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A brief review on graphene and its Applications

A K MAHAPATRA and K L MOHANTA*

Department of Physics, Faculty of Engineering and Technology (ITER),
Siksha 'O' Anusandhan Deemed to be University, Bhubaneswar-751030, Odisha, India,
**Corresponding author,Email:kamalmohanta@soa.ac.in*

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Abstract : Occasional attempts to decipher the mystery of graphene can be seen back from mid 20th century. There has been a certain bombardment in the research around the globe, in the field material science in the year of 2004 , when Prof. Andre K Geim and Prof. Kstoya Novoselov who belong to the University of the Manchester, discovered as well as isolated a single atomic thin film of carbon for the first time by scotch tape procedure which is also known as micro mechanical cleavage or mechanical exfoliation technique. The two body team collected the Nobel prize in physics in the year 2010 in recognition of their break-through. Materials based upon graphene and its composites have a noteworthy applications in electronics, biomedical aids, actuators, membranes, flexible wearable sensors. This review article summarizes various scientific published data and research papers so as to present a comprehensive analysis of the state of art.

Keywords: Graphene , flat bandas , multiphased band structures, quantum hall effect, physiochemical properties

1. Introduction

Graphene is an allotropic form of single layered Carbon atoms in 2-D hexagonal lattice with sp^2 bonds, in which the vertex is formed by one atom.

Graphene being wonder material has got many superlatives to its name. It is the strongest as well as thinnest material ever, The charge carriers show massive mobility by the virtue of smallest effective mass which is approximately equal to zero and traverse about a few micrometer long distances with no scattering at room temperature. Graphene can withstand current density of 6 order higher than that of copper. A record thermal conductivity is noted as well as the rigidness, which is not possible in gases. Again it reconciles the two conflicting characteristics i.e. the brittleness and ductility. In order to grasp the relativistic quantum phenomena Dirac-like equations are proposed upon the transport of electron through graphene which in turn becomes an astounding experiment in itself. This review paper helps to concrete the idea over graphene research, applications and attempts to seek those paths on which the field is likely to develop. Lots of papers do appear every day. If the bibliometric prediction [1], is to be trusted, the amount of literatures on graphene are going to increase at higher rates over the upcoming years. More specialized papers on graphene include quantum Hall effect, Raman properties, physiochemical properties and epitaxial growth on SiC[2]. The availability of large bundles of literatures on graphene research become so high that, now a systematic update is necessary to organize every single little achievement in a synchronous way. Its highest surface area compare to all other known materials of its class enhances the interaction between polymer materials and sheets[3]. Graphene based composite materials are the materials of scientist interest today for their structural factor .The role of reinforcing agent better suits to graphene in composite material and increase performance and properties[4]. We also add all the environmental application and toxicity so that one can master the act of safe handling.

Monolayer Graphene

New and efficient synthetic techniques are the base for the new discovery . For instance laser vaporization is the reason for the discovery of C_{60}. Carbon nanotubes are produced in discharged evaporation method[5]. Isolation of single layered graphite by scotch tape method not only shows that this planet is a big reservoir of mysterious materials but also begans a new era in material science and technology since. These properties can only be observed, if there is an availability of sufficient synthetic technique. Till now many sophisticated techniques are in the use to produce graphene. Though mechanical exfoliation is the first option for extraction of monolayer graphene, the low yield made it handicap. The two new methods like liquid exfoliation and reduction of graphene oxide were used currently for the bulk preparation the graphene. However these methods have numerous defects and their own limitations. Not upto the mark yields are obtained even in these two methods. The chemical vapor deposition method had come into rescue for developing the synthesis process. But its maintenance like high temperature, gas phase, catalytic metal substrate had made it too expensive as compared to its output. Therefore a search is still on for the efficient extraction of monolayer graphene economically at a large scale level. In this case pyrolytic conversion of organic molecules may be a suitable pathway for mass production . For an instance 3D highly oriented pyrolytic graphite (HOPG) was first obtained by the pyrolysis of poluycrylonitrile in presnce of montmoillonite. Using copper as substrate, pyrolytic preparation of mono layer graphene is done from a (poly methyl methacrylate) thin film . But the quality and the production cost become an obstacle for the process. The update is required regarding technological innovation and development of pyrolytic conversion method for mono layer graphene preparation analogy. The improved direct pyrolytic conversion approach is in progress for the gram scale preparation of high quantity monolayer graphene from sodium carboxylate in presence of $Na_2Co_{3.}$

Bilayer Graphene

As the name suggests it is a version , where two individual layers of graphene are merged together . Current study upon hybrid twisted 2 D Vanderwaal materials shows an interest due to its exotic quantum phases that arises from strong correlation of electrons. It has also shown some possibilities of superconductivity which is rather unconventional within twisted bilayer graphene . This enhances the hope for new fields of understanding the complexities of the system. In tBG, the variation is seen in spatial arrangements of interlayer coupling which changes intrinsic Dirac cone band structures of graphene in such a way that the dispersion of band hardly appears at the magic twisted angles[6]. The condition $U/w \leq 1$is possible to achieve which shows significant rule for Coulomb repulsion(U), where ‘w’ is the band width and it is sufficiently narrow for these low energy band. In order to explain the nature of superconducting phases, a good amount of literature has been found recently on the Coulomb interaction driven broken symmetry phases and superconductivity in tBG flat bands similar to observations of Coulomb interaction driven correlated phases. Superconductivity has been noticed in ABC three layered Graphene on hexagonal Boron Nitride(HBN) where flattening of the low energy bands is carried out by the presence of vertical electric field that introduces a band gap at the primary dirac point of a chiral two dimensional electron gas or twisted gapped Dirac Material[7]. Valley cern Number could be a right option to define the low energy flat bands[8] and a spontaneous quantum hall phase will rise when the coulomb interaction come into act during band degeneracy lifting[9]. Several types of multi-layered graphene material found in two dimensional material combinations with respect to appropriate intrinsic electronic structures of each layer and inter layer coupling scheme[10]. This work concerned with flat band width phase diagram of twisted B.G/ B.G systems.

The two major quantities for the assessment are the interlayer coupling strength and interlayer potential difference in between the layers of the resulting band width of low energy flat bands. As per the expectation, the smaller parabolic band Dispersion slopes at low energy in a B.G can favor the construction of flat bands upon interlayer hybridization.

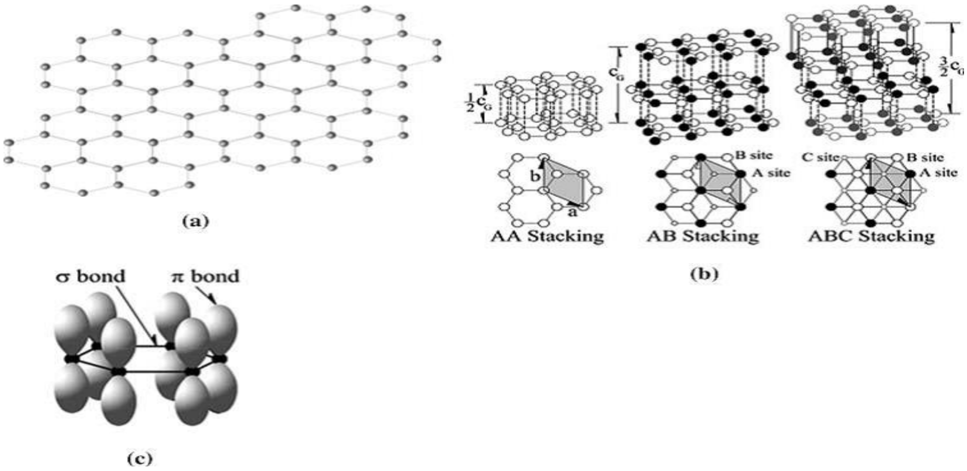

Fig.. 1: (a) A single two-dimensional hexagonal graphene structure sheet of carbon atoms, (b)Three most common structures and

Stacking sequences of graphene and (c) σ bonds and the π orbitals perpendicular to the plane presented in schematic diagram

2. Methods of Synthesis

Till now graphene hasn't been used in its pure (pristine) form due to its limited yield. So many graphene-derivatives such as GO, hGO , and frGO have become more commonly available for their similar properties to that of the graphene. They too possess their own disadvantage such as heteroatomic irregularities, impurities, structural defects. So it is deceptive to denote those materials act like Graphene. There are several number of modes of preparation of graphene which are not that effective for large scale production.

i. Mechanical Method of micro exfoliation

The procedure is also known as top to down approach. It is the method which is employed to extract graphene for the first time successfully. Pyrographic graphite is used to carry out this method effectively by peeling layer by layer with help of a scotch tape . Novoselov[3] used this technique to extract the single layer graphene from the graphite, though the yielding is low still considered as the parent method. In other words we can have monolayer of graphene oxide in large quantities by the two successive processes i.e. chemical oxidation followed by exfoliation method involved ultra-sonication. Hummer and Offman have some significant contribution towards building a systematic method to produce graphene oxide in 1958 which is still in use[11].

ii. ***Method of chemical exfoliation***

A mixture of mineral acid (sulphuric acid and nitric acid) is prepared where the graphite is allowed to immerse that results oxidation and cleaving process. Penetration of acid inside the graphite gives rise to cleaving, which results in the formation of alternating layers of graphene and intercalate. With passage of time the thickness reduces to below 4-5 layers ,again a low yield.

Brbrodie [12] is the first person to prepare graphene oxide successfully. Staudenmair again broadens the idea of Brodie by changing the acidity of Graphite and HNO_3 mixture .It is also famous for prolonged duration for the whole process to be completed and the product in the reaction i.e. chlorine dioxide gas from nitric acid and potassium chlorate are also used in the formation of Carbon[13] tubes and fullerenes[14]. The Oxidation Process results addition of oxygen functional Group and evolution of toxic nitrogen dioxide(N_2O_4) which is a bit of misfortune. Therefore these are not handy methods for production.

As a successor Hummer developed an oxidation process to produce Graphene Oxide[15] by taking the help of concentrated sulphuric acid (H_2SO_4), potassium permanganate($KMNO_4$) and sodium nitrate($NaNO_3$).The process had taken around two hours of duration under 45̊ Celsius with mid string . The material formed higher degree of oxidation than that of the Staudmaier's method. A pre-treatment is also required to improve the oxidation in Hummer's method which has come in to notice while Kvtyukhova[16] reported in her paper. It involves adding graphite to the mixture of concentrated H_2SO_4 , potassium sulphate (K_2SO_8) and phosphorus pent-oxide (P_2O_5) at 80 degree Celsius for a long duration . The pre-oxidised graphite was then washed, filtered and again washed in deionised water followed by air drying that produce better GO.

3. Chemical Vapor Deposition (CVD)

For the production of large scale level of graphene the CVD technique is found to be promising. Roll to roll transferring process was done at first and SLG (single layerd Graphene) were Synthesized and FLG (few layer graphene) were synthesized using Ni foil (30μm in thickness, Ni laco Corp) as the substrate. The major differentiating aspect between carbon nano tube(CNTs) and graphene production applying this method is involvement of catalyst for the decomposition of nanofeed into an atomic carbon. Because for the preparation of CNTs the catalytic nano particles are important, where as the graphene synthesis utilises foil. Due to the dimensional effect the shape of CNTs is decided by shape and size of the catalyst nanoparticle and for graphene, the sheet is responsible for preparation and growth. Though a few scientists working on CVD have reported the formation of single metallic crystals.

Reduction of graphite oxide[17] results partially reverting, to its primary stage improving its properties especially in electrical conductivity[18]. This process plays crucial role in the synthesis of graphene oxide. Other methods like plasma enhanced chemical vapor deposition synthesis (PECVD), Liquid phase exfoliation, Epitaxial growth on silicon carbide substrate are some honorable mentions which have fundamental relationship with CVD process. While laser based chemical vapor Deposition, Laser growth directly upon Quartz and Silica substrate are some methods which are very less in use for its high cost factor.

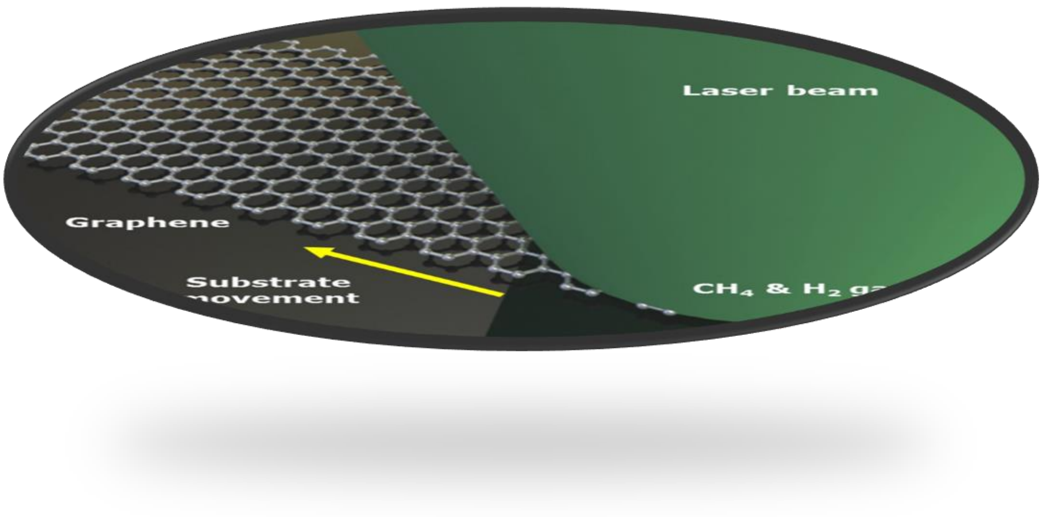

Fig-2. Schematic diagram representing the laser induced CVD process

Properties

Graphene exhibits so many properties which makes it superior in various aspects from its contemporary elements. So we shall now be going to discuss the properties of the material.

1. Mechanical Properties

The first systematic study of elastic properties of graphene at its pristine form has been done by lee et. al[19]. with demonstration of strength. It is experimentally shown that brittleness and non elastic behavior. Min et al.[20] have measured that shear strength, fracture strain and shear modulus, of this substance as a new function of temperature and chirality of the same by molecular stimulation and reported that fracture stress by molecular stimulation and reported that fracture stress 97.45GPa and strength of shear 60 GPa are highly flattened graphene sheet. Another paper by Ovidko et al[21] have shown different mechanical properties of graphene. On the other basis of experimental conclusions, purest graphene possesses Young's modulus of 1TPa along with an intrinsic strength 130GPa, that is exactly equals to computer simulation. Frank at al.[22] have given a report which tells these mechanical properties were inconsistent but still it has some really promising properties for the further research and application in composite field. on the other hand graphene does not have any kind of defects like voids, gain beads and dislocations that may cause fractures in an arm chair and zig zag pattern around the limits. So the understanding new types of defects and former defects at fundamental level needed to be done in order to research ideas that will positively impact its application. Suk et al.[23] developed a method named as finite element method for the analysis of mechanical properties of graphene odxides by the help of atomic microscope (AFM) in contact mode. The young's modulus for the GO ultra thin films were found to be 207 ±23.4 GPa with thickness maintained at 0.7 nm. This was considered as an equivalent of pristine graphene oxide films. The pre-stressed graphene oxide films was obtained to be at 39.7768 MPa, which was noted to be 1. Order of magnitude lower than that of mechanically exfoliated graphene. So, in short, we can say that we awere using the combination of AEM and FEM mapping for the finding of elastic modulus and pre stress in case of graphene oxide.

2. Electrical Properties

While we are considering the electrical properties, the first and foremost term comes into our mind is electrical conductivity. And already significant amount of literatures is found on graphene and polymer composites on incorporating or improving electrical conductivity. Some of the common observations are techniques such as melt bending, casting solutions, insitu processing and chemical vapor deposition (for sensor application) now in use for electrical conductivity but with low order i.e. 1x $10^{-8}cm^{-1}$. Conductivity can further be increased by adding Polymer of second order as Filler[24]. Now the obstacle is, in graphene particle dispersion in a polymer matrix. There exists a restriction on the addition of graphene at certain level. It gives development of agglomerates. This results in poor conductivity. Prior work based upon simpler composite blend are more complex blends or hybridization to jump over the limitation of adding graphene material above exact levels. This leads to a new path for addition of different substances to the graphene structure and forming composition that is beyond expectation and materials of desire qualities.

The mechanical properties and thermal stability of the composites have an eye catching improvements. Due to versatile nature of graphene, it reinforced the polymer nanocomposite points to its future application in packing detectors and agile devices[25].

3. Thermal properties:

The atomic structure of a material determines the conductivity, while the thermal property defines its characteristics. When we arrange them in nanometer scale, the thermal properties get changed from the theoretical values Graphene possesses infinitely large intrinsic thermal conductivity[26]. Thermal conductivity (K) of the material is directly related to the heat flux per unit area . Q'' (e.g. in w /m^2) and inversely proportional to temperature gradient . $Q'' = -\nabla T$ .The heat flowing from high to low temperature is negatively indicated in this relation . Specific heat can be related to thermal conductivity directly by, $K=\sum Cv\lambda$ where v and λ are suitably averaged phonon group velocity and mean velocity and mean free path, respectively[27].Thermal conductivity K as a function of temperature for suspended graphene is shown in the figure below.

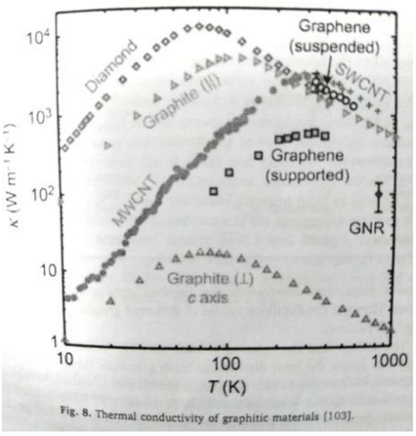

Fig. 3: Thermal conductivity of graphene Materials

Induction of a steep anisotropy of its thermal properties in the plane inside and that at the outside is the result of 2D nature of Graphene. The inner plane direction confinement shows an excellent thermal conductivity (>1000$wm^{-1}k^{-1}$) and the outer plane is constrained by weak Vander waal interaction for the thermal coupling. So all depend upon the interface. And it doesn't disappoint. All the interactions, atomic defects and the phonon dispersion have taken place here to determines the thermal conductivity of graphene. Simulation outcome is improved in such a way that thermal properties are tunable now a days, considering the graphene composites and 3D Architecture.

4. Optical Properties

Polyamides are the reduced graphene Nano composites and they are again used for LED thermal magnet by titanate coupling agent. This increases the load transfer across the polymer and graphene, thermal conductivity as well. High thermal dissipation along with better durability made LED lamp possible. A simple layer of grapheme is found to have thermal conductivity 5300 w/mk. The thermal conductivity is going to increase upto a level of 53% in the current work.

4.0 Limitations:

From the advent of the research on this topic, the safety and the toxicity remain as the most important topic of discussion. Although there are several traits of graphene that enables it to be used as biomedicine, the deep study in this topic suggests that graphene based materials (GBMs) show hydrophobic forms. They accrue on the cell membrane surfaces and are highly toxic. Therefore the toxic effects of the GBMs are still unaddressed[28].

Application

1. Sensors

It is seen that the characteristics of the graphene have made it extremely sensitive to environment. These properties enables it foe their sensor application which examines the the DNA sequencing. Careful monitoring of velocity of adjacent liquid to strain gauges with either electrical or optical statistics helps in counting applications. Another advantage of using crystalline form of graphene is its 20 % ductility which increases the working range of the such sensor substantially.

2 Battery

The renewable and clean nature of Li-ion batteries are made them vital part of hand held devices. Graphite is considered as anode material in Li-ion battery as it has good value for specific capacity and reversibility. However the ever developing modern scientific field world wants more energy density, durability, higher capacity and stability from all the carbonceous material, graphene based anode. Graphene is expected to be best substitute for Li-ion batteries as Graphene has an edge over Li-ion regarding its conductivity, high surface area and chemical tolerance etc. The authors (122,141,146-147 et al.) have made graphene nano sheets embeded with SNO_2 nano particles by dispersing reduced nano graphene sheets in the ethylene glycol and regathering in presence of SNO_2 nano particles. The SNO_2 -Graphene has shown 810 mAh/g reversible heat capacity and its cycling performance is drastically enhanced that from bare SNO_2 nano particle. Wang et Al. have shown self assembled TiO_2-graphene hybrid nano structure and thereby increase the rate of performance of electrochemical active materials. They have used anionic sulphate surfactants to assist the stabilization of graphene in aqueous solution and facilitated self assembly of insitu grown nano crystalline TiO_2-Graphene . The capacity is 87mAh/g for TiO_2-graphene which is sufficiently large from normal TiO_2 (which is about 35mAh/g). The specific capacity of anatase TiO_2- functionalized graphene at 30^o C is higher as 96mAh/g comparing 25mAh/g of controlled anatase TiO_2.

3. Membrane

Microscopic membrane separation technolgy now becomes over hot topic in these recent years. Graphene membrane possesses a unique gift of nanopores and feasibility to be functionalized. By virtue of this property, graphene becomes ideal for the higher selectiveness, permeate flux and improved stability through manipulation of the shape and size of those pores. For further higher value of permeability and to achieve an increased output leading to enhanced membrane performance[29], the widen thickness has to be reduced.

Sin et al. have under gone the study of the diffusing ions (Li^+, Na^+, K^+, Cl, Br) through` graphene monolayer with functionalized nanopores with a diameter of 5Å. Molecular dynamics simulation observation, suggested that, the passage of cataion favored by the pore dismissed by negatively charged F-N, whereas anaion passing is eased by H-terminated nanopores with positive charges. Their study verified the viability of nanoporous graphene mono layer as ion separation membrane for desalination and energy storage applications.

The hydrogen terminated nanopores had better water sensitivity and hydroxyl functionalized graphene pores had double the water flux which accredited to their hydrophilic character and ability to substitute water molecule in the hydration shells of ions .The water permeability through the nanoporous graphene is appraised to be 66 Lcm^2.

The salt rejection is 99%in conventional reverse osmosis, this value is higher by 2-3 orders of magnitude. These values demonstrate the potential of using functionalized nanoporous graphene sheets as high permeability desalination.

All the other applications of the graphene are now on rudimentary stage such as Graphene in Piezoelectric Materials, Graphene in Self-Healing Materials and Graphene in Shape Memory Materials.

3. Conclusion

The research on graphene is the reason for the considerable enrichment of our comprehension and also the applications of 2-D crystal atoms. The mixture of unachieved chemical and physical traits, showing enormous strength, Electrical(as well as thermal)conductivity, and mechanical ductility (and malleability) , have lured scientists for further digging.

To study in detail of its actual potential in building and modifying different devices in pure and applied scientific fields. And technological developments of industrial sector lie a hope upon it ,ranging from material science, chemical engineering, physics, even in molecular biology making the spectrum very large. To be particular, we can stick to a field electrical and electronic domain. The mechanical properties, thermo electricity, memory shap, self healing activation, are enhancing day by day using different material. But graphene could be most eligible candidate to serve the purpose. Now the hurdles to be crossed are the same old ones. Graphene always become cumbersome substance, while we think of its mass production within a reasonable amount of investment of money since a proper method hasn't been discovered yet which satisfied our need with its efficiency. The second important point is utilization of graphene in various field and how to connect different fields on the basis of graphene application for interdisciplinary connection. So that we can use the advance properties of graphene in a more controlled manner. That also develop our fundamental understanding of the origin and states of developments through which different branches have been arisen in science and technology. Last but certainly not the least, we have to think pragmatically about the fabrication of multifunctional systems that retaliates multiple stimuli. In space, we need strong and durable object which can withstand large amount of stress and strain keeping its highly sensitive thermal, electrical, mechanical properties intact. Graphene is seen as a suitable substitute for designing different space craft in the near future when all its properties are examined thoroughly by repeated experiments. So that we can built strong, sensitive, cost effective, reproducible equipments for the space exploration or any other field . Smart application of the graphene and its functional groups is necessary for the evolution of human race .

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