Graphene: A New Generation Smart Material

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Abstract -The graphene is the two dimensional carbon sheets made from the ghiphite. The π-conjugation in graphene shows extraordinary thermal, mechanical and electrical properties. It is the materials of new generation in the scope of scientific, industrial interest. In present review, the basics of graphene are highlighted with reference to its advantages with respect to other carbon based materials. The preparation of graphene at different methods is summarized with their comparative advantages. The emerging properties of the graphene are narrated with other materials of comparative behavior. The possible applications of graphene and related materials are established with reference to their structural properties.

INTRODUCTION

Graphene is the first two dimensional crystalline sheet material having sp^2-hybrized carbon to be extracted (Fig-1). It is the parent of all graphite form and is an interesting topic of research in the last three to four years [1]. It can be stacked to form 3D graphite, rolled to form ID nanotubes and wrapped to form 0D fullerenes. The long-range π-conjugation in graphene shows extraordinary thermal, mechanical and electrical properties. In graphene all the carbon atoms are covalently bonded by sp^2-hybridization in a hexagonal honeycomb lattice with inter-atomic distance of about 0.14nm [2]. It is distinctly different from carbon nanotubes (CNTs) and fullerenes and exhibits unique and interesting properties which fascinate the scientist for both theoretical and experimental research. Three different types of graphenes are reported. They are single – layer graphene (SG), Bilayer graphene (BG) and Few-layer graphene (FG, number of layers<10). The single layer graphene and by layer graphene were obtained by micro-mechanical cleavage [3]. Up-to-date various effective techniques have been developed for producing graphene micromechanical exfoliation [4], epitaxial growth [5] and chemical vapour deposition [6] can produce graphene with high quality for fundamental studies and potential applications in nanoelectronics [7-8].

To understand graphene research it is useful to consider graphene as simply the fewest layer limit of graphite. In this light the extraordinary property of the honeycomb carbon (graphite) are not nearly new [9]. Abundant and naturally occurring graphite has been known as mineral for nearly 500 years. Even in the middle age the layer morphology and weak dispersion forces between adjacent sheets were utilized to make instruments much in the same way that we use graphite in pencil today. After the discovery of fullerenes and nanotubes in 1990's the interest in all kinds of carbon materials were renewed. This promoted electron microscopists and scanning probe microscopists to investigate graphene experimentally [10-11].
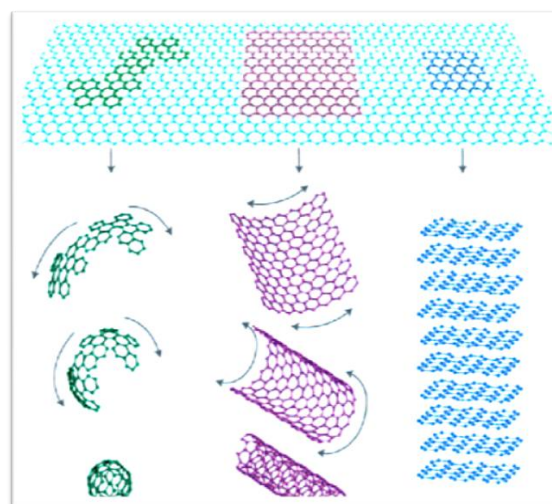

Figure1. Graphene: the parent of all graphitic forms. [1]

PREPARATION OF GRAPHENE

Single layer graphene has been generally prepared by micro-mechanical cleavage in which highly oriented pyrolytic graphite (HOPG) is used which is deposited on to a silicon substrate. Besides the mechanical cleavage of graphite, the other important methods employed to produce graphene samples are epitaxial growth on an insulator surface (SIC), Chemical vapor deposition (CVD) on the surface of single crystal of metals (i.e Ni)

are discharge of graphite under suitable conditions, use of interrelated graphite as the starting material, preparation of appropriate colloidal solution in selected solvents and reduction of graphene oxidized sheets[12]. A second focus of experiments on graphite has been substitutional doping replacement of carbon with other elements. This includes work by Bantlett and coworker at Berkley in which substitution of carbon with boron and nitrogen resulted in p- and n-type graphite respectively. In light of recent progress with CVD of single layer graphene, such work will almost certainly by revisited as an alternative to external gating for controlling electronic behavior in graphene based devices or perhaps to form graphene-only p-n junctions. Single and few layer graphene taken from freshly cleaved HOPG surfaces by scotch tape technique can be readily transferred on to a given substrate using electrostatic deposition [13].
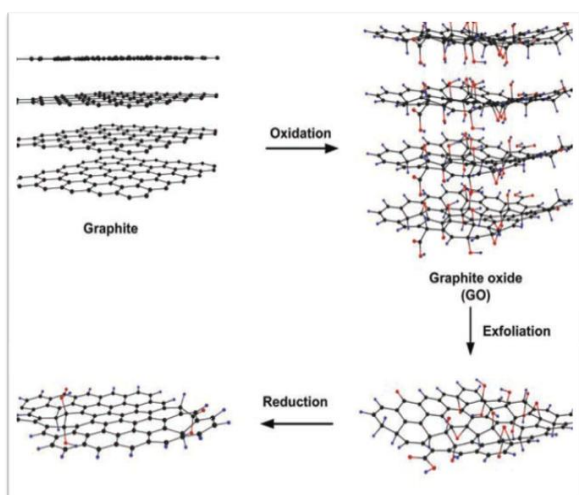

Figure 2. Preparation of chemically converted graphene (CCG) by reduction of graphene oxide(GO)[12]

While the mechanical cleavage of graphene crystal has afforded the study of properties of single –layer graphene or bi layer graphene, the method is not suitable for large scale synthesis of single layer graphene or of few layer graphene (FG). Two categories are distinguished for synthesis of large scale graphene [14]. Those which starts with graphite or a comparable starting material which does not contain oxygen as functional group and other are those which involve the exfoliation of graphite oxide (GO) followed by reduction (Figure 2). Graphene suspension can easily prepared by dispersing graphite in surfactant-water solution [15]. Highly conducting graphene sheets produced by the exfoliation re intercalation –expansion of graphite are readily suspended in organic solvents. The average size of the single-layer graphene sheet was 250 nm and the average tropographic height was 1 nm.

CHARACTERIZATION OF GRAPHENE

Graphene has been characterized by a variety of microscopic and other physical techniques including

Atomic force microscopy (AFM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), X-ray diffraction and Raman spectroscopy (Figure 3). It is interesting phenomenon that as single – layer graphene if placed on a silicon wafer with a 300nm thick layer of SiO_2 it becomes visible in an optical microscope (Fig 3 a and b)[10] while AFM directly gives the number of layers(fig 3c), STM(3d) and Tem (3 e) images useful in determining the morphology and structure of graphene. Raman spectroscopy has emerged to be an important tool for the characterization of graphene sample. Hence various aspects of graphene i.e its synthesis, structure, properties, fictionalization and polymer composite are easily studied.
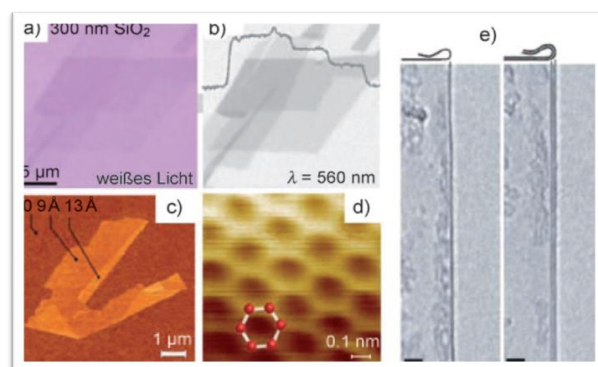

Figure 3. Microscopy images of graphene crystallites on 300 nm SiO2 imaged with a) white and b) green light. Figure (b) shows step-like changes in the contrast for single-, bi-and tri-layer graphenes. c) AFM image of single-layer graphene. The folded edge exhibits a relative height of approximately 4 indicating that it is single-layer. d) High resolution STM image. e) TEM images of folded edges of single- and bi-layer graphenes. ([29], [30], [31])

The dispersion behavuas of graphene oxide in different categories of organic solvents such as DMF, NMP, ethylene glycol, THF has been studied[16].The graphite oxide undergoes full exfoliation intro single-layer graphene oxide under sonication forming stable dispersion in all the above solvents.The sample prepared from dispersion in DMF yields sheets of uniform thickness (1.0-1.4nm) The single layer and bilayer graphene are obtained by using a substrate –free-atmospheric pressure microwave plasma reactor, where the liquid ethanol droplets are passed through an oxygen plasma. High quality graphene sheets of 1-3 layer has been synthesized on stainless steel substrates at $500^{\circ}C$ by microwave plasma chemical vapour deposition (CVD) in an atmosphere of 10% CH_4 and 90 % H_2 at a pressure of 30 torr and a flow rate of 200 SCCM (standard cubic centimeter per min).

Starting with graphite by employing chemical exfoliation, high quality graphene with a predetermined number of layers can be obtained [17]. With artificial graphite and natural flake graphite as starting materials nearly 80% of the final product has been found to be

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single-layer, single and double layer, double and triple layer and 4-10 layers graphene respectively.

The structure of graphene oxide is often described as graphene sheet bonded to oxygen atom in the form of carbonyl , hydroxyl or epoxy group (Fig-4). However the exact identity and distribution of oxide functional groups depend strongly on the extent of oxidation . The ratio of epoxy to hydroxyl group increases with increasing oxidation (theoretically).The structure of graphene oxide studied experimentally by chemical analysis, X-ray photoelectron spectroscopy (XPS), ^{13}C NMR spectrum etc [18]. The result of scanning transmission electron microscopy studies indicates that a graphene oxide film is with 1:5 O/e atomic ratio , about 40 % SP^3 C-O bonds. The high fraction of SP^3 C-O bonds induces structural distortion, suggesting that the atomic structure of graphene oxide sheets should resemble a mostly amorphous 2D sheet of carbon atoms with some of them bonded to oxygen, rather than ideal sheet of graphene with surface oxidation[19].
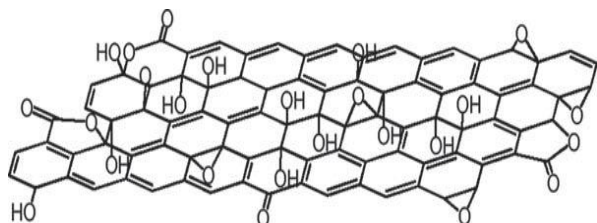

Figure 4: Structure of graphene oxide [34]

PROPERTIES OF GRAPHENE

Magnetism with carbon network material of SP^2 hybrid carbon atoms has been controversial, because of possible contamination with magnetic impurities. The edge in graphene ribbons plays a crucial role in determining the electronic structure. Paramagnetism as well as certain other magnetic switching phenomena has been observed in nanographite particles [20-22]. Hydrogenated nanographite is predicted to show spontaneous magnetism .The edge states as well as of adsorbed or intercalated species of nanographite and nanographite plays an important role in determining the magnetic behavior. Adsorption of different guest molecules on graphene gives rise to a reversible low spin /high spin magnetic switching phenomenon, which depends upon the nature of guest species.

Magnetic properties of few –layer graphene EG (prepared by exfoliation of graphite oxide) , DG (prepared by conversion of nanodiamond) and HG (prepared by evaporation of graphite) have been compared [23]. The temperature dependence of magnetic susceptibility for these three samples is compared in figure-3.The graphene show curie-Weiss behavior, similar to activated carbon –fiber with a negative Weiss temperature. Few-layers graphene and nanographite particles show semiconducting or insulating behavior with their resistance showing little change in the range of 100-300k .This resistivity

increases sharply below 50 K and decreases if graphene is heated to high temperature .Thus graphene nano-fibers prepared from exfoliation of graphite shows semi-conducting properties and hence predicted as half metallic. This behavior is realized in-plane if homogeneous electric field is applied across zig-zag edges [24]. Graphene sheets prepared from graphene oxide show well-behaved field affect transition (FET) properties. The charge carrier nobilities for electrons and hoes are in the order of 10 cm2V^{-1}S^{-1}. Although graphene is not superconducting by itself, when placed between super conducting electrodes it shows supper currents over a short distances. By using the non-equilibrium Green's function method, the transmission of super conductor –graphene-superconductor junction has been examined theoretically [25]. Palladium sheets sand witched between graphene sheets give rise to a superconducting transition around 3.6K and in this case superconducting observed in the palladium sheets.

The electrochemical properties of different graphenes (EG, CG, DG) have been investigated using redox reaction with potassium ferrocyanide)[26]. Chemically modified graphene sheets obtained by reduction of graphene oxide with hydrazone have also been investigated as electrode material in super capacities. Graphene nanosheets show a high lithium-storage capacity with values reaching 540 mAh g^{-1} which is interesting for lithium secondary battery. By incorporating CNTs and C60, this value can be extended upto 730 mAh g^{-1} and 740 mAh g^{-1} respectively.

APPLICATIONS OF GRAPHENE

Carbon nonmaterials have been widely used as substrates for immobilizing catalysts. This is mainly due to that they have unique structures and inherent properties including highest specific surface area, chemical and electrochemical inertness and easy surface modification etc. Like other newly discovered allotropes of carbon (fullerenes, CNTs), CCG and its composites have also been widely exfoliated as catalysts for chemical and electrochemical as well as photochemical reactions [27].

CCG and its composites have been widely applied to the field of electro catalysis due to their high specific surface area, high conductivities and unique graphitic basal plane structures. The multi layered graphene nanoflake (MGNF) and CCG films process have high electron mobility. Thus the use of CCGs as substrates of catalyst provides a new opportunity for designing and constructing the next generation catalysts. These composites can decrease the over potential of some important electrochemical reactions such as methanol oxidation and oxygen reduction for fuel cells [28]. For example CCG-Pt nanocluster or CCG/Pt-Pd composites exhibited enhanced catalytic activity and improved stability towards methanol oxidation comprising with Pt/Carbon black catalyst. Glassy carbon electrodes modified by a composite of PVP-Capped CCG and PEI-

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functionalized ionic liquid also have a high electrolytic-catalytic activity towards the reduction of oxygen or H_2O_2. CCG/GCL composite modified electrode exhibits highly improved conductivity and electro catalytic performance on oxygen reduction reaction.

Lithium-ion batteries (LIBs) have been widely used in portable electronics, which was first of all commercialized by Sony electronics in 1991. During last two decades many efforts have been devoted to improve the performance of traditional LIB focusing on its energy density, durability, cost and safety [29]. Generally graphite powder used as most commercial materials for anode but it has low specific capacity, Therefore a new anodic material graphene-based materials could be promising alternatives because of superior of electrical conductivity, high specific surface area, chemical tolerance and broad electrochemical windows. Now a days CCG composites with metal or metal oxides have been exfoliated as anodic material for LIBs.

CCG/noble metal composites can be employed as fuel cell electro catalysts in which CCG plays an important role in improving the charge transfer efficiencies and decreasing the over potential of electrochemical reactions [30]. A prototype hydrogen fuel cell by using carbon modified with CCG/Pt nanoparticles composites as the cathode and carbon black/Pt nanocomposites as anode. This fuel cell delivers a maximum power of 161 mW cm^{-2} which is much higher than that of an unsupported Platinum based fuel cell (96 mW cm^{-2}) which signifies that the immobilization Pt-catalyst on CCG is an effective approach for achieving fuel cells with improved performance.

Super capacitor represents another kind of energy storage devices with high power capacitances, long cycling lives, low maintenance cost and fast dynamics of charge propagation. Although the energy densities of super capacitors are much higher than those of conventional dielectric capacitors, still they are lower than those of batteries and fuel cells [31]. Hence a great deal of efforts have been devoted for manufacturing advanced electrode materials for super conductors. CCG-based composites have been proven to excellent material for this purpose. Among this CCG/PANi has received a great attention and was synthesized by chemical oxidative polymerization of aniline in the presence of CCG sheets. CCG/CB composites were also used as electrode materials for super capacitors.

CCG composites have been widely used as electrode materials for solar cells. The CCG composites with PSS doped PEDOT (CCG/PEDOT: PSS) on indium tin oxide (ITO) substrate by spin coating at room temperature. The ITO sheets coated with thin CCG/PEDOT: PSS films were applied as the counter electrodes of dye-sensitized solar cell (DSSCs). The cell with a CCG/PEDOT: PSS counter electrodes showed energy conversion efficiency 4.5 % much higher than that of the

cell with PEDOT: PSS counter electrode (2.3%) [32-33]. Now a days CCG/TiO$_2$ composites was applied the photoanode of DSSCs, which increases the light collection efficiency and charge transport rate and decreases the charge recombination of the cells.

Graphene-based composites materials have been applied in various biotechnologies such as drug delivery, cellular imaging and antibacterial materials. CCG/Ag composites with a homogeneous distribution of silver nanoparticles (5-10 nm in size) on CCG sheets have been applied to be as an anti bacterial material [34]. It was found that the bacterial cultures (Coli-bacillus, Staphylococcus aurecus and canidia albicans) were almost completely destroyed when the concentration of CCG/Ag was 0.05 mg/ml.

REFERENCES

[1] K. Geim, K. S. Novoselov, Nat. Mater. 2007, 6, 183.

[2] D.Li, R. B. Kaner, Science 2008, 320, 1170.

[3] K. S. Novoselov, Z. Jiang, Y. Zhang, S. V. Morozov, H. L. Stormer, U. Zeitler, J. C. Maan, G. S. Boebinger, P. Kim, A. K. Geim, Science 2007, 315, 1379.

[4] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science 2004, 306, 666.

[5] P. W. Sutter, J.-I. Flege, E. A. Sutter, Nat. Mater. 2008, 7, 406.

[6] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B. H. Hong, Nature 2009, 457, 706.

[7] S. Park, R. S. Ruoff, Nat. Nanotechnol. 2009, 4, 217.

[8] C.-Y. Su, Y. Xu, W. Zhang, J. Zhao, A. Liu, X. Tang, C.-H. Tsai, Y. Huang, L.-J. Li, ACS Nano 2010, 4, 5285.

[9] Kam N.W.S, Liu. Z, Dai H.J.J, J. Am. Chem. Soc. 2005, 127, 12492.

[10] S. Roddaro, P. Pingue, V. Piazza, V. Pellegrini, F. Beltram, Nano Lett. 2007, 7, 2707.

[11] T. T. Baby, S. S. J. Aravind, T. Arockiadoss, R. B. Rakhi, S. Ramaprabhu, Sens. Actuator B-Chem. 2010, 145, 71.

[12] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, J. M. Tour, ACS Nano 2010, 4, 4806.

[13] Gupta, G. Chen, P. Joshi, S. Tadigadapa, P. C. Eklund, Nano Lett. 2006, 6, 2667.

[14] E. Rollings, G.-H. Gweon, S. Y. Zhou, B. S. Mun, J. L. McChesney, B. S. Hussain, A. V.

Fedorov, P. N. First, W. A. de Heer, A. Lanzara, J. Phys. Chem. Solids 2006, 67, 2172.

[15] M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. T. McGovern, G. S. Duesberg, J. N. Coleman, J. Am. Chem. Soc. 2009, 131,3611.

[16] J. I. Paredes, S. Villar-Rodil, A. Martinez-Alonso, J. M. D. Tascon, Langmuir 2008, 24, 10560.

[17] Z. Wu, W. Ren, L. Gao, B. Liu, C. Jiang, H. Cheng, Carbon 2009, 47, 493.

[18] D. R. Dreyer , S. Park , C. W. Bielawski , R. S. Ruoff , Chem. Soc. Rev. 2010 , 39 , 228 .

[19] J. J. Mack, L. M. Viculis, A. A. R. Luoh, G. Yang, H. T. Hahn, F. K. Ko, R. B. Kaner, Adv. Mater. 2005, 17, 77.

[20] B. Das, K. E. Prasad, U. Ramamurty, C. N. R. Rao, Nanotechnology 2009, 20, 125705.

[21] A. Yu, P. Ramesh, M. E. Itkis, E. Bekyarova, R. C. Haddon, J. Phys. Chem. C 2007, 111, 7565.

[22] A. G. Cano-Marquez, F. J. Rodrguez-Macias, J. Campos-Delgado, C. G. Espinosa-Gonzalez, F. Tristan-Lopez, D. Ramrez- Gonzalez, D. A. Cullen, D. J. Smith, M. Terrones, Y. I. Vega-Cantu, Nano Lett. 2009, 9, 1527.

[23] H. S. S. R. Matte, K. S. Subrahmanyam, C. N. R. Rao, J. Phys. Chem. C 2009, 113, 9982.

[24] Y. W. Son, M. L. Cohen, S. G. Louie, Nature 2006, 444,347.

[25] Q. Liang, J. Dong, Nanotechnology 2008, 19, 355706.

[26] K. S. Subrahmanyam, S. R. C. Vivekchand, A. Govindaraj, C. N. R. Rao, J. Mater. Chem. 2008, 18, 1517

[27] N. Mohanty, V. Berry, Nano Lett. 2008, 8, 4469.

[28] Y. Cao , J. Feng , P. Wu , J. Mater. Chem. 2010, 20 , 5605 .

[29] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A. K. Geim, Proc. Natl. Acad. Sci. USA 2005, 102, 10451

[30] E. Stolyarova, R. K. Taeg, S. Ryu, J. Maultzsch, P. Kim, L. E. Brus, T. F. Heinz, M. S. Hybertsen, G.W. Flynn, Proc. Natl. Acad. Sci. USA 2007, 104, 9209.

[31] J. C. Meyer, C. Kisielowski, R. Erni, M. D. Rossell, M. F. Crommie, A. Zettl, Nano Lett. 2008, 8, 3582.

[32] X. Li,G. Zhang, X. Bai, X. Sun, X.Wang, E.Wang, H. Dai, Nat. Nanotechnol. 2008, 3, 538.

[33] Dato, V. Radmilovic, Z. Lee, J. Phillips, M. Frenklach, Nano Lett. 2008, 8, 2012.

[34] W. Gao , L. B. Alemany , L. Ci , P. M. Ajayan , Nat. Chem. 2009, 1, 403.

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