

A Review on Synthesis and Utilization of Graphene

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Abstract- The one-layer thick entity, graphene, associates solitary physico-chemical characteristics, extending from its mechanical attitude to electrical and even thermal dynamism. Hence, correctly graphene is looked upon as a miracle material by the world. In this review paper, in contemplation of the latest progress of semiconducting graphene, some important synthesis and its emerging intelligent applications are highlighted. Emphasis is put on the methods of production including exfoliation techniques, Chemical Vapour Deposition on various metals, different ways of reduction of graphene oxide. Employment of graphene in multifarious devices like solar cell, supercapacitor, thermoelectric devices, fuel cell and even its bioapplications are featured.

Keywords- Graphene, Allotrope

I. INTRODUCTION

Graphene, proclaimed as a wonder material, is a single two-dimensional layer of carbon atoms bound in a hexagonal lattice structure. This wonder material has been studied broadly in the past several years, but was only isolated for the first time in 2004. It was first isolated by Andre Geim and Konstantin Novoselov at the University of Manchester, England in the year 2004. [8]The method adopted was micromechanical cleavage / Scotch tape, where they pulled out graphene layers from graphite and transferred them on SiO₂ layer. Graphene is specified to be serious substitute to outpace many conventional materials in numerous applications and would enable many disruptive innovations in potentially existing markets. It has appraised far-reaching attention in scientific society for its surprising electrical, mechanical, optical and thermal properties.[3]

An allotrope of carbon with a single layer of sp² - bonded carbon atoms, which are densely packed to get a 2-dimensional honeycomb lattice of graphene, comprising of 6-membered rings. The sheets have interplanar spacing of 0.34 nm. Each carbon atom has 1s and 3p orbitals, of which 1s and 2 of the 2p orbitals (ps and py) from the structure hybridizes to form a strong covalent sp² C-C bond. The pz orbital overlaps the neighbouring C-atom to get a filled π orbital (valence) and vacant π* orbital (conduction). Graphene's structure serves as the primary shape of other crucial allotropes, it can be stacked to form 3D graphite, coiled to form 1D nanotube and even wrapped to get 0D fullerenes. [3]

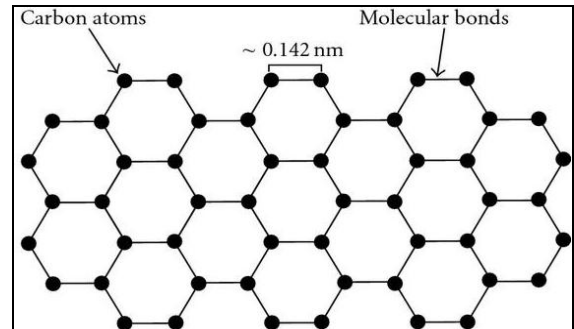


Fig 1: Schematic of the structure of a graphene sheet (reprinted from [3]; copyright 2010, Hindawi Publishing Corporation, Journal of Nanotechnology).

Graphene is extraordinary strong (the strongest material ever known or tested) , supernaturally light, almost completely transparent, extremely light and electrically super-conductive. Carbon is a non-metal, so one would expect graphene to behave the same too. As a matter of fact, it behaves much more like a metal, but the way it conducts is very unique, which led some scientist to describe it as a semimetal or a semiconductor. The flat, hexagonal lattice of graphene bid relatively little resistance to electrons, carrying electricity better than even conductors like Copper. Even though graphene possess various exceptional characteristics, but because of the absence of a substantial bandgap, its use in semiconducting electronic devices is restricted, where appropriate bandgap is a necessity. Breaking the adjacent, in-place lattice symmetry is the better way to open up a bandgap. This could be achieved by various structural and chemical transformations. If for instance, an atom substitutes the carbon atom, it may result in the creation of gap between π and π* bands, the method can be described as doping. Other methods to enhance the surface properties of graphene include chemical functionalization and controlled reduction, which introduces remarkable prospects for the development of graphene-based semiconducting materials with unique electronic properties. [15]

II. METHODS OF PREPARATION

1. Mechanical exfoliation

Commonly known as Scotch-tape method, first developed by Novoselov and Geim in 2004. Peeling off graphene, from a graphite crystal is done using an adhesive tape. After peeling, there are multiple layers of graphene, which need to be peeled off repeatedly to obtain few-layers of graphene.



Fig 2: Monolayer graphene produced by mechanical exfoliation. Large sample with length of 1mm on Si/SiO₂ (reprinted from [6]; copyright 2012, International Scholarly Research Network ISRN Condensed Matter Physics).

These thin flakes are then released in a solvent acetone and later captured on the surface of Si/SiO₂ wafer to obtain single layer graphene flakes with dimensions of upto 10 μm. [2]

Liquid-Phase exfoliation

A solvent is used to exfoliate graphene in liquid-phase exfoliation by ultrasonication. Basically used solvents include acetic acid, sulphuric acid, and hydrogen peroxide and even organic solvents N,N-dimethylformamide, o-dichloro benzene. The role of solvent would be to minimize the interfacial tension (γ) between liquid and graphene flakes. However, it was able to separate the sheets by density gradient ultracentrifugation, which enables the isolation of graphene from few layers graphene. [2]

2. Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a process of depositing gaseous reactants onto a substrate. CVD works by combining gas molecules in a reaction chamber at high temperature.[3]

For the synthesis of graphene, a transition metal catalyst is used as the substrate, and then a gaseous source of carbon is mixed with another solid, liquid or gas containing heteroatom in the furnace. Ni, Cu, Pd are typically used as the substrate with methane as precursor gas. On cooling the substrate, solubility of carbon on substrate decreases and carbon precipitates to give mono to multilayer graphene sheets.[2]

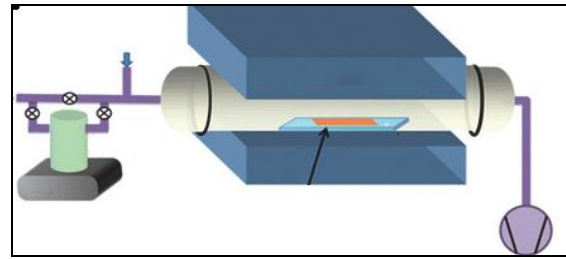


Fig 3: CVD doping experimental setup (reprinted from [3]; copyright Hindawi Publishing Corporation, 2010, Journal of Nanomaterials.

Graphene grown on Nickel

Ni films deposited on SiO₂ / Si are annealed in H₂ flow at 900-1000 °C to get a smooth surface.[16] The Ni films are then exposed to a mixture of H₂ and CH₄ to make C-atoms dissolve into Ni film forming a solid solution, then the substrate is cooled in Argon environment, which is important to get rid of O₂ contamination.[2,16] On cooling, the carbon atoms diffuse from Ni-C solid solution and precipitates onto the Ni surface to form graphene films. Even if H₂ is used in the cooling gas, it accelerates cooling and helps to remove loosely bound C from the surface. [16]

Graphene grown on Palladium

Graphene films can also be grown on another metal surface like Pd by CVD approach. The Pd layer taken was 2 mm thick and 10× 3 mm surface area. The carbon-doped metal sample was heated by electron-back bombardment. The temperature can be monitored by a pyrometer. Then, the Pd surface is cleaned by Ar ion at 900 °C to dissolve all remaining surface carbon into the bulk.

Graphene grown on Copper

Ruoff's group at University of Texas reported high-quality monolayer graphene grown on polycrystalline Cu foils with relative high carrier mobility. On a 25 μm thick foil, H₂ gas was ejected and heated to 1025 °C and pressurized. Consequently, CH₄ was added to the flow, the tube was allowed to cool. After growth, the samples were exposed to air in lab, supervised and characterized. The techniques used were optical microscopy, Raman spectroscopy, Auger-e-spectroscopy (AES), STM. By using various transfer methods, the grown graphene films can be migrated to another substrate like SiO₂/ Si or glass substrate. Graphene films relocated on glass substrate were found optically uniform. The uniformity and quality were assessed by Raman spectroscopy. [12]

3. Reduction of Graphene oxide

The most appealing property of graphene oxide(GO) is that it can be partly reduced to graphene-like sheets by eliminating the O-containing groups with the recovery of a conjugated structure.[10] On reduction, graphene oxide undergoes the modulation from insulator to semiconductor and then to semimetal with large scale reduction. Chemical reduction can be performed at room temperature or by moderate heating.[3] Numerous reduction methods have been proposed for the synthesis of graphene, which are discussed.

Chemical reduction

The use of chemical hydrazine to prepare graphene was first reported by Stankovich. [10] Hydrazine and its derivatives, eg: hydrazine hydrate and dimethylhydrazine can be incorporated to reduce GO by further adding the liquid reagents to a GO aqueous dispersion, resulting in the accumulation of graphene-based nanosheets, which on drying gives electrically conductive black powder.

Even demonstration of NaBH_4 as a reductant in this process is effective, but results show it is kinetically slow. Fernandez-Merino came out with GO reduced by ascorbic acid/Vitamin C, giving graphene of appreciable conductivity, as equivalent as those produced by hydrazine. Also ascorbic acid is non-toxic as compared to hydrazine. Pei and Moon proposed HI as reducing agent for GO, where GO can be used in any form of colloid, powder or film in a gas or liquid environment. Results have proved HI has a better reducing effect than hydrazine. [10]

Thermal reduction

Thermal reduction of GO can be achieved by heat treatment in the presence of inert atmosphere. The increased temperature makes the oxygen containing functional groups on carbon-plane disintegrate into gases creating huge pressure between the stacked layers. at decreased temperature, a transportation gas was observed for reduced GO. Proper regulation in the heat treatment is able to achieve bandgap in GO and induce semiconducting properties. [7,10]

Microwave and Photoreduction

Heating of GO powders in a commercial microwave oven for about 1 min leads to the synthesis of reduced GO. [10] Uniformity and pace are the primary advantage of microwave irradiation over conventional heating methods.

Photoreduction of GO films is accomplished by using single flash irradiation from a xenon lamp. After the procedure, GO films expand 10 times, on account of rapid degassing with electrical conductivity of 10 S/cm. Zhang revealed a femtosecond laser irradiation of GO. The laser beam has higher power density than a xenon lamp flash and the heated area is much localised in the range of 10^{-1} to $10^1 \mu\text{m}$. [4,10]

Photo catalyst reduction

Kamat and co-workers have showed reduction of GO with the help of TiO_2 nanoparticles, suspensions in ethanol, which is a UV- assisted photo catalyst method. TiO_2 is most preferably used photo catalyst because of its relatively high activity, nontoxicity, chemical stability and is cost impressive. M. Choobtashani and O. Akhavan reported the photo catalyst reduction of GO nanosheets deposited on tungsten oxide, the thin films were irradiated by UV lamp for 24 h at room temperature.[10,16]

Electrochemical reduction

Electrochemical approach can be undertaken by 2 different routes. First route involves direct electrochemical reduction of GO in suspension onto the substrate electrode. and the second route include pre-deposition of GO onto the substrate electrode before electrochemical reduction. [17]

4. Epitaxial growth

Epitaxial growth is a substrate-based method, wherein isolated monolayer of graphene is developed on a single-crystal Silicon carbide (SiC) by the method of vacuum graphitization. The carbon-enriched surface experience reorganization and graphitization resulting in graphene islands over the entire surface of SiC wafers by the particular control of sublimation. The dimensions of graphite layers were controlled mainly by annealing temperature and time. [2,9] A complementary approach was applied to other metallic substrate like Ruthenium to get graphene layers. Yannopoulos reported a process using CO_2 laser as the heating step for a single -step growth process of large consistent graphene film on SiC, the method is cost effective as it do not involve any kind of pretreatment or high vacuum process.[2] The growth mechanism need to be further investigated , which will lead to enhanced electronic properties of graphene. [2, 9]

III. UTILIZATIONS OF GRAPHENE

Graphene has a apparently boundless potential for improving existing products as well as inspiring new ones. Numerous research has been carried regarding the application of graphene, some of which are discussed.

1. Solar cells

Solar cells require materials that are conductive and allow light to pass through, thus benefiting from graphene's superb conductivity and transparency. Atomic doping may confer graphene with n-type or p-type semiconducting properties. Studies reveal boron -doped graphene being used as p-type electrode in solar cells with interfacing boron-doped graphene with n-type Si. Functionalised graphene-based materials can also be used in solar cells. Recently, research on graphene- based solar cells led to the creation of hybrid perovskite-graphene solar cells, which showed good stability upon exposure to sunlight. Still research on solar cells with graphene in its structure is still at laboratory scale. [2, 3, 18]

2. Thermoelectric devices

Thermoelectric devices bring about the conversion between thermal and electrical energy. Thermoelectric properties of graphene have attracted increased attention as it can convert heat to electricity and vice-versa. A high thermopower value of $80 \mu\text{V/K}$ was noted for graphene. Reduction of thermal conductivity of graphene nano-ribbons can be done by introducing pores in them , which ultimately enhances their thermoelectric performance.[3]

3. Supercapacitor

Supercapacitors are regarded as the most proposing electrochemical energy storage devices, having prospects to supplement or eventually replace the batteries for energy storage applications. Ruoff instigated the chemically modified graphene as electrode material. It was found that the specific capacitances of 135 and 99 Fg^{-1} could be obtained in aqueous and organic electrolytes respectively. [19]

Metal oxides can be used as composites with graphene. Hydrothermally reduced graphene-MnO₂ composites exhibit a specific capacitance value of 211.5 Fg⁻¹. Literature study shows that heteroatom doped graphene (B,N and P doped graphene) bid increased stability, conductivity and better chemical reactivity as compared to pristine graphene. [3] A specific capacitance of 101.9 uF cm⁻¹ was noted by a solid electrochemical capacitor made of fiber-based rGO coated on Au wires. [19]

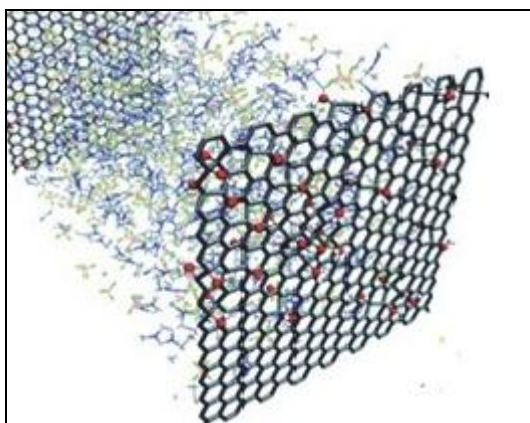


Fig 4: Illustration of a supercapacitor model which consists of GO electrodes (ten percent oxidation)(reprinted from [3]; copyright Hindawi Publishing Corporation 2016, Journal of Nanomaterials.

4. Fuel cells

Graphene based membrane could be used as proton-conducting membranes, which are of importance to the functioning of fuel cells by conducting protons through it. Exorbitant noble metals such as Pt,Au,Ru and their alloys are known cathode materials for oxygen-reduction reaction(ORR).[20] Doping of graphene with heteroatom may enhance the catalytic activity of graphene in ORR. Thus, graphene doped with heteroatom have possibility of being exercised in fuel cells to alter the high-priced Pt catalysts. [3] N,B,S can be used to dope graphene. Greater stability was reported from N-doped graphene nanosheets in contrast to regular Pt/C catalysts.[2] Even use of Ni and Co salts in addition to graphene to obtain nanocomposite based graphene for fuel cells was reported. The prepared cobalt oxide-graphene nanocomposite has been used flourishingly for methanol oxidation as fuel cell utilization. [20]

Enhanced research in this developing area may prove to be beneficial for fuel cell technology with metal-free graphene based ORR technology.

5. Bioapplication

Apart from wide range of applications in electronics and other field, graphene has also fascinating properties to be used in bio-medical applications.

Graphene-derivative / oligonucleotide nanocomplex is used as a foundation for DNA recognition and scrutiny, detection of heavy metals, pathogens. Even GO magnetic nanoparticles can be used for complementing MRI. Due to the aromatic character of graphene and its potential to keep

various ionic components above its basal plane, graphene nanomaterials can become exemplary biosensors in near future. Inhibition effect of bacterial growth on the surfaces of graphene-based nanocomposites, because of the synergistic effect and oxidative stress induced by membrane disruption is also reported. Few reports have been published on the in vivo test of graphene nanomaterials as delivery carriers and therapeutic applications via phototherapy.

Exploration of the outcome of graphene on the immune system, nervous system, reproductive system is yet to be done systematically. [21]

IV. CONCLUSIONS AND PERSPECTIVE

Review of the synthesis and various applications is been done in this paper. As discussed, the anomalous mechanical and electrical properties of graphene make it an upcoming material for application in several energy storage and other devices. In spite of tremendous progress made in the field of semiconducting graphene materials, still many difficulties are associated with their preparation and usage. Further efforts for synthesis of graphene and achieving desired surface functionalisation or preparation into desired shapes, will generate novel structures with many applications.

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