SURFACE FUNCTIONALISATION OF GRAPHENE OXIDE

SURFACE FUNCTIONALISATION OF GRAPHENE OXIDE

A literature review submitted in partial fulfillment of the
requirements for the degree of **Master Of Science In Chemistry**
(Organic Chemistry).

BY

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APRIL 2022

DECLARATION

I declare that the literature review titled **"Surface functionalization Of Graphene Oxide"** has been carried out by me in the Chemistry Department, School of Chemical Sciences, Goa University. The information derived from the literature has been duly acknowledged in the text and a list of references is provided.

CERTIFICATE

I certify that the literature review titled: **“Surface Functionalisation Of Grahene Oxide”** has been successfully completed under the guidance of Dr. Kashinath Dhumaskar during the year 2021-2022 in the partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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ACKNOWLEDGEMENT

The literature review titled: “Surface Functionalisation Of Graphene Oxide” has been successfully completed under the guidance of Dr. Kashinath Dhumaskar sir during the year 2021-2022 in the partial fullfilment of the requirements of the degree of Master Of Science In Chemistry.

I had a good learning experience learning the applications and future prospects of undertaking a literature survey which was possible due to the timely guidance of Dr. Kashinath Dhumaskar Sir and our respected Dean Dr. Vidhyadatta Verenkar Sir. I also thank the entire library faculty for helping me out for searching different books relevant to my topic.

Last but not the least I thank my parents, friends and other people who are directly or indirectly in the successful completion of my Literature survey.

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ABSTRACT

The chemistry of graphene oxide is explained in this review. Particular emphasis is directed towards functionalization of graphene oxide. Functionalized graphene oxide increases its solubility in various organic solvents. Graphene oxide (GO) with oxygen containing functional groups can be selectively modified by small biomolecules to achieve heterogeneous surface properties such as hydrophilicity, electrical conductivity, and selectivity for electrochemical sensing applications etc. However, parent graphene oxide (unmodified) shows less solubility in water as well as other organic solvents and does not exhibit good conductivity.

INTRODUCTION

Graphene is a two-dimensional material made of carbon atoms which is sp^2 hybridized that are bonded together in a repeating pattern of hexagons (honeycomb like structure). Graphene is good conductor of electricity and heat and therefore has wider applications in almost every field like electronics, medicine, graphene batteries etc. Due to its expensive nature and because of some of its limitations like its hydrophobic nature graphene is replaced with its derivative or related material that is Graphene oxide (GO).[1] The molecular structure of GO consists of carbon, hydrogen and oxygen and it is an oxidized form of graphene with a single layered carbon structure, incorporated with oxygen containing groups such as carbonyl (C=O), hydroxyl (-OH), carboxyl (-COOH), alkoxy(C-O-C) and epoxy groups (fig. 2). GO flakes does not have a regular shape and its size depends on different

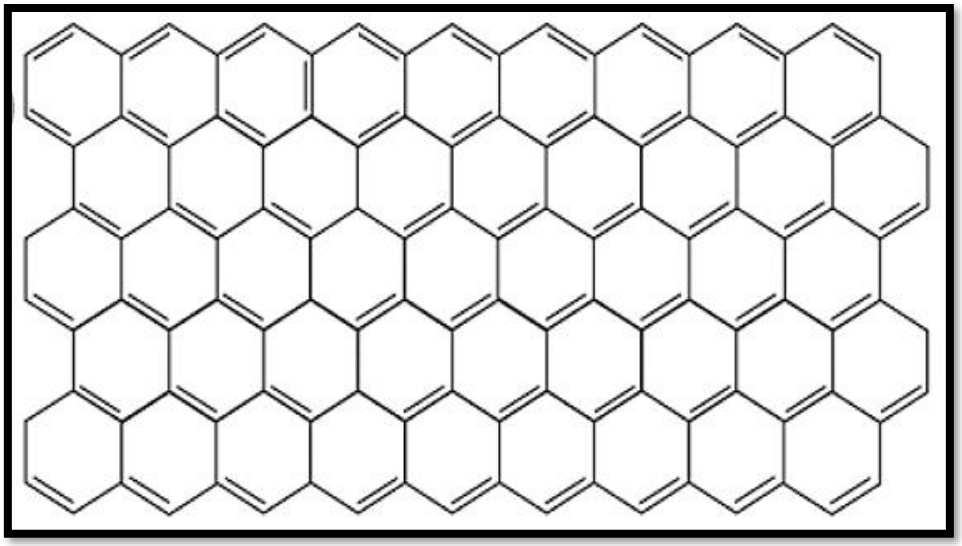

Figure 1: Structure of Graphene

parameters such as domain size of graphite, oxidation procedure, and oxidation time and it ranges from few nm to few mm. [2]

GO was first reported by Schafhaeult in 1840 and was first synthesized by oxford chemist Brodie in 1859.[3] GO synthesize through two main routes they are top-down method and bottom-up method. But bottom-up method has some disadvantages and also it is time consuming therefore top-down method is selected for the synthesis of GO. There are many other routes to synthesize GO they are, Chemical synthesis in which graphene is treated with CrO_3 as the oxidizing agent instead of $KMnO_4$, Mechanochemical synthesis, Electrochemical synthesis, Biosynthesis.[1]

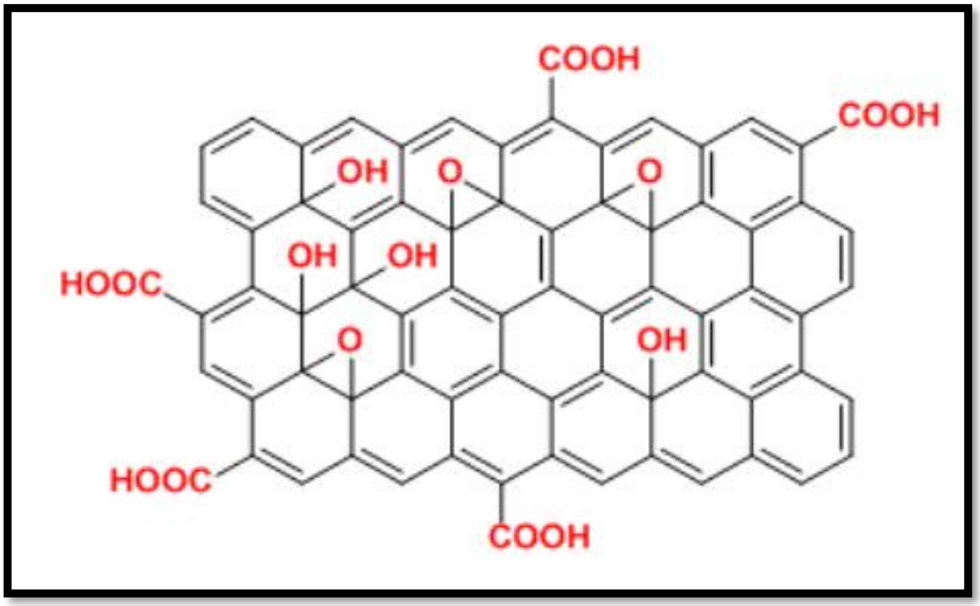

Figure 2: Structure of Graphene Oxide [3]

Graphene oxide becomes hydrophilic in nature due to incorporation of these oxygenated groups and therefore used to prepare various water and organic solvent-based suspensions. Also, there is a possibility for surface functionalization of GO, and is reported to have wider applications.[4] Highly oxidized forms of GO are poor conductor of electricity.[3] Researchers have reported upon reduction of GO to form reduced graphene oxide (rGO) its electrical and thermal properties can be greatly improved.[5] Also mixture of GO and rGO are prepared to achieve mechanical properties such as tensile strength etc.

Functionalization occurs by reacting two different functional groups such as functional group of organic compound with epoxy or carbonyl or other oxygenated group on GO.

GO has wider applications in biomedical fields such as in drug delivery, cancer therapy, bioimaging, and biosensor.[3] It is best suited for hydrogen storage. Also used as stabilizing agent in oil-in-water emulsions. GO membranes are widely used as prominent materials for water treatment application because of its hydrophilic nature. Also used as corrosion resistance. The study has reported that GO was better than rGO in long term corrosion protection of steel substrates.[6]

LITERATURE REVIEW

SYNTHESIS OF GO

Staudenmaier and Brodie's method of synthesis of GO has some disadvantages and are hazardous in nature therefore Hummer's method is followed.[4] Hummer and Offeman are the two well-known chemists from Mellon institution of Industrial Research, synthesized GO in 1958 by oxidizing graphite with concentrated H_2SO_4, $KMnO_4$, and $NaNO_3$ mixture.[3]

They have taken mixture of graphite flakes and $NaNO_3$ in volumetric flask containing sulfuric acid and kept in ice bath(0-5°C) for 2 hrs. Then slowly $KMnO_4$ as oxidizing agent was added to the mixture and the ice bath was then removed and they kept the mixture for two days with stirring at 35°C. The reaction temperature shoots up rapidly to 98°C with effervescence when water was added for dilution. Again, they have added water for diluting the content and then they treated this mixture with hydrogen peroxide to stop this reaction. A GO powder was obtained when dried after centrifugation with HCl.[7]

But this method also has some disadvantages as it generates some hazardous gases like NO_2, N_2O_4 etc. Then to overcome these disadvantages modified Hummer's method was proposed where sodium nitride was replaced with phosphoric acid and amount of $KMnO_4$ added was increased, so that it can eliminate the generation of hazardous gases, with a greater number of hydrophilic carbons and identical conductivity with Hummer's method.[3] Then modified Hummer's method of synthesis was proposed in which oxidation and exfoliation of graphite sheets was performed.[7]

Gaur and its co-worker emphasized on applications of GO in many fields of science and technology. GO has many properties over other carbon-based materials like graphite, diamond, pristine graphene due to its exceptional properties like high surface area, exceptional biocompatibility, water loving nature, resistance to corrosion, the profusion of the low-cost source material, easy synthesis methods. They mentioned that there are some issues in the yield of graphene from GO due to addition of diverse chemicals induces scums that affect the properties of graphene oxide.[3]

FUNCTIONALISATION OF GRAPHENE OXIDE

The current accessibility of water-soluble graphene oxides (GOs) by acid oxidation of graphite powder has permitted the functionalization of graphene sheets through several solution reactions. Lately, ample struggle has been made to synthesize organic soluble graphene oxide by integrating organic moieties onto oxygen-containing groups (e.g., −OH, −COOH, C=O, C-O-C, epoxy) of graphene oxide.

Examples involve the integration of octadecyl amine (ODA), 9 phenyl isocyanate, and 2-amino-4,6-didodecylamino-1,3,5-triazine (ADDT) on graphene oxide to extend its solubility in organic solvents.[8] Cautious functionalization of GO increases its conductivity, stability, and selectivity in applications of electrochemical sensing, in addition to this it enhanced the sensitivity of GO by increasing the surface area.[9]

Researchers have stated that the chemical structure of GO has been examined using carbon nuclear magnetic resonance (13C NMR), IR, XRD, Raman, AFM etc.[10] Which confirms that there are many oxygen containing groups present on the sheets. Yet, GO sheets which is reduced are hydrophobic in nature and display less conductivity than graphene because some of the oxygen moeties have not been removed. In order to avoid accumulation of graphene sheets, covalent or non-covalent functionalization is achieved. Due to oxygen-bearing functionalities, it is more susceptible to functionalized GO via covalent interactions, that is, esterification, amidation, amination, or urethane linkage. Covalent functionalization is done via two means ''grafting from'' and ''grafting to'' methods.[2]

Recently, researchers have reported the functionalization of Graphene Oxide with Hyperbranched Polyamide-Amine and Microcrystalline Cellulose (MCC) for Effective Adsorption of Heavy Metal Ions. Hyperbranched polymers have ample of terminal active groups and various internal cavities shaped by branched molecular structures. Hyperbranched polyamide-amine (HPAMAM) grants a spherical branched molecular structure with several terminal amino groups and advanced nanocavities. HPAMAM was grafted on top of GO by making an amide bond amid the carboxyl group of GO and amino group of HPAMAM. For effective adsorption, the favorable condition is grafting of cellulose on GO which increases the number of hydroxyl groups and contact area with pollutants.[11]

This study suggests to incorporate HPAMAM and MCC on the surface of GO to expand the contact area and affinity amid the adsorbent and pollutants to further progress the adsorption capacity of GO. The HPAMAM and MCC functionalized GO adsorbent was synthesized via the synthesis method shown in Figure 3, for the adsorption of heavy metal ions in water like Pb (II), Cd (II), and Cu (II).

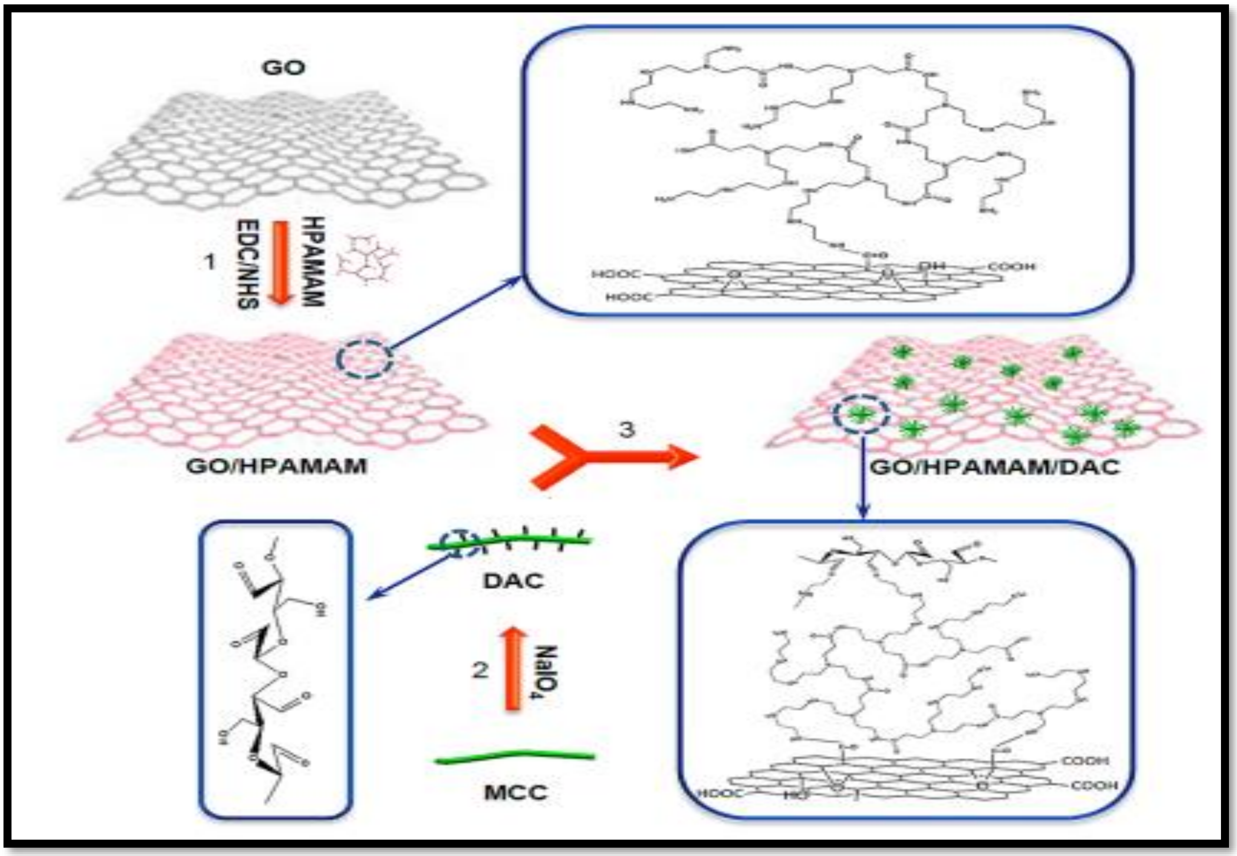

Figure 3: Schematic of the synthesis of GO/HPAMAM/DAC Adsorbent[11]

It contains the following steps: (1) In the existence of a catalyst (EDC/NHS), HPAMAM was grafted on top of GO by formation of an amide bond so that the number of active groups should increase. (2) Then oxidation of MCC to DAC (Dialdehyde cellulose) using $NaIO_4$ for incorporating aldehyde groups on the cellulose molecular chain for the grafting of DAC on GO/HPAMAM. (3) The DAC was grafted onto GO/ HPAMAM and this was done by forming a Schiff-based structure amid the aldehyde group of DAC and the amino group of HPAMAM to developed micro bumps on the surface of GO.[11]

To confirm the covalent grafting of HPAMAM and DAC on GO, Fourier-transform infrared spectroscopy (FT-IR) spectra were carried out. To study the crystallographic structure of GO-based adsorbent X-ray diffraction (XRD) spectra were carried out. Then thermogravimetric analysis (TGA) was performed to determine the weight loss at variable temperature.[11]

The adsorption performance was observed, it was reported that the plane GO which is unmodified without any functionalization had the worst adsorption capacity that is 42.4, 28.7, and 10.8 mg/g for Pb (II), Cd (II), and Cu (II), respectively, the adsorption capacity of GO was enhanced to 112.8, 58.9, and 24.3 mg/g for Pb (II), Cd (II), and Cu (II), respectively after grafting HPAMAM. And it was primarily due to the incorporation of several nitrogen- and oxygen-involving groups on GO. And finally, the adsorption capacity of GO exhibited more enhancement that is 401.5, 242.8, and 131.4 mg/g for Pb (II), Cd (II), and Cu (II), respectively after grafting DAC. So, the adsorption performance of GO with hyperbranched polymers and cellulose may deliver an innovative strategy for enlightening the further process.[11]

S. Wang et al, reported the synthesis of functionalized GO using polymethyl methacrylate (PMMA) and polystyrene (PS) which was grafted on graphene material. Graphene oxide (GO) was coated with polydopamine (PDA) which is a reactive underlayer as well as a reducing agent. The incorporation of polymer brush-decorated rGO in the PMMA or PS matrix increases the glass transition temperature (Tg), thermal conductivity and thermal stability of the polymer matrix. The raise in Tg of PMMA/rGO-g-PMMA and PS/rGO-g-PS nanocomposites was about 15° C and 13° C more than that for PMMA and PS, correspondingly.[12] The temperature equivalent to 10% weight loss of PMMA/rGO-g-PMMA nanocomposites was boosted to 344.8°C. In addition, thermal conductivity of PMMA nanocomposites was 66% greater than PMMA at 25°C. The study offers a simplistic path to synthesise polymer brush-functionalized rGO, which can improve the compatibility with the polymer matrices for a wide range of applications.[12]

Wang and his co-workers combines the interaction of surface functionalized amino acids with immobilized enzymes and GO. The surface properties of GO are structured via a green reducing agent, amino acid, thus regulating the catalytic activity of the enzyme. The hydrophobic properties and surface charge of GO can be controlled by using a variety of amino acids. The modified GO with amino acid is significantly reduced, and the water repellent nature increased under control. Amongst all amino acids, arginine (Arg) and lysine (Lys) both has strong adsorption and reducibility on GO. In accordance, cysteine (Cys) has the weakest reducibility on GO. Because of the interesting activation process of Thermomyces lanuginosus (TL) lipase, on altering the surface hydrophobicity and charge properties of the carrier, the TL lipase can be halted on the carrier like a lid opening. Glu-GO-Lipase (glutamic acid-graphene oxide) has the uppermost comparative enzymatic activity amid other immobilized samples. Via adsorption isotherm and thermo- dynamic studies, it was found that the adsorption of lipase on rGO and GO is reliable with the Freundlich model, and phenylalanine-GO (Phe- GO) and cysteine-GO (Cys-GO) have the major enzyme weightage. The adsorption volume rises on heating up to 70 °C.[13]

Rooyanian et al, work on surface functionalization of graphene nanosheets by benzoic acid and its application toward Pb (II) sensing. They first obtained the GO by Hummer's method. Then by means of environment friendly and easy technique with glucose the GO was reduced and converted into graphene nanosheets and the surface of the graphene nanosheets was functionalized with benzoic acid (BA) diazonium salt and characterized by physical techniques like FT-IR, XRD, SEM, AFM etc. The modified carbon paste electrodes (CPE) by means of graphene oxide (CPE/GO), graphene nanosheets (CPE/GNS) and graphene nanosheets functionalized with benzoic acid (CPE/GNS-BA) shown in figure 4 were characterized electrochemically.[14]

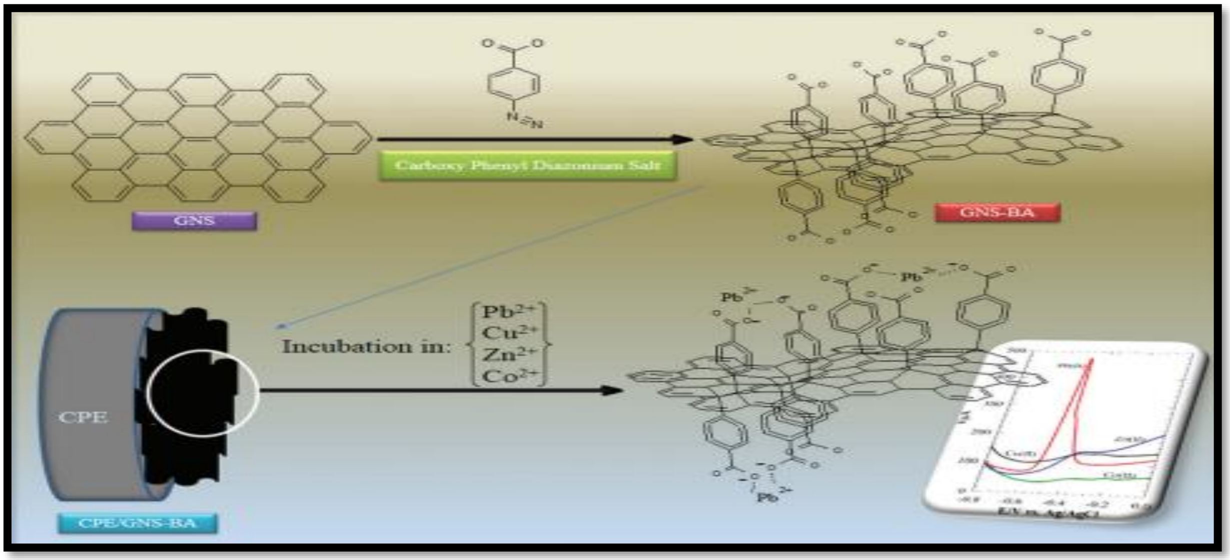

Figure 4: Fabrication steps for the preparation of a CPE/GNS-BA electrode and its application in the selective detection of Pb (II)[14]

For the first time, the synthesized improved carbon paste electrode was studied for quantitative purpose of Pb (II). OSWV for detection of Pb (II) was established. a detection limit of 1.5×10^{-10} M and a linear response from 1.0×10^{-9} to 1.0×10^{-3} M Pb (II) were attained, which shows that in absorbing Pb (II) ions, there is a high competence of the CPE improved with graphene nanosheets functionalized with benzoic acid (GNS-BA). The study offers a simple approach for building of innovative sensors and ion adsorbents based on the molecular functionalization of graphene nanosheets through a diazonium grafting route.[14]

V. Georgakilas et al, works on functionalization of graphene and reported that there is so much work to be done to understand the properties of graphene and functionalized graphene, thus opening innovative avenues of research. One just have to focus on the structure of GO to understand that there are multiple manipulations that can be chemically accomplished, if the structure is understood fully. The review offers insight into the several ways to functionalize graphene and graphene derivatives, thereby increasing the number of potential applications for graphene-based materials.[6] The modes of functionalization can be classified according to the method and materials used and as such have been categorized as covalent functionalization, noncovalent functionalization, substitutional doping of graphene, and hybridization with nanoparticles, nanowires, and other materials.[15] These several methods of functionalization provides various ways to increase the present usages of graphene, that is, bioimaging or band gap opening, which can be used in electronics. Following are the organic covalent functionalization reactions of graphene and its derivatives, which includes two general routes: (a) the covalent bond formation between the free radicals or dienophiles and C=C bonds of pristine graphene and (b) the formation of covalent bonds between oxygen groups of GO and organic functional groups. [16]

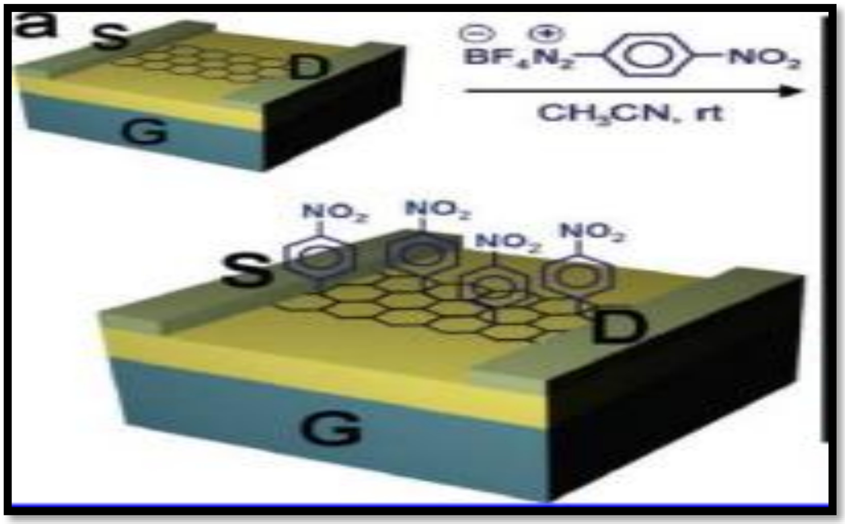

Figure 5: Chemical doping of graphene with 4-nitrophenyl groups [16]

Functionalized graphene can be produced upon heating of a 4-nitrophenyl diazonium salt. A highly reactive free radical is produced, which attacks the sp2 carbon atoms of graphene forming a covalent bond in presence of CH3CN (fig. 5).[16]

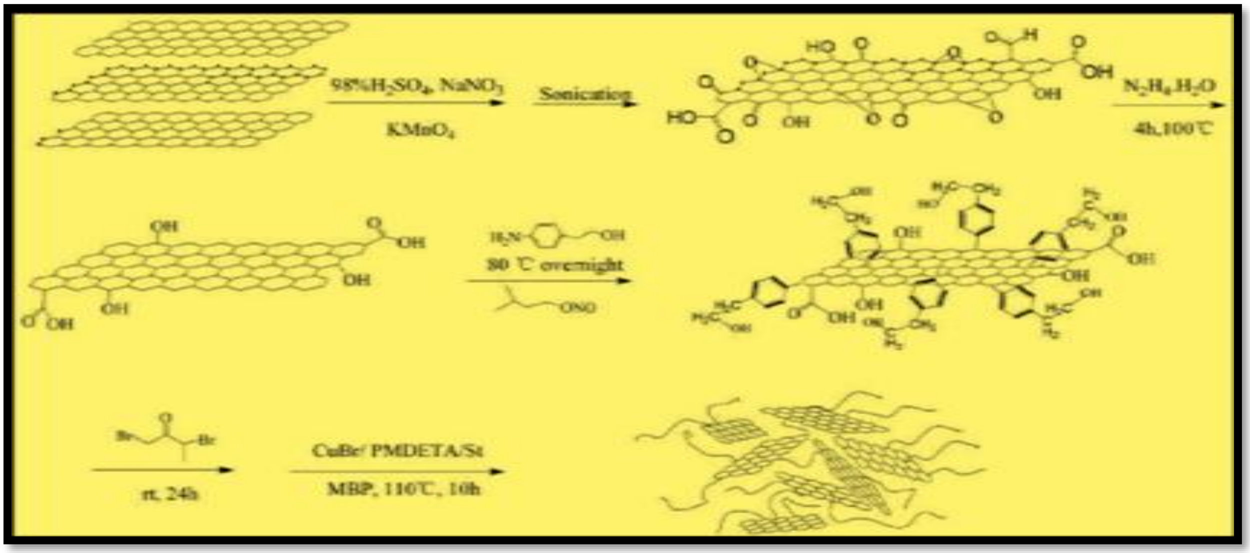

Figure 6: The attachment of aryl groups on graphene nanoplatelets and the formation of polystyrene chains grafted on graphene nanoplatelets [16]

Graphene was oxidized to GO in presence of oxidizing agent, then hydroxylated aryl groups grafted covalently on graphene by the diazonium addition reaction which act as initiators for the polymerization of styrene via the atomic transfer radical polymerization (ATRP) method (Figure 6). The polymeric chains are covalently grafted on the graphene surface. [16]

Graphene sheets substituted with pyrrolidine rings in presence of azomethine ylide. The azomethine ylide was formed by the condensation of 3,4-dihydroxybenzaldeyde and sarcosin (fig. 7). The hydroxyl groups incorporated onto a graphene sheet increases its solubility in polar solvents such as ethanol and N, N-dimethylformamide (DMF).[15]

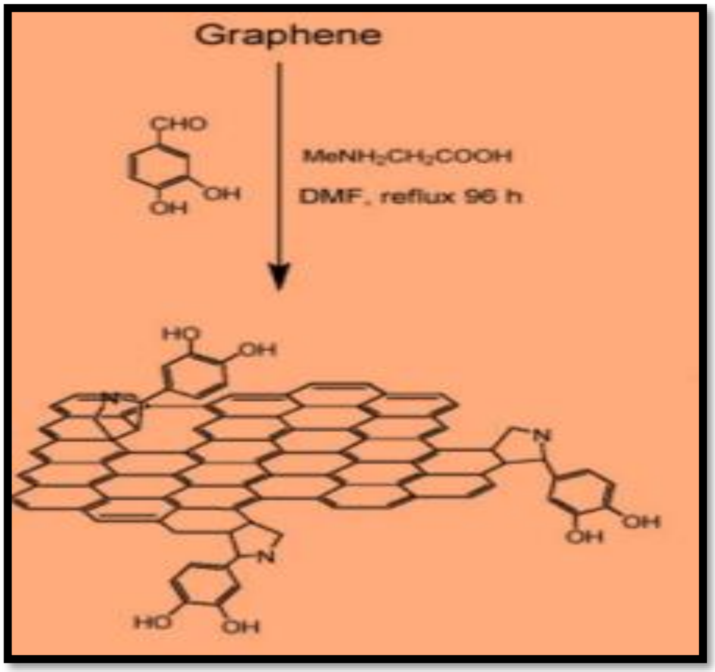

Figure 7: Schematic representation of 1,3 dipolar cycloaddition of azomethine ylide on graphene

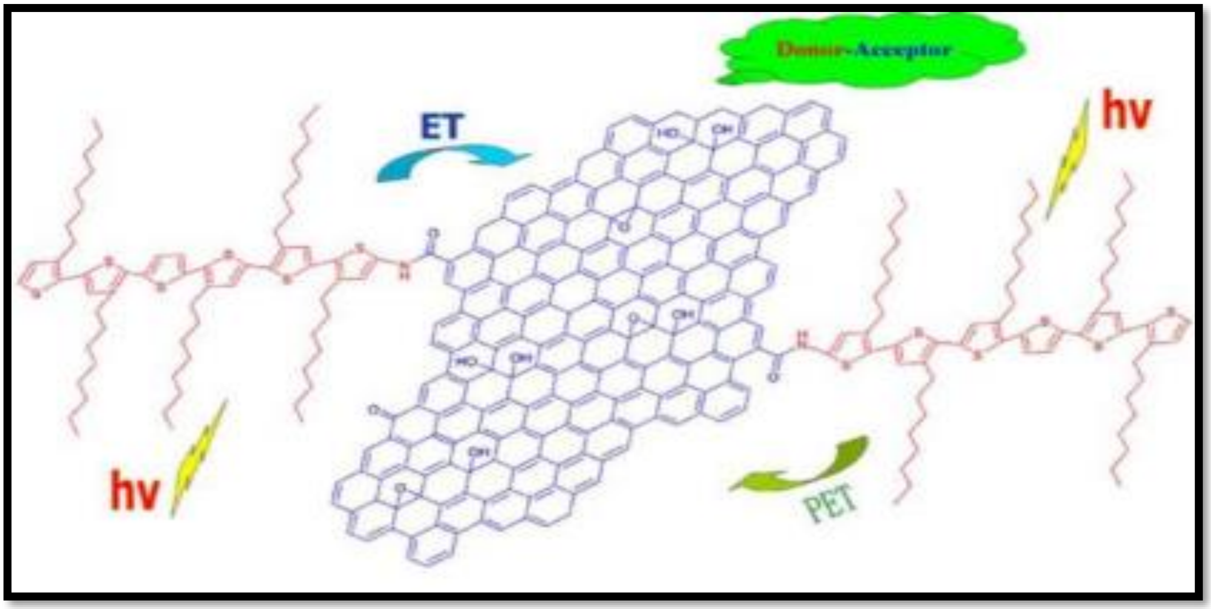

Figure 8: Structure of oligothiophene functionalized GO [16]

Amine-terminated oligothiophenes can be grafted on GO nanoplatelets through the formation of covalent amide bonds between carbonyl group of GO and amine group of oligothiophene (fig. 8). There is a strong interaction between GO and oligothiophene.[16]

Figure 9: The reaction between GO and CH2OH terminated P3HT chains through an esterification reaction [16]

Yu et al, reported functionalization of GO with −CH2OH terminated regioregular poly(3- hexylthiophene) (P3HT) through the formation of ester bonds with the carboxyl groups of GO nanoplatelets in presence of triethylamine base and THF solvent (fig. 9). P3HT-GO was soluble in common organic solvents due to presence of large number of hydroxyl groups.[16]

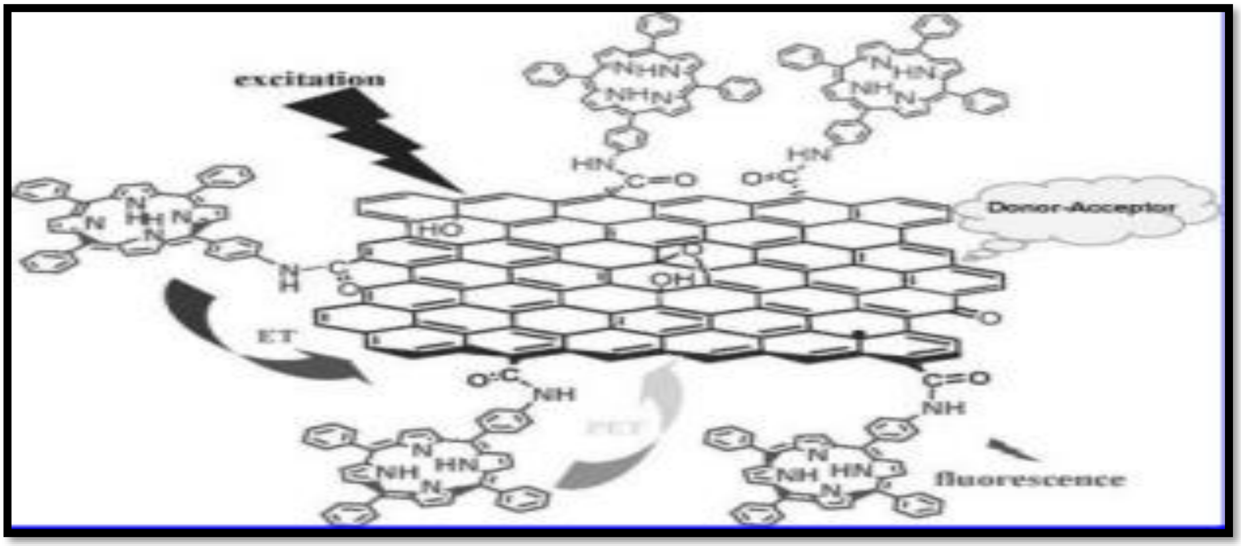

Figure 10: Schematic representation of the product of the reaction between GO and amine functionalized porphyrin [16]

Apart from conjugated polymers, organic chromophores such as porphyrins, functionalized on GO through the formation of amide bonds between amine functionalized porphyrins and carboxylic groups of GO (fig. 10).[15,16]

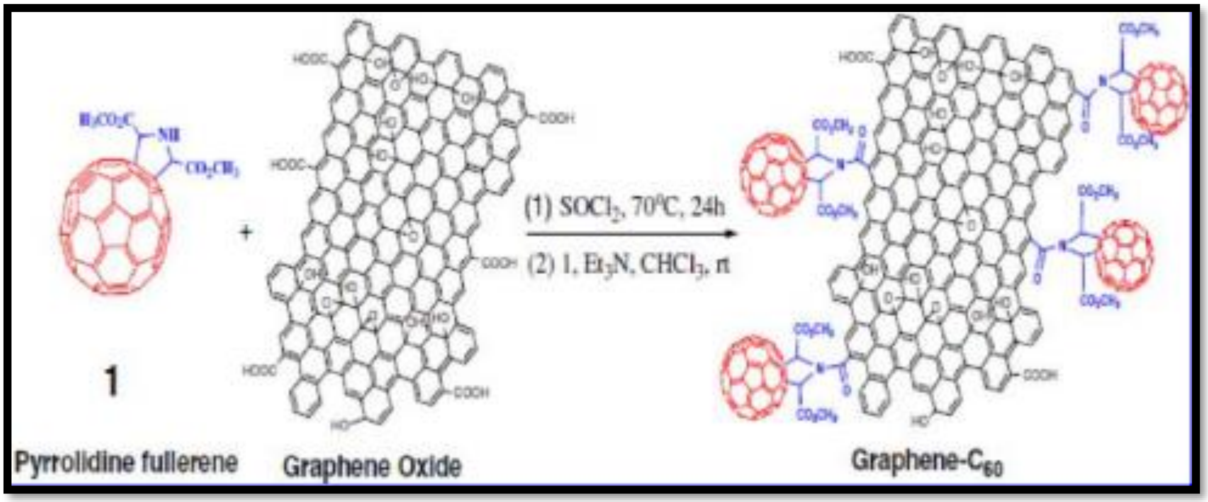

Figure 11: Representation of the formation of C_{60}-GO composite [16]

Zhang et al, have reported the formation of a hybrid material by covalent linking of C_{60} with GO via an amide bond formation between a pyrrolidine ring modified C_{60} and the carboxyl groups on the GO surface (fig. 11).[16,15]

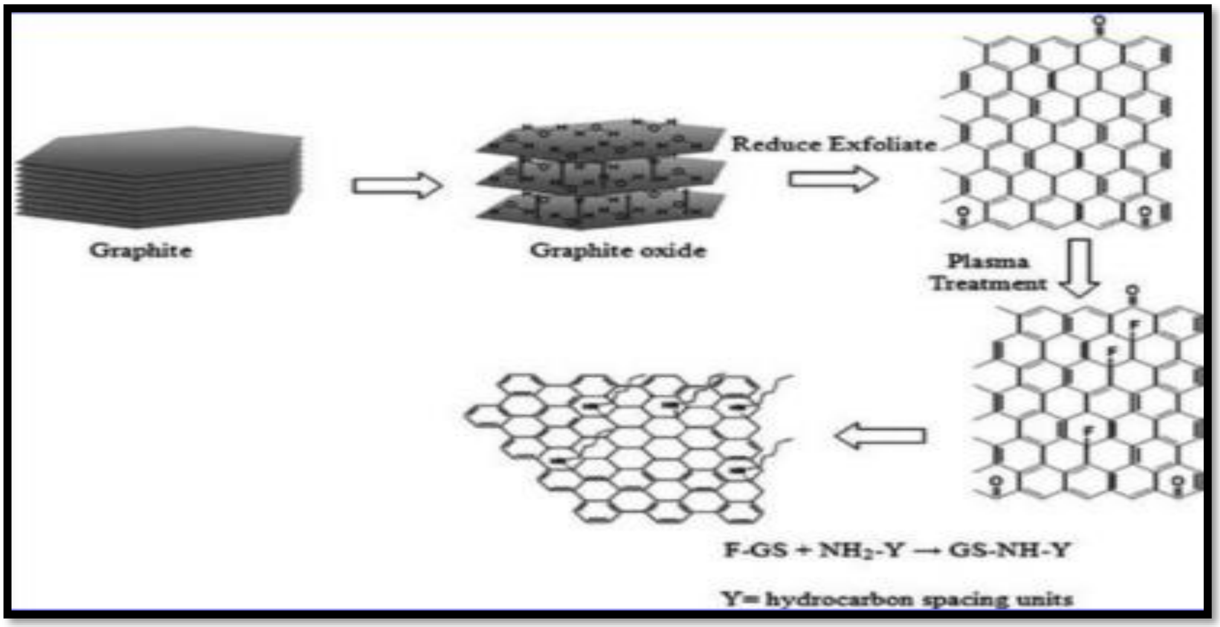

Figure 12: Preparation of butylamine-functionalized rGO nanoplatelets. [16]

rGO nanoplatelets were first functionalized by fluorine using plasma-assisted decomposition of CF_4 for introduction of butyl amine onto graphene sheets. The fluorinated GO was then converted to butylamine-functionalized GO by replacing fluorine atoms with butylamine groups (fig.12).[16]

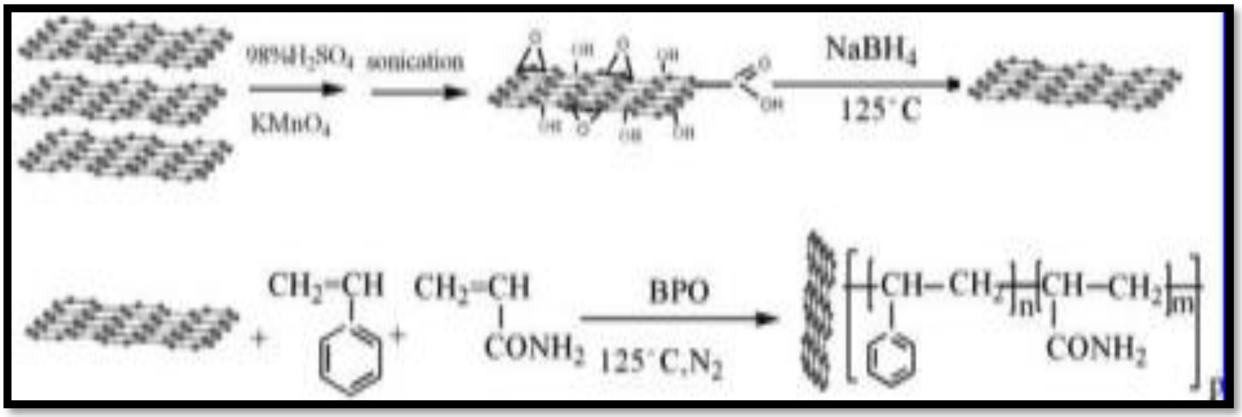

Figure 13: Schematic representation of covalent attachment of PS/PAM copolymer to rGO [16]

Shen et al, used rGO for the preparation of “amphiphilic” graphene. They used $NaBH_4$ for the reduction of GO to rGO nanoplatelets, which were incorporated with polystyrene−polyacrylamide copolymer (PS−PAM) by in situ free radical polymerization, in presence of benzoyl peroxide initiator (fig. 13).[16]

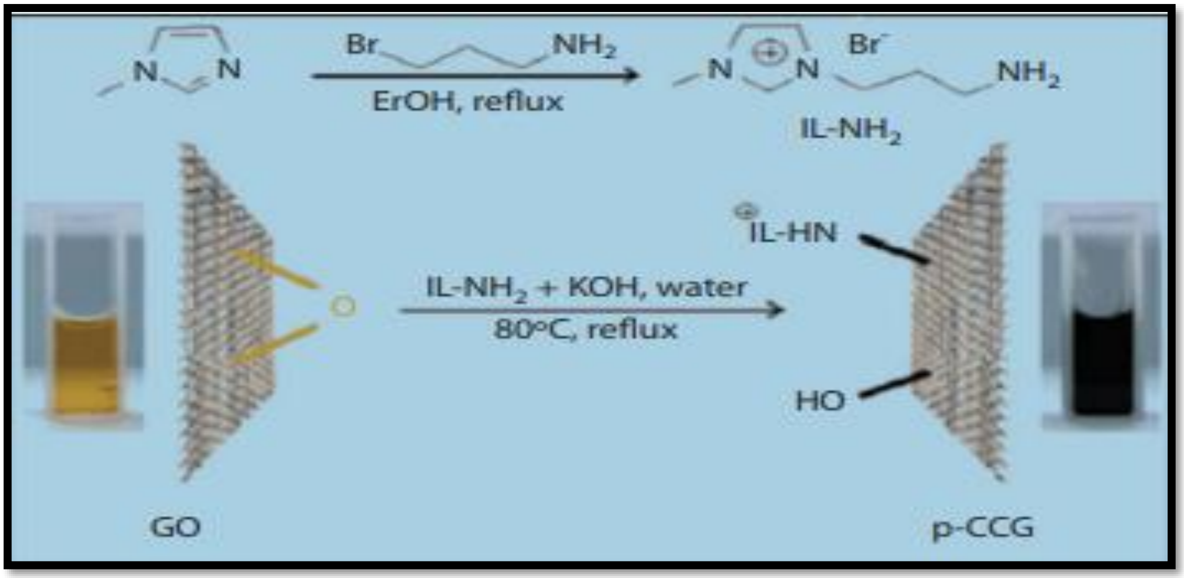

Figure 14: Illustration of preparation of imidazolium-modified GO [15]

Yang et al, modified the partially rGO with imidazolium derivatives such as 1-(3-aminopropyl)-imidazolium bromide (IL-NH_2), which can be attached to the epoxy groups of GO nanoplatelets by refluxing the mixture at around 80°C in presence of KOH and water (fig.14).[15]

B. Sung et el, reported a method of simultaneous reduction and surface functionalization of graphene oxide by a one-step poly(norepinephrine) functionalization. To functionalize the GO a new mussel-inspired surface chemistry was developed. It is based on the oxidative polymerization of norepinephrine (fig.15), which was resulted in simultaneous reduction and surface functionalization of GO (fig. 16). The poly(norepinephrine)-coated rGO converted to a multi-purpose platform for graphene nano-composite materials through the ability of ring-opening polymerization of caprolactone and establishing silver nanoparticles on rGO surfaces. The mussel-inspired surface alteration is non-hazardous as it uses water as a solvent. The study demonstrates several advantages employing mussel-inspired surface chemistry to GO.[17]

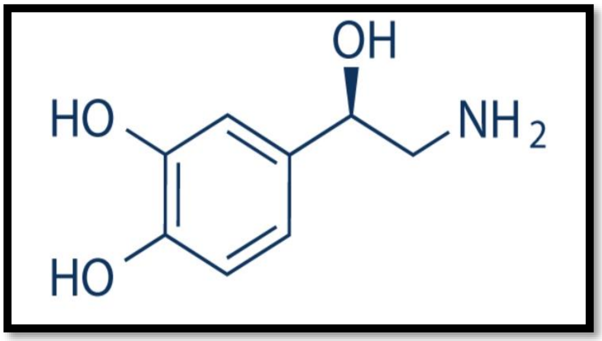

Figure 15: Structure of norepinephrine

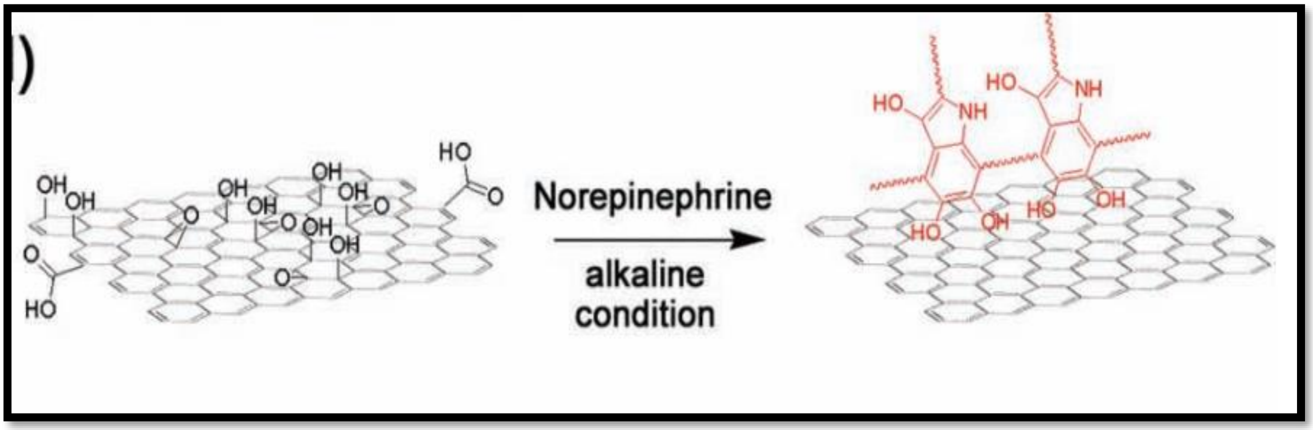

Figure 16: Poly(norepinephrine) coating on the surface of GO [17]

CONCLUSION

Graphene Oxide films were successfully prepared via modified Hummer’s method and characterized using XRD, IR, Raman, 13CNMR spectroscopy. The presence of oxygen bearing functional groups provided more opportunities for potential applications of GO in many areas. Here we discovered a convenient methodology for synthesizing functionalized GO with various organic compounds via covalent functionalization method. It is interesting to note that the functionalized graphene oxide with organic compounds increases its solubities in various organic solvents such as DMF, THF, chloroform, toluene etc. This data will provide a reference to further study the nature of graphene and graphene oxide.

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