Biological and Medical Applications of Graphene Nanoparticles

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Abstract— *Graphene which is one of the latest additions to nanocarbon family has peculiar band structure, extraordinary thermal and electronic conductance and room temperature quantum Hall effect. It is used in for various applications in diverse fields ranging from catalysis to electronics. In addition to being components in electronic devices, GO have been used in nanocomposite materials, polymer composite materials, energy storage, biomedical applications, catalysis and as a surfactant with some overlaps between these fields Graphene oxide is a unique material that can be viewed as a single monomolecular layer of graphite with various oxygen containing functionalities such as epoxide, carbonyl, carboxyl and hydroxyl groups.*

Keywords— ***Graphene oxide, catalysis, Applications.***

I. INTRODUCTION

Carbon materials are known to be eco friendly and less toxic than inorganic materials. Graphene, a single layer of graphite[1-3] would also be safe and useful for biomedical research. The high surface area and rich abundance of functional-groups present make (GO) Graphene oxide and reduced graphene oxide (rGO) or chemically converted graphene an attracting candidate in biotechnology and environmental remediation [4-10]. The properties easy synthesis, low cost and non-toxicity of graphene can be turned to suit applications such as sensing, drug delivery or cellular imaging. Graphene with its high surface area can act as a good absorbent for pollutant removal. In this review some of the relevant efforts undertaken to utilize graphene in biology, sensing and water purification are discussed.

II. SYNTHESIS OF GRAPHENE NANOPARTICLES

Synthesis of GO are based on the method first reported by Hummers in which graphite is oxidized by a solution of Potassium permanganate in sulphuric acid [11]. Graphite oxide chemistry was first studied by Brodie [12-14] in 1859. There are various methods reported on synthesis of graphene sheets which include mechanical cleavage of graphite, unzipping carbon nanotubes, chemical exfoliation of graphite solvo thermal synthesis, epitaxial growth on Sic surfaces and metal surfaces, CVD of hydrocarbons on metal surfaces, bottom up organic synthesis, electric arc discharge method, Sonochemical approach, reduction of graphene oxide (GO) obtained from graphite oxide by chemical reducing agents are aqueous and environment-friendly greener reduction methods. Yang et al [15-17] have developed PEG lated nano-reduced graphene oxide for ultra-low power photo thermal therapy. Gurunathan et al [20-22] w.r.t. green synthesis and bioactivity related studies of graphene using Bacillus marisflavi as reducing agent and studied the cytotoxic effects of graphene oxide and bacterially reduced graphene oxide (rGO) in human breast cancer cells. Novoselov et al in 2004 [23-24] by the mechanical exfoliation of highly oriented pyrolytic graphite (HOPG). Wang et al [18-20] combined chemotherapy and photo thermal targeted therapy for the deisgn of multifunctional, mesoporous silicate coated graphene nanosheets as a drug delivery system. Advent of chemical processes and self-assembly approaches for the synthesis of graphene analogues have opened-up new avenues for graphene based materials.

Chemical reduction of GO is carried out by reducing agent such as hydroquinone, sodium borohydride, hydrazine and hydrazine with NH_3 [47-50]. Chemical reduction of exfoliated graphite oxide is a common method employed for obtained high-yield synthesis of graphene. In this method graphite is treated with strong oxidizers, the obtained graphite oxide has layered structure but is lighter in colour than graphite due to change in hybridization of carbon atoms occur from planar Sp^2 to tetrahedral Sp^3. Liu and gong [26-30] reported the reduction of Polyaniline-intercalated graphite oxide in aqueous hydrazine hydrate. Ruff and co-workers [31-33] prepared the stable graphitic nano platelets in the presence of poly (sodium 4 styrene sulfonate) also used hydrazine hydrate for the reduction of graphite oxide nanoplatelets prepared by exfoliation of the graphite oxide. GO is synthesized by the strong oxidation of flake graphite using acid via Hummers method. It is decorated by hydroxyl and epoxy functional groups on the hexagonal network of carbon atoms with carbonyl and carbonyl groups at the edges, [41-45]. GO can be reduced via thermal, chemical, electrochemical and laser scribbling methods. Thermal reduction process requires heating up to 1050ºC in an oven under Argon gas up to 800oC under hydrogen gas or up to 700oC in a quartz tube. The thermal reduction of GO was accompanied by the elimination of epoxy and carboxyl groups in the forms of O_2, CO, CO_2 and H_2O as predicted from thermogravimetry data. Shimizu and Coworkers [34-35] produced GNRS through the oxidization and longitudinal unzipping of MWCNT in concentrated sulphuric acid with KMno4. Graphene nano ribbons were synthesized by the oxidative unzipping of SWCNTS using a mixture of concentrated HNO3/H2So4 in a 1:3 volume ratio. Wei Huang [46] synthesized high performance graphene nanosheet by thermal reduction of GO under ethanol atmosphere at 900ºC and under N_2 atmosphere for super capacitor application. Microwave irradiation (MWI) has been used for the synthesis of a variety of nanomaterials with controlled size and shape without the need for high temperature or high pressure. The main advantages of MWI are (i) rapid reaction velocity (ii) clean and energy efficient and (iii) uniform heating of the reaction mixture [51-60]. By using this method many types of metallic and bimetallic nanoparticles can be dispersed on the graphene sheets via simultaneous reduction of GO and a variety of metal salts to create novel nano catalysts supported on the large surface area of the thermally stable 2D graphene.

Electro chemical reduction is done by adjusting the external power source to change the fermi energy level of the electrode surface that reduces GO in the presence of direct current bias. The electrochemical synthesis of Graphene was carried out via two steps GO being first assembled on the electrodes by solution deposition methods then being subjected to electro chemical reduction by scanning the potential [60-65] or by applying constant potential (bulk electrolysis) [66, 67]. The reduction of GO can be confirmed from the colour of GO electrodes that changes from yellow to black. Laser-scribing technology is simple, rapid, energy efficient and free from poisonous material and high temperature. Feng-Shou Xiao [68] fabricated graphene microcircuits by direct reduction and patterning. Scotch Tape or Mechanical exfoliation method was used to obtain Highly oriented pyrolytic graphene (HOPG) [25] which is time consuming and only small quantities can be obtained with this method. They can be used as sensors to detect individual gas molecules. CVD is used for Large-Area graphene synthesis. It is a simple and cost-efficient method to prepare single and few layer of graphene on various substrates. Many forms of CVD like hot wire, CVD, thermal CVD, plasma-enhanced CVD, radio-frequency CVD and ultrasonic spray pyrolysis are generally used. Arc discharge is a versatile and low cost method for production of graphene flakes enhanced with a specially shaped magnetic field and accustom-designed catalyst was reported [36-40]. Fan et al [69-70] proposed a novel nano carrier based on Fe3O4-graphene nano composite for effective drug delivery and pH-responsive release system for cancer treatment.

III. BIOLOGICAL AND MEDICAL APPLICATIONS OF GRAPHENE

Graphene, a mono layer of Sp^2-bonded carbon atoms arranged in a honey comb lattice has attracted tremendous attention from both the theoretical and experimental scientific communities in recent years because of its unique nanostructure and extraordinary properties [71-73]. It has become a novel and very promising material for nanoelectronics, nano composites, opto-electronic devices, electro chemical super capacitor devices, fabricated field effect transistors, drug delivery systems, solar cells, memory deices and constructed ultra sensitive chemical sensors such as pH sensors, gas sensors, bio sensors [74-76]. Catecholamine neuro transmitters and their detection in the human body has been of great interest to neuro scientists. Zhang and Coworkers [84] reported simple, efficient and green method for the deoxygenation of exfoliated graphite oxide by strong alkali at moderate temperatures Wang et al [85-86] reported a one pot solution phase green method without using any reducing agent or capping agents for the synthesis of Pt/CeO2/graphene nanomaterials for ultrasensitive detection of biomarkers. The heparin-rGO hybrid has a potentially wide range of uses in the biomedical field such as for the treatment of thrombosis [87-89]. The simultaneous reduction of metal salts and GO by focused solar radiation results in a novel hybrid composite composed of 2D and 3D graphene nanoparticles. Yuehe Lin et al [76-80] presented an electro chemical sensor for paracetamol based on the electro catalytic activity of functionalized graphene. Graphene modified GCE obviously promotes the sensitivity of the determination of paracetamol with a low detection limit of 32nm and a satisfied recovery from 96.4% to 103.3% [81-83]. Graphene-PEG-Fe3O4 hybrid has been studied for application on MRI and localized photo thermal therapy of magnetically guided cancer cells [92]. Nanoscale graphene oxide has been used for protecting DNA from cleavage and its effective cellular delivery due to less-toxicity of graphene oxide and strong absorption of DNA on graphene surface [90-91] nanopores of 22nm diameter in graphene studied the translocation of individual DNA molecule through the nanopore confirmed by the change in the conductance of the nanopore. Jia don Huang [100] developed an ultrasensitive electrochemical immunosensor based on nano gold particles. (AuGN-HRP-Aab) was used as the label for the immunosensor. An electro chemical immunosensor for the sensitive detection of carbohydrate antigen 1.5-3 (CA 15-3) was fabricated based on ionic liquid functionalized graphene and Cd+2 nanoporous TiO2.

Drug bio sensor using Graphene and Nafion film modified GCE was fabricated for the detection of codeine displaying an excellent analytical performance and enhanced applicability for code in detection in wine samples and cough syrup. A nano composite of Gr and CoFe2O4 nanoparticles modified CPE was proved to be an ultrasensitive electrochemical sensor for codeine and ACOP with low detection limits of 0.011 and 0.025nm respectively. Chandra et al [97] reported the synthesis of magnetite- rGO hybrid which is superparamagnetic and shows very high binding capacity for AS(III) and AS(v) which can be used for metal removal from the contaminated environment. Wang et al [98] investigated the synergistic adsorption of humic acid and heavy metal ions, specifically pb(II) and cd(II) using mesoporous silica-graphene oxide composites. Graphene based materials are Good for photo thermal agents as they absorb strongly in NIR region. Wang et al [93] reported the synthesis of reduced graphene oxide red composite (rGO-R) as electrodes for CDI process in brackish water desalination and drinking water purification. Wen etal [94] prepared graphene based hierarchically porous 3D carbon by a dual template strategy and explored its electrode performance for CDI. 3DGHPC presents a higher electro sorption capacity of 6.18 mg-g-1 and an increased desalination efficiency of 88.98%. Zho et al [96] prepared graphene sponges by hydro thermal treatment using thiourea. These (GSS) show a tumble pore structure surface properties and high adsorption ability for various types of water contaminations including the presence of arsenic in drinking water.Sin et al [95] designed functionalized nanopores in graphene monolayers using MD simultaneous and showed that they could serve as ionic sieves of high selectivity and transparency. Xiaoli Zhang [99,100] fabricated graphene/Au nanoparticles modified GCE (GR/Au/GCE) for the detection of EP, a harmone secreted by the medulla of adrenal glands is an important catecholamine inhibitory neurotransmitter with high sensitivity. GR as well as pd nanoparticles presented perfect characteristics for the proposed sensor like excellent electro catalytic activity for the oxidation of NE.

IV. CONCLUSIONS

Graphene based materials have a profound impact on electro analysis, electrocatalysis sensors and bio sensors. In sensing application, graphene-based materials featured with good conductivity and large specific area have demonstrated accurate, rapid, selective, sensitivity. Due to high mechanical strength and surface area electronic and thermal properties and its wide range of applications in various fields of graphene has become one of the well-studied. The electronic properties of graphene synthesized by wet chemical routes have to be improved for large scale applications.

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