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REVIEW

A Brief Overview on Facile Synthesis and Challenging Properties of Graphene Nanocomposite: State-of-the-art

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This review work aims to present a brief study on the unique carbon allotrope graphene and its composite with nanoparticles. Graphene plays an important role in physics, chemistry, biotechnology, medical science, materials science and many more fields. The wide applications of graphene are based on its unique structure, exceptional physical properties, chemical tunability and dramatically electronic arrangement. The current world demands the energy conversion, digital technology and medical diagnoses in lower potential value, low cost, high reproducibility and high portability. Graphene nanocomposite possessing the above criteria and able to fulfill the worlds demand and become the most rising shining star in the horizon of material science research field. This review elaborates about historical background, structural feature, developed synthesis process, unique properties, characterizations and its different magnificent biosensor applications. In particular, the general overview study of its different fascinating properties such as mechanical, optical, magnetic, quantum hall effect, electronic transport properties and these makes graphene nanocomposite a rising tool for different biosensor applications.

Keywords: Graphene, Nanoparticles, Quantum Hall effect, Field-Effect devices, Biomedical.

INTRODUCTION

Graphene is a single layer of sp^2 hybridized carbon with p_z orbital out of plane of a two-dimensional sheet bonded together in a hexagonal lattice. Many layers of graphene stacked over to form a giant 3D substance called graphite. Graphene spined on to construct 1D carbon nanotubes (CNT) and wrapped to make 0D fullerenes [1]. Graphene shows high rich of unique properties like expanded theoretical specific surface area of value 2630 $m^2\ g^{-1}$, high electrical conductivity, high intrinsic mobility of value 200000 $cm^2\ v^{-1}\ s^{-1}$, high Young's modulus of value ~1.0 TPa, high mechanical strength, high thermal conductivity of value ~5000 $Wm^{-1}\ K^{-1}$, high impermeability to gases and optical transparency (~97.7%), enhancing transport phenomena such as the quantum hall effect and fracture strength (125 GPa) [2-4]. These specific properties of graphene make itself as a thrilling material in research field. The flexible membrane of graphene extends for functionalization modification of its carbon backbone [5,6].

Graphene and chemically modified graphene (CMG) play an unique precursor component material in application to many fields of energy storage materials, mechanical resonators, polymer composites, liquid crystal devices and many more. Graphene oxide offers the potential of very cost effective with large scale production than other carbon based materials [7-9]. Graphene posses zero band gap with nanoscopic overlap between conduction and valence band, charge potential carrier concentration of up to value 10-13 cm^{-2}, room temperature mobilities value of ~10 000 $cm^{-2}\ s^{-1}$ and most exceptional of an absorption of nearly 2.3% towards the visible light [10-13]. These properties of graphene caused for the Dirac fermions and as a massless relativistic particles [14,15]. The most favourable hydrophilic property of graphene forms stable colloidal suspensions of thin sheets in water [16,17]. Graphene with a scale of oxygen functional groups called graphene oxide, which furnishes it a better candidate in many fields [7]. Graphene oxide on fully dispersed in water shows light yellow colour where as graphite on dispersed with same solvent forms black colour.

As widely known, graphene shows flat hexagonal sheet with carbon-carbon bond length of 1.42 Å and having van der Waals force of attraction present between different layers of graphite of 3.35 Å [14]. In addition, it have the exfoliation energy (well depth) of 42.6 meV, compressibility value of 2.97 × 10^{-12} cm^2 $dyne^{-1}$ and phonon frequency value of 1.26 THz (E_{2g1} shear mode) [18,19]. The interlayer interactions energy is the energy each layer per area required to separate 3D graphite into individual 2D graphene sheets. At first, exfoliation method employed for the separation of different layers of graphite to form graphene. In general experiments focused on the insertion of chemical species between the different layers of graphite planes to separate multiple stacked sheets to a single sheet [20-24] (Fig. 1). Organic precursors used through bottom-up methods and attempts to catalyzed growth *in situ* on a subs-trate used for synthesis of graphene [25-28]. In meanwhile, the reduction methods are employed to form graphene from graphite by electrochemical [29,30], photochemical [31,32], thermal [33,34], laser irradiation [35-37], microwave reduction [38,39], reduction by different reducing agents [40,41] pro-cesses.

Graphene oxide undergoes chemical reduction by several green method agents and with some corrosive agents such as vitamin C [42], hydrazine [43], bovine serum albumin (BSA) [44] and sodium borohydride [45], *etc*. The graphene oxide (GO) sheets exfoliated from black coloured graphite are proposed by the Hummers method. This method is the most helpful by the reaction of graphite powder on reacting with oxidizing acids of concentrated sulphuric acid and potassium permanganate followed by hydrogen peroxide [46]. This oxidative methods caused the introduction of oxygen based functional groups of epoxides, alcohols and carboxylic acid groups, which been confirmed by IR and UV instrumental technique [47,48]. Graphene oxide on chemical reduction forms incomplete reduced graphene oxide (RGO). RGO possesses lower electric conductivity than the primitive graphene due to the incomplete reduction of different functional groups and the presence of numerous defects, which disrupt the sp^2 networks present in graphene [49]. Poor conductivity of RGO also caused in different new methods such as the non-oxidation liquid phase exfoliation of graphite [50], reinterpolation and ultrasonication of thermally most exfoliated of expandable graphite [51], one-step electrochemical exfoliation of graphite in ionic liquids [52], arc discharge method [53], even also direct chemical synthesis from non-graphitic substances to graphene [54] and the organic synthesis of graphene [55]. Each of these methods has its own drawbacks.

Besides the 2D graphene single sheet, different shape of graphene also been fabricated such as graphene quantum dots zero dimensional (0D), graphene nano meshes (GNMs) and also 1D graphene nano ribbons (GNRs) [56,57]. These different shaped graphene possesses outstanding optical, magnetic, quantum hall effect and also supreme electronic transport and field effect properties on combination with nanoparticles. This fact is caused since there is the variation in surface to volume ratio, geometry and size. All the credit properties of graphene nanocomposite is due to long range π-conjugation of electronic conjugation, being a single sheet with a fascinating hexagonal dramatically arrangement and acts as a best supported to nanoparticles composite. Currently, nanoparticles attracted more research interest caused by its fashionable properties with ample application in all magnificent research fields [46,47].

Since the electronic arrangement of nanoparticles correlate with the electronic arrangement of graphene, the combination of these two makes an excellent transducer for conductivity, catalytic and for many more applications [48,49]. Literatures survey by researchers observed the well dispersed of single layer of graphene sheet on metal surface acts as a boon for the material science. The observed electronic arrangement of metal nanoparticles on the surface not only enhances the conductivity, catalytically activity also caused for the different shaped

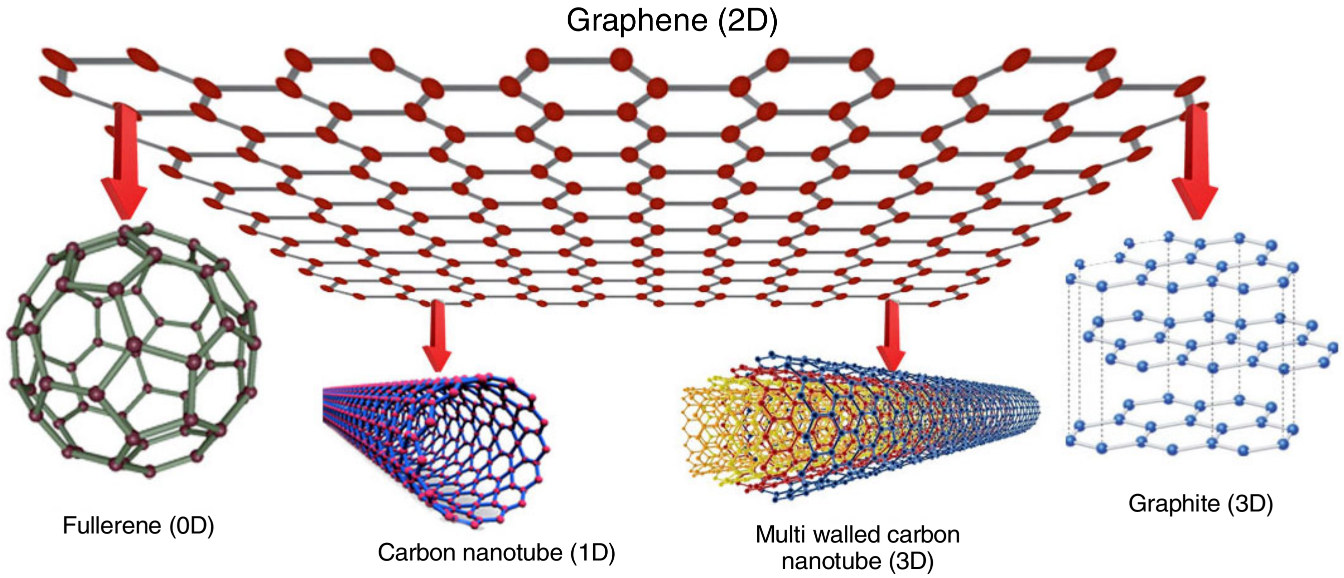

Fig. 1. Graphene: the basic component for graphite (3D), multi wall carbon nanotube (3D), carbon nanotube (1D) and fullerene (0D)

of nanoparticles [56-58]. These different shaped nanoparticles possess unique catalytic activity but having limited life span duration due to their decrease in electrochemically active surface area (ECAS). In order to enhance their storage and operational catalytic activities, nanoparticles are required to support with conductive materials. The fascinating electronic structured of deposited nanoparticles on conductive substrate graphene caused a very unique transducer for catalytic activity [47-50]. This has been the long research area interest in many branch of science and became a pre-eminent area in experiment lists. Graphene supported noble metal nanocomposite has grabbed the most attracting attention in the entire scientific community in the world due to for their extraordinary physiology combination properties and easy methods of preparation.

Brief reports on graphene: Graphite, the parent crystal of graphene was first discovered around in some time of 1556. In 1985, three chemists Kroto, Curl & Smalley discovered buck minster fullerene, zero-dimensional (0D) [1,11]. This molecule can act as a semiconductor, conductor and superconductor under specific conditions and got Nobel Prize in 1996. The carbon allotrope carbon nanotubes (CNTs) was drawn much attention to nearly three decades. This carbon allotrope based carbon nanotubes material first reported by Sumio Iijima in 1991. This is made up of multiple wall tubes nesting in a concentric fashion and then he discovered a single-wall carbon nanotubes in 1993 [59]. Discovery of CNT made a direction with a strong blow to research in materials science field and show a path for discover of different shaped carbon allotropes like carbon nano ribbon, carbon nano rod, *etc.*

Carbon nanotubes (CNTs) have high thermal conductivity, high electrical conductivity with elasticity and having much tensile strength with greater flexibility activity. That CNT can be bent materially without any disfigurement and having low thermal expansion coefficient that caused for good electron field emitters. It has wide application in different fields such as high field emission, greater thermal conductivity, long energy storage, unique conductive properties, conductive adhesive, biomedical applications, air and water filtration, *etc.* [60,61].

Before the discovery of graphene, graphite oxide was synthesized by chemical process in 1859 by Prof. Brodie by mixing graphite, nitric acid with potassium chlorate and heated for 4 h followed by washed and dried up. The yellow coloured substance had carbon:hydrogen:oxygen ratio of 61.04:1.85: 37.11. This carbon allotrope material can be spread over in pure based alkaline water still it failed in acidic media. Hence, called this graphic acid [62]. Later on potassium permanganate used as an oxidant on mixing with concentrated sulphuric acid and followed by sodium nitrate. This process was deployed to avoid the use of highly dangerous fuming nitric acid by Hummers & Offeman in 1958 [46,63]. These two oxidative agents caused for a more injected oxygenated functional groups to form of graphite oxide. The above discussed all methods caused for the evolution of toxic gases like NO_2, N_2O_4 and ClO_2. However, the Hummers method has been played a rising star in the horizon of graphene oxide synthesis. This carbon based material has shown exceptional properties, which show new directions to the phenomena in quantum physics. Since, it is practically good conductor with zero overlap semimetal and used for the producing transparent touch screens, ear phone, light panels, solar cells, *etc.*

Structural features of nanocomposite: More research interest in graphene nanocomposite is due to its peculiar structure than any other carbon allotropes. Carbon, oxygen, hydrogen with other peroxide atoms is the bonded atoms in graphene oxide whereas only carbon and hydrogen are present in graphene. Several structures have been put forwarded over the years by many researchers [64-67].

The atomic structure of graphene/graphene oxide was based on elemental compositions of C, H, O elements and X-ray diffraction (XRD) studies and their chemical reactivity studies. Hofmann & Holst suggested the first model of graphene oxide, which contained repeating units of 1,2-epoxides and other oxygen based functional groups on the entire basal planes of GO of sp^2 hybridized system. This model was contradiction to a new model proposed in 1946 by Ruess made up of sp^3 hybridized basal-planes. In 1969, Scholz & Boehm suggested that in GO, hydroxyl and ketone groups present and then Nakajima & Matsuo proposed proposed a new model, which was structurally related to a graphite intercalation compounds. In fact, on observing from recent reports, graphene oxide and graphene using high-resolution transmission electron microscopy (HRTEM) has suggested the presence of rupture in the position of functional grouped and from AFM study, it was revealed the more thickness of graphene oxide than graphene. Three valence orbitals of carbon atom used to form σ bonds and the unhybridized fourth one forms π bond with adjacent carbon atom. For these exceptional structural features, graphene brilliantly able to accomplished large number of chemical compounds on its hexagonal planner surface.

Graphene drives the motion of electrons in 2D platform and have zero-band gap trans semiconductor. This is due to the convergent of conduction and valence bands at the Dirac points. The Dirac points are considered as primary points of reason while concerning the electronic structural properties of graphene [38]. Daniel *et al.* [68] explained that the two sets of dirac points are labelled as k and k' give degeneracy of gv = 2 for graphene. Here k and k' are considered as two non-equivalent corners of the brillouin zone of graphene with 'M' considered in the midpoint between two adjacent k and k′ points and Γ in the zone centre. On detailed study, we looking closely to any dirac point and observed cone-like linear dispersion relation suggests the Fermi energy different from dirac energy in graphene. The charge carrier's operative mass in that area is zero, which can be well explained by Dirac equation for massless fermions. Electrons in graphene show the property of chirality. This chirality property causes current flow in graphene. The direction along which an electron wave function propagates is not independent, so the electrons in graphene are said to possess the property of chirality or handedness. The experiment set up for testing the chirality of graphene made up of four atom thick boron nitride placed between two sheets of graphene. When voltage applied to one of graphene sheet, it tunneled to other graphene sheet through the middle boron nitride sheet where it could be removed. This experiment stated that right-handed electrons tended to prefer to make it to right-handedness and *vice-versa* for the left-handed electrons. This property of graphene could cause for making new class of chirality electronic devices. The most exotic and counter intuitive of electronic structure in graphene is kelin paradox. The all aforesaid discussed structures causes for to seek more research attention to graphene. Traditional semiconductors such as silicon, germanium and gallium arsenide are opaque and have a terminable band gap while graphene possesses zero band gaps. In addition, Fermi level often falls within the band gap in traditional semiconductors whereas in graphene, the Fermi level is always within the conduction or valence band. Nanoparticles with different shape possess more catalytic activity. On graphene surface, different shape controlled nanoparticles can be synthesized with enhanced catalytic activity [46,47]. The TEM and SEM techniques revealed the different structures such as branched, porous, nano rods structure of nanoparticles with uniformly dispersed on graphene surface.

Synthesis of graphene and its nanocomposite: In recent years, production of graphene in low economic value with large scale amount has turned into more research interest. In the 70's and 80's decades, few layer of graphene was synthesized in the form of skinny and transition metals well dispersed on graphitic layers a single crystal platinum surface [69,70]. Till date various methods been developed for synthesis of graphene but none of can replace mechanical exfoliation method for large and high quality production but this process caused the long time consuming and limited scale of product production is possible. Herein, we discuss elaborately on various methods put forwarded for graphene synthesis such as mechanical exfoliation, chemical vapour deposition, chemical synthesis and some other techniques reported like unzipping nanotube, thermal decomposition of SiC, molecular beam deposition and microwave synthesis.

In mechanical exfoliation transverse stress effect is applied on the surface of the graphite material. Graphene layers stacked off together to form graphite, so graphite can be exfoliated to form graphene. At first, Ruoff *et al*. [71] established the foundation for mechanical exfoliation as well as outlined a wide variety of fundamental studies and applications published in 1999.

Then, Geim & Novoselov [1] developed mechanical exfoliation method to generate high quality of graphene up to 10 mm by using of HOPG (highly oriented pyrolitic graphite) as a precursor material. Then, HOPG was put forwarded to create 2-5 mm deep mosaic spread angle and these mosaic mesas were then compressed into a layer of photosensitive resist. That photo resist was baked and resist to splited of the HOPG. Scotch tape used repeatedly to peel off thin layer flakes of graphite from the mesas and subjected to encapsulated on the surface layer of a Si/SiO_2 wafer. The graphene flakes have high ballistic transport character at room temperature and mobilities value as high as 15,000 $cm^2 V^{-1} s^{-1}$. In certain research articles, they explained the exfoliation of crystal materials can be done by different techniques such as using electric field [72], ultrasonication [73], scotch tape [74-76] and also printing transfer technique [77], *etc.* Graphene synthesized through this techniques studied under optical microscopy, Raman spectroscopy and AFM technique applied to measure thickness layers of graphene flakes and measuring its crystalline quality. Optical microscopy, identified colour contrast of 300 nm thickness on top of Si wafers AFM technique resulted that flakes were randomly diffused on the substrate and a single layer flake films is matter of chance and Raman spectra shows number of layers present. Actually, through this method standard of the synthesized graphene have very high defect less with low difficulties but larger amounts of graphene can't be prepared and hence till now not been used in large area yet to scalable large area. It typically produces graphene 'particles' with lateral dimensions on the order of tens to hundreds of micrometers. However, the process is employed for this method is very limited to small sizes and cannot be measured for industrial production. Hence ability to synthesize large scale of graphene with current methods of industrial technology is much more important to eradicate most energy barriers for future applications.

The transition metals are widely used in chemical vapour deposition (CVD) method for the synthesis of graphene. This technique is the most promising technique for the safety, less defect and large-scaled synthesis of graphene films. The name chemical vapour deposition (CVD), itself determines depositing of gaseous (vapour) reactants onto a surface of substrate, where substrate generally coated in a very small amount, with slower speed, often described in microns of thickness per hour. This used of transition metals as substrates is the important part of this technique. The chemistry behind this technique mostly adopted since oxidizing acid solutions etched to the transition metals, graphene deposited on these materials can be easily transferred to other substrates. The experimental fact of this technique is the as grown graphene can be separated from transition metal surface to other substrate. The first single layer graphite developed on platinum metal surface in low energy electron diffraction (LEED) patterns in 1965 [70]. Recently, more practice goes on CVD method employed on two transition metals Cu and Ni. Nickel metal looks straight forward to form multilayer and non-uniform films whereas Cu metal forms uniform monolayer graphene [75]. Few-layer graphene sheets developed on polycrystalline Ni was first studies by Yu *et al.* [76. In this method, camphor used as the precursor material. Nickel foils were exposure in methane-argon-hydrogen environment at 1000 ºC with atmospheric pressure for 20 min. On cooling down the temperature, 3-4 typically layers of graphene being produced at cooling rate of 10 ºC/s [76]. Graphene layers were separated from Ni by coated the composite in silicone rubber covered with a glass slide followed by Ni etching in HNO_3. The same is followed for Cu transition metal foil, where Li *et al.* [77] heated Cu foil at 1000 ºC followed by exposure of methane 35 standard cubic centimetres per minute with pressure 500 mTorr. The analytical techniques (AFM, Raman spectroscopy and SEM) confirm the growth of graphene monolayer primarily with independent of growth time. Monolayer of graphene was grown on Cu foils (more than 95 %) by CVD of very low solubility of C in Cu. But in case of Ni, polycrystalline substrate graphene films forms gradually from monolayer to tens of layers because of more solubility of C in Ni. This opposed to suppress of C precipitation completely. Graphene growth on Cu surface covers 100 % area with monolayers and stops the process after completion. Due to high temperature the graphene usually strained on the copper foil. Other transition metals like Ni [78], Pd [79], Ru [80], Ir [81] and Cu [82] used vigorously for good quality graphene synthesis with large amount.

The electrical properties can't be measured for graphene formed through CVD method on the conductive metal substrates in *in situ* procedure. Recently, graphene's integrity and quality properties performance can be caused for wrinkle formation, high impurities, tearing in graphene and other structural defects in CVD method. Plasma-enhanced chemical vapour depositions (PECVD) are highly used for large-scale industrial production with catalyst free graphene fabrication [83]. This technique needed RF (AC frequency), microwave, inductive coupling and gas-phase precursor materials which are much costly with large set up of instruments.

Chemical method is one of the best and widely used among all for synthesis of graphene. By this method, polymer composites [84], energy storage materials [85] and transparent conductive electrodes [86] are used for large scale production of graphene with fewer defects. This method is a two step method in which at first to increase the inter space layer in graphite then exfoliates by quick sonication or exposure of light or heating. In this method, GO was first identified by Geim & Novoselov [1] and they credit Boehm and his co-workers for the experimental discovery of graphene in 1962 [87] and first synthesized by Hummer *et al*. [63] and Staudenmaier [88]. GO is useful for graphene synthesis because its individual layers are hydrophilic due to O and OH groups, which can be removed through sonication by increasing the inter space distance from 3.7 to 9.5 Å. Graphene oxide acts as a precursor for graphene synthesis. Graphene oxide prepared by the Hummer's method involved in the oxidation of graphite powder with strong oxidant such as sulphuric acid (conc.), potassium permanganate, sodium nitrate followed by addition of water. This process also known as wet chemical synthesis method [87]. The degree of strongly oxidation caused for introduction of oxygen groups like OH, CO, COOH and epoxide groups, which are covalently bonded to the graphene surface lattice. Here the oxidative group increase the inter space region and interrupts the sp^2 hybridized electron orbital. Reducing agents used for chemically reduction of graphene oxide to graphene such as phenyl hydrazine [89], hydroxylamine [90], glucose [91] ascorbic acid [92], hydroquinone [93], alkaline solutions [97], pyrrole [95], sodium borohydride [96], *etc*. In addition, some of the literature did electrochemical reduction of GO to graphene. Solvothermal method can also be used for synthesis of graphene in a large scale also [97]. Graphene can be produced up to sheets of 10 μm by smoothly detached by pyrolization of sodium ethoxide through sonication and this method is low-cost and needs easy decoration to produce high-purity graphene. But the quantity of graphene could not fulfill the industrial demand and the graphene shows large number of defects.

The graphene nano ribbon (GNR) undergoes chemically reduction by chemical reducing agents to form graphene sheets. At first side walls of multi walled carbon nanotube (MWCNT) were oxidized in H_2SO_4 and then treating with $KMnO_4$ followed by H_2O_2 in step by step process [98]. An electric field was applied to end of the MWCNT and started unwrapping and forming graphene nano-ribbon. This method produces defect free controlled and high quality GNR. The GNRs were conducting and have oxygen defect sites, which caused for electronically inferior to large scale graphene sheets. Some other methods to produce graphene such as electron beam irradiation of nano fibres [99], arc discharge of graphite [100], thermal fusion of PAHs [101], conversion of nano-diamond [102], plasma functionalization [103], radio frequency plasma [104], photoluminescence [105], molecular beam deposition [106], *etc*. All of these methods have their own limitations based on instrumental needs, materials cost, quality and quantity production of graphene. In typical synthesis of graphene nanocomposite, graphene oxide was mixed well by *in situ* and *ex situ* methods. In GO, oxygen functional groups present on their surfaces are caused for electrostatic interactions attachment of free metal ions and allows for the nucleation growth of noble metal nanoparticles like Pt, Au, Ag, Pd and also metal oxide nanoparticles such as Fe_3O_4, TiO_2, ZnO, *etc*. [107-111]. Different methods used to prepare graphene nanoparticles composites are basically summarized to reduction method [107,111], hydrothermal [112,113], electrochemical [114,115] and *ex situ* [116,117] methods. Consequently, in different synthesis methods graphene oxide acts as an intermediate between graphene and graphite [118].

Characterization and properties of graphene and its nanocomposite: Among different techniques at first optical microscope technique are mostly applicable for the quick detection from single-layer to few graphene sheets layers. This technique deeply depends on wavelength of light and thickness of SiO_2. Electronic topography of graphene can be measured by ultrahigh scanning tunnelling microscopy (UHSTM) technique. This technique method shows six carbons in a single layer of graphene are completely equivalent with equal intensity [119]. The TEM and AFM measured the number of layers focusing on the edges of the graphene single-layer swinged on a micro-fabricated scaffold. It was observed that the sample posses a good level of translucency, indicating a high degree of oxidation in GO and related to the stacking of some GO layers, as observed by other researchers. After reduction to graphene, long range crystalline order was observed in graphene even with the lack of a supporting substrate. Raman spectroscopy techniques used for measurement of defects and impurities intensity in graphene. In graphene three prominent bands at ~1580 cm^{-1}, ~2680 cm^{-1} and ~1350 cm^{-1} were observed for G band G′ band and the disorder-induced D band, respectively (G band corresponding to E_{2g} vibrational mode G′ band peak dealings to second-order two-phonon mode and D band peak response the defects in the graphene plane [68]. The G′ band peak shows two low and high shifts peaks components of intensities 1/4 and 1/2, respectively and a single sharp peak observed at lower shift for single layer graphene sheet. Again the ratios of G′ peak intensity are 4 times higher than that of the G peak. The synthesized nanocomposite of graphene nanoparticles was successfully characterized by different techniques. From high resolution TEM, SEM and EDX studies, revealed that nanoparticles were properly dispersed on surface of graphene with the existence of carbon and corresponding nanoparticles [46,47]. The kinetics of electron transfer can be measured by the cyclic voltammetry (CV), redox couple and electrochemical impedance spectroscopy (EIS) techniques and the synergetic effect of graphene and nanoparticles also. This enhanced in electron transfer rate of graphene nanocomposite can be significantly utilized for the electro catalytic applications [68,114].

Mechanical property is the most outstanding property of graphene. Graphene is the hardest materials even than diamond of same thickness and tensile strength found to be of 1 TPa [120]. The origin of graphene's robustness based on the σ bonds, which are connected in a solid honeycomb packed structure. The absence of dislocation of atomic bonds, ensure the strength of graphene sheet. Young's modulus and fracture strength are the primary mechanical properties of graphene. From atomic force microscopy (AFM) technique, it revealed that graphene layer exhibits a weak diffraction peak at 3.9 Å [121]. This diffraction peak varies upon annealing. Annealing at 500 ºC results sharpen diffraction peak near 3.4 Å. The reported value of Young's modulus, electrical conductivity and fracture strength of defect free graphene was 1.0 TPa, ~7200 S m^{-1} and 130 GPa, respectively [122]. These values depend on defect structure and quality of graphene layer. The graphene possesses young's modulus value of 0.25 TPa, which is very stretchable and light weight and can be stretched up to 25% than its original length. In addition weight of 1 m^2 of paper 100 times heavier than 0.77 mg of graphene m^2. This excellent mechanical property is the reason for used in optoelectronic applications.

Thinnest single layer graphene can absorb 2.5 % of light when passed through it [123]. The optically transmittance, T and reflection, R of light through single layer graphene can be derived using the Fresnel equations:

$$T = (1 + 0.5\pi\alpha)^{-2} \text{ and } R = 1/4\pi^2\alpha^2 T$$

here $\alpha = 2\pi e^2/hc \approx 1/137$, e = electron charge, C= speed of light, h = Planck's constant [124].

Infrared spectroscopy is used to measure interband optical transitions in graphene, which is found to be gate-dependent [125]. The absorbance of 2D graphene corresponding to the number of graphene layers and reflectance is very low of 0.5% but increases up to 2% per 10 layers of graphene. Hence absorbance of single layer graphene (SLG) towards light possesses very high value. Graphene on composite with various supported substrates like SiO_2/Si, Si_3N_4/Si, SiC and Al_2O_3/Si used for the fabrication of photo-detectors, touch screens, smart windows, optoelectronic devices, *etc*.

The unique both electronic and magneto properties of SLG mostly is the one of the interesting and studied aspects than any other ones. Electrons in graphene layers move faster (as if zero mass of electrons in graphene) even 100 times than light. The exceptional electronic arrangement possesses unique Quantum Hall effect (QHE) and Klein tunnelling properties. The electrons in graphene are ordered and have very long mean free paths. Field-effect transistors (FETs) experiment performed by Novoselov *et al.* [124] explained that resistivity (ρ) which depends on the gate voltage value (V_g) possess a sharp peak to a value of several kilo ohms. Two- to three-layered graphene with hydrogen atmosphere samples have shown mobility of 10428 cm^2 $(V\ s)^{-1}$. All these unique properties of graphene can be easily enhanced by addition of layers on its surface through the electric and magnetic fields. The special zero band gap semi conductor electronic properties of graphene has been used for fabricating electronic devices.

The magneto transport properties in graphene are all time an important research area today. The electronic motion gives rise to a magnetic moment. The most interesting fact is that magnetic energy of the electrons in graphene 1000 times more than on comparing to other carbon 3D/2D allotropes despite the absence of *d* and *f* subshell electrons in graphene (which causes for magnetic coupling). The defects in graphene lattice (C atom vacancies or additional atom bonded by irradiation of different atomic species) originate magnetic moments. In graphene, the edges of honeycomb lattice introduce magnetic moments in the zig-zag configuration possessing ferromagnetically ordered. Graphene samples show magnetic hysteresis at room temperature. Graphene synthesized in hydrogen atmosphere (HG) possess good hysteretic features with saturation but it synthesized by conversion of nano diamond (DG) shows only saturation magnetization. Epitaxial graphene (EG) have large area and layers than hydrogen atmosphere (HG) and nano diamond (DG). The order is as EG > DG > HG and the variation in magnetic properties of the samples order is as HG > DG > EG. Quantum hall effect (QHE) in graphene found at low temperature in strong magnetic field was suggested by several authors [121-123]. The formation of discrete Landau levels (a series of discrete energy levels of two dimensions in strong magnetic field) in conventional quantum hall effect appears when the filling factor is an integer for quantization of the Hall conductivity and in unconventional phenomenon (1/2 integer QHE) due to the quasi-particle excitation in graphene which can be described by massless dirac's formation equation of the relativistic quantum mechanics [125]. There is much more theoretical and experimental work for single layer graphene and much has should be done for bi/multilayer graphene. Till date QHE is a challenging topic in quantum field theory.

Outlook of graphene nanocomposite: The extraordinary physical, chemical and mechanical properties with extremely unique high surface area and adsorption capacities of graphene nanocomposite developed a wide range of applications in many fields. The advancement king-sized potential of graphene nanocomposite have replaced the precious metals used in common catalysts and can be increasingly used in diversified applications. The structural feature of graphene facilitating chemical functionalization combination with various types of inorganic nanoparticles, including metals, metal oxides, *etc*. This unique combination creates a wide range of enhanced sensitivity, selectivity, activity for biosensor applications, low band gap in photocatalytic applications, accuracy in biomedical, clinical applications, *etc*. The graphene-based materials and their unique properties caused for physical adsorption and direct electron transfer (DET) processes are elaborated for bunch of applications.

Graphene-based nanoparticles in biomedical fields: In the field of medical sciences and healthcare industries, biosensors are important for diagnosing physiological and metabolic parameters with high operational, storage stability, high sensitivity, selectivity and detection of femto/nano/picomolar concentrations of bioanalytes so called low limit of detection (LOD). The graphene has accelerated the said properties on combined with nanoparticles due to its unique physical properties, which includes high electrical conductivity, high specific surface area, high carrier mobility and optical transparency. The common biosensors are amperometric, optical, surface plasmon resonance, enzymatic, bacterial sensors, enzyme based, tissue-based, immune sensors, DNA biosensors, thermal, piezoelectric, *etc*. All these have great applications in many fields such as food, environmental, biomedical fields and marine sectors to detect and remove certain contaminants, weather non-living or living entities within femto- or piccomolar concentration of analytes molecule.

Biosensors: The different types of biosensor used for the detection of lower or higher limits with high precision values of bioanalytes and other hazardous compounds present in our daily used materials or in environment. Now days, the detection of bio-analytes like glucose, uric acid, H_2O_2, ascorbic acid, hydrazine, NADH, nitrate, *etc*. exhibit a interesting part in the field of medical science and environment for a fit and pollution free society. There are various techniques such as electrochemical, spectrophotometer, chemiluminescence, fluorometry and titrimetry used for the detection of these bioanalytes but all are the traditional methods and have much limitation for the detection of sub-nano molar level. Among them, electrochemical method plays a rising star in the horizon of other methods [126,127]. In recent years, implementation of electrochemical method by using graphene as transducer is the most promising research method to detect various bioanalytes at sub-nano molar level. The excellent electronic properties of graphene nanocomposite have high sensitivity, easy operability able to detect bioanalytes through the electrochemical method. The advanced properties of graphene like thermal/electrical conductivity, chemical inertness, optical transmittance and super hydrophobicity at nanometre scale present itself as a king in the kingdom of biosensors.

Here we put much attention for non-enzymatic (free from oxygen limitation) amperometric sensing of above mentioned bio-analytes by graphene and it's composite with nanoparticles. Nanostructured electrodes (rougher surfaces, which causes to wider electrode area) have high electrochemically active surface area (ECSA), which generating large currents and hence generally advantageous in terms of sensitivity for biosensing. There are a number of reports on detection of bioanalytes in fields of biosensors implementing graphene or graphene based nanoparticles composites as substrate. The graphene based nanostructured electrodes generally have great advantageous for the oxidation/reduction of bioanalytes in terms of sensitivity than the other carbon based substrate like carbon black, carbon nanotube, carbon nano-horn, fullerene, *etc*. It has been observed that the graphene nanoparticles composites show excellent nanomolar detection level of analytes than the single one graphene.

Recently, Behera *et al.* [46] fabricated branched platinum decorated graphene (GPtNs) and derived their potentiality towards electrochemical biosensing for hydrogen peroxide. Graphene supported Pt nanoparticle electrode revealed high sensitivity and also enable to detect very low nanomolar concentration of H_2O_2.

Hydrogen peroxide is used as an essential vital oxidizing agent in various potential fields such as the biomedical, clinical, pharmaceutical, food preserving process and so on. In addition this, the concentration of H_2O_2 beyond the permit able level caused harmful effects and caused for diseases so the detection of H_2O_2 is of great importance. This RGO/Pt/GCE electrode detects a very sensitive limit of detection value of 5 nM level. In addition this, this group also developed RGO-Pd electrode towards H_2O_2 sensing with very sensitive lower limit of detection of 1 nM [47]. Here porous Pd nanostructures shows highly electrocatalytically activity on decorated over the graphene sheet uniformly. The RGO-Pd/GCE electrode possessed a current density of 445.267 $\mu A/cm^2$, which was much higher than that of bare GO and also bare Pd nanostructures electrode. RGO supported porous Pd glassy electrode reduces to H_2O_2 at 0.126 V. This lower reduction potential caused due to the unique morphologic combination of porous palladium nanoparticles with graphene. The RGO-Pd nanostructures modified electrode possessed the amperometric sensing lower than 5 nM with high storage and operational stability.

The antibacterial properties of graphene layers are due to the combined mechanisms of bacterial membrane perturbation caused by sharp edges and oxidative stress induction. Recently, functionalized graphene used for bioselective detection of bacteria at cellular levels. Akhavan & Ghaderi [128] demonstrated the antibacterial activity of graphene nano walls deposited on stainless steel substrates. This experiment suggests that graphene sheets acts as an encapsulating material for delivery of microorganisms. In this experiment, bacteria entrapped within the aggregated sheets were biologically isolated from their environment for which they do not proliferate. The bacteria become reactive after removing graphene sheet and alive for 24 h. Recently, Ji *et al.* [129] reported the antibacterial activity of the graphene as a novel green broad-spectrum antibacterial material. Wu *et al.* [130] exploited the antibacterial activity of graphene oxide effectively for controlling eradicated bacteria and can prolong mice survival and again can cause less tissue injury and subdued inflammatory response. In general, three types of bacteria such as *Klebsiella pneumoniae*, *Escherichia coli* and *Pseudomonas aeruginosa* were used for *in vitro* study. Among them *Klebsiella pneumoniae* was considered for multidrug resistant (MDR) bacterium for *in vivo* study but GO nanoparticles effectively eradicated *Klebsiella pneumoniae* in agar dishes from *Klebsiella pneumoniae* infection in the culture. And hence, GO able to eradicate the growth and spread of *Klebsiella pneumoniae* resulting in significantly increased cell survival rate, less tissue injury, subdued inflammatory response and prolonged mice survival [130].

The mechanisms for antibacterial action of graphene nanocomposite may be due to production of reactive oxygen species, oxidative stress or vigorous extraction of large amounts of phospholipids from the membrane of the bacteria under consideration. The flat face and electronic modulation of graphene nanocomposite caused a disturbance to the protein–protein bonding in the cell membrane. This disrupts leading to the destabilization of 3D structure of protein, causing its functional failure and hence the bacterial metabolic activity increased causing the GO to be reduced to a form of graphene that was bactericidal *via* a glycolsis process [131].

However, the antibacterial activity of graphene sheet mechanism is not yet explored perfectly remains as a unexplored research area. In addition to this, graphene antibacterial activity can be enhanced by making composite with nanoparticles. The electronic feature of these two correlates to each and makes an excellent transducer for antibacterial activity. From last decades, silver based nonmaterial have emerged an important position as antimicrobial agents due to its excellent activity such as at low concentrations amount it is toxic to microbes but are safe for human cells. However, the aggregation of silver nanoparticles caused for some challenges which compromise their antimicrobial properties and thus limit their efficient use. By attaching silver nanoparticles to graphene significantly improved antibacterial activities [132]. In addition this, RGO-Au [133], RGO-Cu [134], nanoparticles also possesses synergistic antimicrobial effect with good biocompatibility. Due to the superior antibacterial properties and good biocompatibility of graphene supported nanocomposites have wide range of applications, in field of antibacterial packaging, water disinfection and wound dressing.

Conclusion

Graphene appreciated worldwide attention due to its effortless manufacturing methods and remarkable striking properties. Two-dimensional graphene offers the unique multifunctional properties due to which it shows the most promising material in field of materials science, engineering and technology. The journey from the study of synthesis methods to biomedical applications is considered as tremendous impact on scientific and technological on science community. By use of graphene nanocomposite cased for changeling engineering properties, engineers are able to make novel devices and designing photo catalytic technology. And the most tremendous biochemists enthusiastically are working on new synthetic routes in organic and material science and scientist busily minutely functioning on very lower detection of bioanalytes for a safe environment. Despite of these various applications, production of graphene nanocomposites in large amount with high purity and low cost is still immature.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A.K. Geim and K.S. Novoselov, *Nat. Mater.*, **6**, 183 (2007); https://doi.org/10.1038/nmat1849
2. M. Orlita, C. Faugeras, P. Plochocka, P. Neugebauer, G. Martinez, D.K. Maude, A.L. Barra, M. Sprinkle, C. Berger, W.A. de Heer and M. Potemski, *Phys. Rev. Lett.*, **101**, 267601 (2008); https://doi.org/10.1103/PhysRevLett.101.267601
3. S.K. Tiwari, S. Sahoo, N. Wang and A. Huczko, *J. Sci. Adv. Mater. Devices*, **5**, 10 (2020); https://doi.org/10.1016/j.jsamd.2020.01.006
4. C. Lee, X. Wei, J.W. Kysar and J. Hone, *Science*, **321**, 385 (2008); https://doi.org/10.1126/science.1157996
5. V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril and K.S. Kim, *Chem. Rev.*, **112**, 6156 (2012); https://doi.org/10.1021/cr3000412
6. L. Rodríguez-Pérez, M.Á. Herranz and N. Martín, *Chem. Commun.*, **49**, 3721 (2013); https://doi.org/10.1039/c3cc38950b
7. O.C. Compton and S.B.T. Nguyen, *Small*, **6**, 711 (2010); https://doi.org/10.1002/smll.200901934
8. A.T. Smith, A.M. LaChance, S. Zeng, B. Liu and L. Sun, *Nano Mater. Sci.*, **1**, 31 (2019); https://doi.org/10.1016/j.nanoms.2019.02.004
9. H. Chen, M.B. Muller, K.J. Gilmore, G.G. Wallace and D. Li, *Adv. Mater.*, **20**, 3557 (2008); https://doi.org/10.1002/adma.200800757
10. M.S. Nevius, M. Conrad, F. Wang, A. Celis, M.N. Nair, A. Taleb-Ibrahimi, A. Tejeda and E.H. Conrad, *Phys. Rev. Lett.*, **115**, 136802 (2015); https://doi.org/10.1103/PhysRevLett.115.136802
11. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos and A.A. Firsov, *Nature*, **438**, 197 (2005); https://doi.org/10.1038/nature04233
12. Y.B. Zhang, Y.W. Tan, H.L. Stormer and P. Kim, *Nature*, **438**, 201 (2005); https://doi.org/10.1038/nature04235
13. A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao and C.N. Lau, *Nano Lett.*, **8**, 902 (2008); https://doi.org/10.1021/nl0731872
14. P. Wallace, *Phys. Rev.*, **71**, 622 (1947); https://doi.org/10.1103/PhysRev.71.622
15. M.I. Katsnelson, K.S. Novoselov and A.K. Geim, *Nat. Phys.*, **2**, 620 (2006); https://doi.org/10.1038/nphys384
16. J. Rafiee, X. Mi, H. Gullapalli, A.V. Thomas, F. Yavari, Y. Shi, P.M. Ajayan and N.A. Koratkar, *Nat. Mater.*, **11**, 217 (2012); https://doi.org/10.1038/nmat3228
17. C.J. Shih, Q.H. Wang, S. Lin, K.C. Park, Z. Jin, M.S. Strano and D. Blankschtein, *Phys. Rev. Lett.*, **109**, 176101 (2012); https://doi.org/10.1103/PhysRevLett.109.176101
18. F. Rozpaloch, J. Patyk and J. Stankowsk, *Acta Phys. Pol. A*, **112**, 73 (2007).
19. C.A. Coulson, Valence, The University Press, Oxford, vol. 2, p. 391 (1965).
20. H. Shioyama, Synth. Metals, 114, 1 (2000); https://doi.org/10.1016/S0379-6779(00)00222-8
21. S. Stankovich, R.D. Piner, X.Q. Chen, N.Q. Wu, S.T. Nguyen and R.S. Ruoff, *J. Mater. Chem.*, **16**, 155 (2006); https://doi.org/10.1039/B512799H
22. S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen and R.S. Ruoff, *Carbon*, **45**, 1558 (2007); https://doi.org/10.1016/j.carbon.2007.02.034
23. D. Li, M.B. Muller, S. Gilje, R.B. Kaner and G.G. Wallace, *Nat. Nanotechnol.*, **3**, 101 (2008); https://doi.org/10.1038/nnano.2007.451
24. S. Gilje, S. Han, M. Wang, K.L. Wang and R.B. Kaner, *Nano Lett.*, **7**, 3394 (2007); https://doi.org/10.1021/nl0717715

25. M. Muller, C. Kubel and K. Mullen, *Chem. Eur. J.*, **4**, 2099 (1998); https://doi.org/10.1002/(SICI)1521-3765(19981102)4:11<2099::AID-CHEM2099>3.0.CO;2-T
26. N. Tyutyulkov, G. Madjarova, F. Dietz and K. Mullen, *J. Phys. Chem. B*, **102**, 10183 (1998); https://doi.org/10.1021/jp982651b
27. C. Berger, Z. Song, T. Li, X. Li, A.Y. Ogbazghi, R. Feng, Z. Dai, A.N. Marchenkov, E.H. Conrad, P.N. First and W.A. de Heer, *J. Phys. Chem.*, **108**, 19912 (2004); https://doi.org/10.1021/jp040650f
28. W.A. de Heer, C. Berger, X. Wu, P.N. First, E.H. Conrad, X. Li, T. Li, M. Sprinkle, J. Hass, M.L. Sadowski, M. Potemski and G. Martinez, *Solid State Commun.*, **143**, 92 (2007); https://doi.org/10.1016/j.ssc.2007.04.023
29. C.Y. Su, A.Y. Lu, Y. Xu, F.R. Chen, A.N. Khlobystov and L.J. Li, *ACS Nano*, **5**, 2332 (2011); https://doi.org/10.1021/nn200025p
30. N. Liu, F. Luo, H. Wu, Y. Liu, C. Zhang and J. Chen, *Adv. Funct. Mater.*, **18**, 1518 (2008); https://doi.org/10.1002/adfm.200700797
31. G. Williams, B. Seger and P.V. Kamat, *ACS Nano*, **2**, 1487 (2008); https://doi.org/10.1021/nn800251f
32. O. Akhavan, M. Abdolahad, A. Esfandiar and M. Mohatashamifar, *J. Phys. Chem. C*, **114**, 12955 (2010); https://doi.org/10.1021/jp103472c
33. O. Akhavan, *Carbon*, **48**, 509 (2010); https://doi.org/10.1016/j.carbon.2009.09.069
34. H.B. Zhang, J.W. Wang, Q. Yan, W.-G. Zheng, C. Chen and Z.-Z. Yu, *J. Mater. Chem.*, **21**, 5392 (2011); https://doi.org/10.1039/c1jm10099h
35. V. Strong, S. Dubin, M.F. Elkady, A. Lech, Y. Wang, B.H. Weiller and R.B. Kaner, *ACS Nano*, **6**, 1395 (2012); https://doi.org/10.1021/nn204200w
36. R. Trusovas, K. Ratautas, G. Raciukaitis, J. Barkauskas, I. Stankeviciene, G. Niaura and R. Mazeikiene, *Carbon*, **52**, 574 (2013); https://doi.org/10.1016/j.carbon.2012.10.017
37. Y.L. Zhang, L. Guo, H. Xia, Q.-D. Chen, J. Feng and H.-B. Sun, *Adv. Opt. Mater.*, **2**, 10 (2014); https://doi.org/10.1002/adom.201300317
38. W. Chen, L. Yan and P.R. Bangal, *Carbon*, **48**, 1146 (2010); https://doi.org/10.1016/j.carbon.2009.11.037
39. D. Voiry, J. Yang, J. Kupferberg, R. Fullon, C. Lee, H.Y. Jeong, H.S. Shin and M. Chhowalla, *Nanomaterials*, **353**, 1413 (2016); https://doi.org/10.1126/science.aah3398
40. C.K. Chua, A. Ambrosi and M. Pumera, *J. Mater. Chem.*, **22**, 11054 (2012); https://doi.org/10.1039/c2jm16054d
41. E.C. Salas, Z. Sun, A. Luttge and J.M. Tour, *ACS Nano*, **4**, 4852 (2010); https://doi.org/10.1021/nn101081t
42. X. Zhu, Q. Liu, C. Li, M. Xu and Y. Liang, *J. Electrochem. Sci.*, **7**, 5172 (2012).
43. S. Park, J. An, J.R. Potts, A. Velamakanni, S. Murali and R.S. Ruoff, *Carbon*, **49**, 3019 (2011); https://doi.org/10.1016/j.carbon.2011.02.071
44. P. Yang, Q. Liu, J. Liu, H. Zhang, Z. Li, R. Li, L. Liu and J. Wang, *Ind. Eng. Chem. Res.*, **56**, 3588 (2017); https://doi.org/10.1021/acs.iecr.6b04532
45. Z. Yang, Q. Zheng, H. Qiu, J. Li and J. Yang, *N. Carbon Mater.*, **30**, 41 (2015); https://doi.org/10.1016/S1872-5805(15)60174-3
46. T.K. Behera, S.C. Sahu, B. Satpati, B. Bag, K. Sanjay and B.K. Jena, *Electrochim. Acta*, **206**, 238 (2016); https://doi.org/10.1016/j.electacta.2016.03.046
47. S.C. Sahu, T.K. Behera, A. Dash, B. Jena, A. Ghosh and B.K. Jena, *New J. Chem.*, **40**, 1096 (2016); https://doi.org/10.1039/C5NJ02555A
48. T.K. Behera, P.K. Satpathy and P. Mohapatra, Nanoparticles: Excellent Transducer for Electrochemical Biosensor, Arcler Publishing, pp. 215-249 (2018).
49. T.K. Behera, P.K. Satpathy and P. Mohapatra, Methanol and Formic Acid Oxidation: Selective Fuel Cell Processes, Apple Academic Press (AAP), Inc., Canada, A Taylor & Francis Group (2019).
50. Y. Wei and Z. Sun, *Curr. Opin. Colloid Interface Sci.*, **20**, 311 (2015); https://doi.org/10.1016/j.cocis.2015.10.010
51. M. Cai, D. Thorpe, D.H. Adamson and H.C. Schniepp, *J. Mater. Chem.*, **22**, 24992 (2012); https://doi.org/10.1039/C2JM34517J
52. J.N. Coleman, *Acc. Chem. Res.*, **46**, 14 (2013); https://doi.org/10.1021/ar300009f
53. K.S. Subrahmanyam, L.S. Panchakarla, A. Govindaraj and C.N.R. Rao, *J. Phys. Chem.*, **113**, 4257 (2009); https://doi.org/10.1021/jp900791y
54. K.F. Kelly and W.E. Billups, *Acc. Chem. Res.*, **46**, 4 (2013); https://doi.org/10.1021/ar300121q
55. F.M. Koehler and W.J. Stark, *Acc. Chem. Res.*, **46**, 2297 (2013); https://doi.org/10.1021/ar300125w
56. Y.N. Xia, Y.J. Xiong, B. Lim and S.E. Skrabalak, *Angew. Chem. Int. Ed.*, **48**, 60 (2009); https://doi.org/10.1002/anie.200802248
57. M. Terrones, *Proc. Natl. Acad. Sci. USA*, **109**, 7951 (2012); https://doi.org/10.1073/pnas.1205024109
58. J. Lu, Y. Li, S. Li and S.P. Jiang, *Sci. Rep.*, **6**, 21530 (2016); https://doi.org/10.1038/srep21530
59. D.B. Shinde, M. Majumder and V.K. Pillai, *Sci. Rep.*, **4**, 4363 (2014); https://doi.org/10.1038/srep04363
60. A. Eatemadi, H. Daraee, H. Karimkhanloo, M. Kouhi, N. Zarghami, A. Akbarzadeh, M. Abasi, Y. Hanifehpour and S.W. Joo, *Nanoscale Res. Lett.*, **9**, 393 (2014); https://doi.org/10.1186/1556-276X-9-393
61. V.N. Popov, *Mater. Sci. Eng. Rep.*, **43**, 61 (2004); https://doi.org/10.1016/j.mser.2003.10.001
62. B.C. Brodie, *Philos. Trans. R. Soc. Lond.*, **149**, 249 (1859); https://doi.org/10.1098/rstl.1859.0013
63. W.S. Hummers Jr. and R.E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339 (1958); https://doi.org/10.1021/ja01539a017
64. U. Hofmann and R. Holst, *Ber. Dtsch. Chem. Ges. B*, **72**, 754 (1939); https://doi.org/10.1002/cber.19390720417
65. G. Ruess, *Monatsh. Chem.*, **76**, 381 (1947); https://doi.org/10.1007/BF00898987
66. W. Scholz and H.P. Boehm, *Z. Anorg. Allg. Chem.*, **369**, 327 (1969); https://doi.org/10.1002/zaac.19693690322
67. T. Nakajima and Y. Matsuo, *Carbon*, **32**, 469 (1994); https://doi.org/10.1016/0008-6223(94)90168-6
68. D.R. Cooper, B. D'Anjou, N. Ghattamaneni, B. Harack, M. Hilke, A. Horth, N. Majlis, M. Massicotte, L. Vandsburger, E. Whiteway and V. Yu, *Int. Schol. Res. Notices*, **2012**, 501686 (2012); https://doi.org/10.5402/2012/501686
69. M. Eizenberg and J.M. Blakely, *J. Chem. Phys.*, **71**, 3467 (1979); https://doi.org/10.1063/1.438736
70. B. Lang, *Surf. Sci.*, **53**, 317 (1975); https://doi.org/10.1016/0039-6028(75)90132-6
71. X. Lu, M. Yu, H. Huang and R.S. Ruoff, *Nanotechnology*, **10**, 269 (1999); https://doi.org/10.1088/0957-4484/10/3/308
72. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva and A.A. Firsov, *Science*, **306**, 666 (2004); https://doi.org/10.1126/science.1102896
73. X. An, T. Simmons, R. Shah, C. Wolfe, K. Lewis, M. Washington, M. Nayak, S.K. Talapatra and S. Kar, *Nano Lett.*, **10**, 4295 (2010); https://doi.org/10.1021/nl903557p
74. X. Liang, Z. Fu and S. Chou, *Nano Lett.*, **7**, 3840 (2007); https://doi.org/10.1021/nl072566s
75. A. Reina, S. Thiele, X.T. Jia, S. Bhaviripudi, M.S. Dresselhaus, J.A. Schaefer and J. Kong, *Nano Res.*, **2**, 509 (2009); https://doi.org/10.1007/s12274-009-9059-y
76. Q. Yu, J. Lian, S. Siriponglert, H. Li, Y.P. Chen and S.-S. Pei, *Appl. Phys. Lett.*, **93**, 113103 (2008); https://doi.org/10.1063/1.2982585
77. X.S. Li, W.W. Cai, J.H. An, S. Kim, J. Nah, D.X. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo and R.S. Ruoff, *Science*, **324**, 1312 (2009); https://doi.org/10.1126/science.1171245
78. K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.H. Ahn, P. Kim, J.Y. Choi and B.H. Hong, *Nature*, **457**, 706 (2009); https://doi.org/10.1038/nature07719
79. M. Choucair, P. Thordarson and J.A. Stride, *Nat. Nanotechnol.*, **4**, 30 (2009); https://doi.org/10.1038/nnano.2008.365
80. P.W. Sutter, J.I. Flege and E.A. Sutter, *Nat. Mater.*, **7**, 406 (2008); https://doi.org/10.1038/nmat2166
81. J. Coraux, A.T. N'Diaye, C. Busse and T. Michely, *Nano Lett.*, **8**, 565 (2008); https://doi.org/10.1021/nl0728874
82. A. Reina, X.T. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. Dresselhaus and S. Kong, *Nano Lett.*, **9**, 30 (2009); https://doi.org/10.1021/nl801827v

83. N.G. Shang, P. Papakonstantinou, M. McMullan, A. Stamboulis, M. Chu, A. Potenza, S.S. Dhesi and H. Marchetto, *Adv. Funct. Mater.*, **18**, 3506 (2008); https://doi.org/10.1002/adfm.200800951
84. S. Stankovich, D. Dikin, A. Dommett, G.H.B. Kohlhaas, K.M. Zimney, E.A. Stach, R.D. Piner, S.B.T. Nguyen and R.S. Ruoff, *Nature*, **442**, 282 (2006); https://doi.org/10.1038/nature04969
85. M.D. Stoller, S. Park, Y. Zhu, J. An and R.S. Ruoff, *Nano Lett.*, **8**, 3498 (2008); https://doi.org/10.1021/nl802558y
86. X. Wang, L. Zhi and K. Mullen, *Nano Lett.*, **8**, 323 (2008); https://doi.org/10.1021/nl072838r
87. W.S. Hummers, The Oxidation of Graphite to Graphitic Oxide, US Patent 2,798,878 (1967).
88. L. Staudenmaier and V.Z. Darstellung, *Eur. J. Inorg. Chem.*, **31**, 1481 (1988).
89. V.H. Pham, T.V. Cuong, T.D. Nguyen-Phan, H.D. Pham, E.J. Kim, S.H. Hur, E.W. Shin, S. Kim and J.S. Chung, *Chem. Commun.*, **46**, 4375 (2010); https://doi.org/10.1039/c0cc00363h
90. X. Zhou, J. Zhang, H. Wu, H. Yang, J. Zhang and S. Guo, *J. Phys. Chem. C*, **115**, 11957 (2011); https://doi.org/10.1021/jp202575j
91. C. Zhu, S. Guo, Y. Fang and S. Dong, *ACS Nano*, **4**, 2429 (2010); https://doi.org/10.1021/nn1002387
92. J. Zhang, H. Yang, G. Shen, P. Cheng, J. Zhang and S. Guo, *Chem. Commun.*, **46**, 1112 (2010); https://doi.org/10.1039/B917705A
93. G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu and J. Yao, *J. Phys. Chem.*, **112**, 8192 (2008); https://doi.org/10.1021/jp710931h
94. X. Fan, W. Peng, Y. Li, X. Li, S. Wang, G. Zhang and F. Zhang, *Adv. Mater.*, **20**, 4490 (2008); https://doi.org/10.1002/adma.200801306
95. C.A. Amarnath, C.E. Hong, N.H. Kim, B.C. Ku, T. Kuila and J.H. Lee, *Carbon*, **49**, 3497 (2011); https://doi.org/10.1016/j.carbon.2011.04.048
96. H.J. Shin, K.K. Kim, A. Benayad, S.M. Yoon, H.K. Park, I.-S. Jung, M.H. Jin, H.-K. Jeong, J.M. Kim, J.-Y. Choi and Y.H. Lee, *Adv. Funct. Mater.*, **19**, 1987 (2009); https://doi.org/10.1002/adfm.200900167
97. W. Qian, R. Hao, Y. Hou, Y. Tian, C. Shen, H. Gao and X. Liang, *Nano Res.*, **2**, 706 (2009); https://doi.org/10.1007/s12274-009-9074-z
98. L.Y. Jiao, X.R. Wang, G. Diankov, H.L. Wang and H.J. Dai, *Nat. Nanotechnol.*, **5**, 321 (2010); https://doi.org/10.1038/nnano.2010.54
99. K.S. Subrahmanyam, L.S. Panchakarla, A. Govindaraj and C.N.R. Rao, *J. Phys. Chem. C*, **113**, 4257 (2009); https://doi.org/10.1021/jp900791y
100. L.S. Panchakarla, A. Govindaraj and C.N.R. Rao, *Inorg. Chim. Acta*, **363**, 4163 (2010); https://doi.org/10.1016/j.ica.2010.07.057
101. Z.S. Wu, W. Ren, L. Gao, J. Zhao, Z. Chen, B. Liu, D. Tang, B. Yu, C. Jiang and H.M. Cheng, *ACS Nano*, **3**, 411 (2009); https://doi.org/10.1021/nn900020u
102. K.S. Subrahmanyam, S.R.C. Vivekchand, A. Govindaraj and C.N.R. Rao, *J. Mater. Chem.*, **18**, 1517 (2008); https://doi.org/10.1039/b716536f
103. X. Fang, J. Donahue, A. Shashurin and M.Keidar, *Graphene*, **4**, 53151 (2015); https://doi.org/10.4236/graphene.2015.41001
104. J.L. Qi, W.T. Zheng, X.H. Zheng, X. Wang and H.W. Tian, *Appl. Surf. Sci.*, **257**, 6531 (2011); https://doi.org/10.1016/j.apsusc.2011.02.069
105. P. Yang, L. Zhou, S. Zhang, N. Wan, W. Pan and W. Shen, *J. Appl. Phys.*, **116**, 244306 (2014); https://doi.org/10.1063/1.4904958
106. E. Moreau, F.J. Ferrer, D. Vignaud, S. Godey and X. Wallart, *Phys. Status Solidi., A Appl. Mater. Sci.*, **207**, 300 (2010); https://doi.org/10.1002/pssa.200982412
107. W. Gao, L.B. Alemany, L.J. Ci and P.M. Ajayan, *Nat. Chem.*, **1**, 403 (2009); https://doi.org/10.1038/nchem.281
108. Q. Zhuo, Y. Ma, J. Gao, P. Zhang, Y. Xia, Y. Tian, X.X. Sun, J. Zhong and X. Sun, *Inorg. Chem.*, **52**, 3141 (2013); https://doi.org/10.1021/ic302608g
109. R. Muszynski, B. Seger and P.V. Kamat, *J. Phys. Chem. C*, **112**, 5263 (2008); https://doi.org/10.1021/jp800977b
110. H. Tien, W. Huang, Y.L. Yang, S.Y. Wang and J.Y. Ma, *Carbon*, **49**, 1550 (2011); https://doi.org/10.1016/j.carbon.2010.12.022
111. Y. Zhou, Q. Bao, L. Tang, L.A.L. Zhong and K.P. Loh, *Chem. Mater.*, **21**, 2950 (2009); https://doi.org/10.1021/cm9006603
112. W. Zou, J. Zhu, Y. Sun and X. Wang, *Mater. Chem. Phys.*, **125**, 617 (2011); https://doi.org/10.1016/j.matchemphys.2010.10.008
113. S. Wu, Z. Yin, Q. He, G. Lu, X. Zhou and H. Zhang, *J. Mater. Chem.*, **21**, 3467 (2011); https://doi.org/10.1039/C0JM02267E
114. S. Wu, Z. Yin, Q. He, X. Huang, X. Zhou and H. Zhang, *J. Phys. Chem. C*, **114**, 11816 (2010); https://doi.org/10.1021/jp103696u
115. F.A. He, J.T. Fan, D. Ma, L. Zhang, C. Leung and H.L. Chan, *Carbon*, **48**, 3139 (2010); https://doi.org/10.1016/j.carbon.2010.04.052
116. T.A. Pham, B.C. Choi and Y.T. Jeong, *Nanotechnology*, **21**, 465603 (2010); https://doi.org/10.1088/0957-4484/21/46/465603
117. P.T. Yin, S. Shah, M. Chhowalla and K.-B. Lee, *Chem. Rev.*, **115**, 2483 (2015); https://doi.org/10.1021/cr500537t
118. B. Garg, T. Bisht and Y.-C. Ling, *Molecules*, **19**, 14582 (2014); https://doi.org/10.3390/molecules190914582
119. 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 and A. Lanzara, *J. Phys. Chem. Solids*, **67**, 2172 (2006); https://doi.org/10.1016/j.jpcs.2006.05.010
120. D.G. Papageorgiou, I.A. Kinloch and R.J. Young, *Prog. Mater. Sci.*, **90**, 75 (2017); https://doi.org/10.1016/j.pmatsci.2017.07.004
121. T. Enoki, M. Suzuki and M. Endo, Graphite Intercalation Compounds and Applications, Oxford University Press (2003).
122. M.S. Dresselhaus and G. Dresselhaus, *Adv. Phys.*, **51**, 1 (2002); https://doi.org/10.1080/00018730110113644
123. N.M.R. Peres, *Condens. Matter*, **21**, 095501 (2009); https://doi.org/10.1088/0953-8984/21/9/095501
124. R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres and A.K. Geim, *Science*, **320**, 1308 (2008); https://doi.org/10.1126/science.1156965
125. F. Wang, Y.B. Zhang, C.S. Tian, C. Girit, A. Zettl, M. Crommie and Y.R. Shen, *Science*, **320**, 206 (2008); https://doi.org/10.1126/science.1152793
126. Y.H. Ng, I.V. Lightcap, K. Goodwin, M. Matsumura and P.V. Kamat, *J. Phys. Chem. Lett.*, **1**, 2222 (2010); https://doi.org/10.1021/jz100728z
127. M. Wang, X. Shang, X. Yu, R. Liu, Y. Xie, H. Zhao, H. Cao and G. Zhang, *Phys. Chem. Chem. Phys.*, **16**, 26016 (2014); https://doi.org/10.1039/C4CP03824J
128. O. Akhavan and E. Ghaderi, *ACS Nano*, **4**, 5731 (2010); https://doi.org/10.1021/nn101390x
129. H. Ji, H. Sun and X. Qu, *Adv. Drug Deliv. Rev.*, **105**, 176 (2016); https://doi.org/10.1016/j.addr.2016.04.009
130. X. Wu, S. Tan, Y. Xing, Q. Pu, M. Wu and J.X. Zhao, *Colloids Surf. B Biointerfaces*, **157**, 1 (2017); https://doi.org/10.1016/j.colsurfb.2017.05.024
131. P. Kumar, P. Huo, R. Zhang, B. Liu, *Nanomaterials*, **5**, 737 (2019); https://doi.org/10.3390/nano9050737
132. B. Marta, M. Potara, M. Iliut, E. Jakab, T. Radu, F. Imre-Lucaci, G. Katona, O. Popescu and S. Astilean, *Colloids Surf. A Physicochem. Eng. Asp.*, **487**, 113 (2015); https://doi.org/10.1016/j.colsurfa.2015.09.046
133. N. Hussain, A. Gogoi, R.K. Sarma and P. Sharma, *ChemPlusChem*, **79**, 1774 (2014); https://doi.org/10.1002/cplu.201402240
134. Y. Ouyang, X. Cai, Q. Shi, L. Liu, D. Wan, S. Tan and Y. Ouyang, *Colloids Surf. B Biointerfaces*, **107**, 107 (2013); https://doi.org/10.1016/j.colsurfb.2013.01.073