation of water through the membrane was attributed to swelling of GO structures, which enables a water penetration path between individual GO layers. GO could also be used as cation exchange membrane KCl, HCl, $CaCl_2$, $MgCl_2$, and $BaCl_2$ solutions. GO film is 500-times thinner than the best filter on the market and ~1000-times stronger than steel, but its permeability is ~100-times greater than the best competitive membrane on the market.

4. Conclusions

In this review, various synthesis processes and applications of GO have been discussed. The paper addresses the continued developments and challenges of GO and their increased use in various applications. Light has also been focused on history, synthesis, application, and oxidation of graphene. GO applications have shown great progress in past research and are still expanding day by day. In GO, various functional groups like carbonyl, carbonate, epoxy, hydroxyl, and certain defects and disorders created during oxidation of graphite oxide are proved to be efficient and have shown broad scope in various researches and are still showing wonders in research projects and applications. Till now exploring GO are surprising, exciting, new, and inspiring. However, there are enormous challenges and need to be overcome. A large number of research papers have been published till date and various projects have been done, they all have proved GO to be promising and proving it as a wonder material which is still surprising the researchers giving them hopes and possibilities day by day.

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