Final Minor research Project submitted to UGC

BY

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TITLE : Synthesis and Characterization of functionalized hybrid nanomaterial of graphene and graphene oxide.

FACULTY : **SCIENCE**

SUBJECT : **CHEMISTRY**

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Synthesis and Characterization of functionalized hybrid nanomaterials of Graphene and Graphene oxide.

The 21st century demands new, renewable, more efficient, more compact, economically viable materials. In 2004 after the discovery of Graphene (1) at the University of Manchester by Andre Geim & Konstantin Novoselov began a new era of the "wonder material". Graphene has wide range of applications including Super-capacitor (2), Super-conductor (3), Energy storage (4), DNA sequencing (5), Desalination process (6), biosensors (7) and many more. The synthesis of Graphene has been classified under two different approaches i.e. Top-Down approach and Bottom-Up approach.

The Top-Down approach refers to using macro molecules like Graphite (which is technically millions of Graphene layers stacked together and breaking down to micro/nano molecules like Graphene. One the method mentioned under Top-Down approach is Chemical exfoliation (8) method also commonly known as Hummers method in which Graphite is Chemical treated with oxidants like $KMnO_4$ etc and highly concentrated acids like H_2SO_4 etc. hence resulting into formation of Graphitic Oxide This Graphitic oxide is later exfoliated using different methods and the resulting product is referred to as Graphene oxide. This Graphene oxide is later reduced using suitable chemical method. The resulting product is Graphene.

The other method included in Top-Down approach is Electrochemical exfoliation (9) in which a typical Electrochemical cell is constructed. The anode of this cell is Graphite sheet/rod and the cathode of this cell is copper sheet or Graphite sheet/rod and both anode and cathode are dipped in electrolytes like Sodium Sulphite etc and a DC current of 10 V is passed through the cell. Soon the Graphite rod/sheet starts depleting and later the entire electrode is disintegrated in solution which is later sonicated to obtain dispersion of high purity Graphene.

The Bottom-Up approach refers to usage of molecule precursors like methane, ethene, ethyne and other hydrocarbons to accumulate and form highest purity single layer Graphene under suitable temperature and pressure. One of the methods classified under Bottom-Up approach is Chemical Vapor Deposition (CVD) method. In this CVD process a substrate is diffused on thermally disintegrated precursors at high temperature. It deposits on thin films, crystalline, solid, liquid or gaseous precursors on the surface of the substrate. The deposit of high quality Graphene from CVD process is usually done onto various transition metal substrate like Ni (10), Pd(11), Ru(12), Cu(13) etc. CVD growth of graphene has been mainly practiced on copper and nickel substrates. The metal is exposed to methane gas and hydrogen gas under extreme temperature and pressure causing the growth of single layer of graphene as separate islands eventually growing and forming perfect singular layer i.e. extra pure.

The other method Classified under Bottom-Up approach is Epitaxial growth of Graphene on SiC substrate (14). The SiC substrate is heated at a temperature (around 1200 degree Celsius) and the conditions of the chamber are set accordingly. UHV (Ultra High Vacuum)

hinders the uniform growth of MLG (Multi-layer Graphene) and favors the bilayer Graphene. The Si atom evaporates due to the thermionic emission leaving behind carbon atoms on the remaining substrate. Carbon layer accumulating on the substrate are controlled by controlling the temperature and pressure. The final SiC substrate is covered with carbon layers which can either be monolayer, bilayer, or multilayer Graphene.

However, all of the above mentioned methods have their specific limitations; some were moreover not eco-friendly, where as some were not economically viable. This lead to furthermore research into such methods which where economically viable, bulk producing and also eco-friendly. Thereby further research lead to the evolution of Microwave assisted mass scale production of Graphene.

In 2007 One of the first method included in this category was based on Microwave exfoliation of Graphite intercalated compounds (15). The reported work suggest formulation of potassium-THF graphite co-intercalation compound and unlike other ancient methods there was no usage of H_2SO_4 or SO_3. Later this compound was microwave exfoliated and the idea behind this referred to THF being more volatile than H_2SO_4, the sudden heating by microwave irradiation would lead to higher degree of exfoliation and increased surface area hence providing an effective way to obtain high quality of Graphene.

In the year 2010 Yanwu Zhu published research on a simple yet versatile method to simultaneously achieve the exfoliation and reduction of graphite oxide (16) was designed. By treating graphite oxide powders in a commercial microwave oven, reduced graphite oxide materials could be readily obtained within 1 min. Extensive characterizations showed that the as-prepared materials consisted of crumpled, few-layer thick and electronically conductive graphitic sheets Using the microwave exfoliated graphite oxide as electrode material in an ultracapacitor cell, specific capacitance values as high as 191 F/g have been demonstrated with KOH electrolyte.

In the year 2011 Jiang Long and Ming Fang published research on a facile and highly efficient microwave-assisted method was used to synthesize water-soluble Graphene (17) from graphene oxide involving pre-reduction, grafting and post-reduction. Polyacrylamide (PAM) chains have been rapidly grafted onto the graphene sheet via free-radical polymerization under sequential microwave irradiations. Grafting of PAM chains on the sides of the Graphene sheets increased the thickness of the sheets and improved the water-solubility of the Graphene sheet.

D.Raghavan in the year 2015 published method on a fast, cost effective method for synthesis of high quality reduced Graphene Oxide sheets was reported by microwave assisted chemical reduction (18) using Hydro Iodic acid/Acetic acid as reducing agent. Exposure of graphene oxide (GO) with microwave irradiation (4 and 7 h) was found to be more rapid and sustainable reduction as compared to that of the conventional chemical reduction process (48 h).

In 2016 Graphene Nanoplatelets were fabricated from expandable graphite by rapid microwave exfoliation (19). Expandable graphite was irradiated in microwave in full power for 3 min, then was soaked in mixed nitric acid and sulphuric acid at volume ratio of 1:1 for 24 h and re-irradiated, thus graphene nanoplatelets (GNPs) were obtained.

Recently in the year 2017 Juxiang Lin Huang demonstrated green and fast approach to prepare few layered high quality Graphene sheets based on Microwave exfoliation method. The pure graphite was treated with exfoliant like Ammonium bicarbonate(NH_4HCO_3) (20) and under microwave radiation this Ammonium bicarbonate decomposed into H_2O steam CO_2 gas and NH_3 Ammonia gas thus generating a strong pressure that exceed the van der Waals force between two layers of Graphite and resulting into fewer defect Graphene sheets of high purity.

Objectives of the Research

Since Graphene is the advanced material of the future technology the numerous research paper have been published on the different methodology to scale out the production of graphene, and its derivatives from milligrams to the mass production.

However, all of the above mentioned methods have their specific limitations; some were not eco-friendly, where as some were not economically viable. The CVD is one of the best method to produce high quality graphene but it is not economically viable. The basic hummer's method suffers from serious drawback of hazardous and toxic chemicals, time consuming washing and purification step. The other drawback of this method is the reduced graphene obtained by chemical oxidation and reduction produce severe defects in the graphitic structure affect the electronic properties of graphene.

This lead to furthermore research into such methods which is economically viable, bulk producing and also eco-friendly. The natural graphite available abundantly and economical source to produce the graphene and its derivatives.

The functionalized graphene nano hybrid materials is one of the most promising and rapidly emerging research areas in materials chemistry. Nanoscale hybrid materials can be broadly defined as synthetic materials with organic and inorganic components that are linked together by noncovalent bonds (linked by hydrogen bond, electrostatic force, or van der Waals force) or covalent bonds at nanometer scale. The combinations of the distinct properties of inorganic, and organic heterogeneous phase in a single material, either in molecular or nanoscale dimensions enable versatile and tunable properties of novel graphene based nanohybrid material. Graphene-based hybrid material deposited on the surface of Graphene nanosheet prevent the restacking of graphene nanosheet during the reduction of graphene oxide

We established the Environmental friendly methodology to isolate the graphene sheet or few layered graphene sheet swiftly under mild reaction condition without any serious defects (less defects) in the resulting graphene structure. Hereby we adopted the combined approach of microwave-sonic exfoliation to produce few layered or monolayer of graphene by using organic exfoliant. The functional graphene sheet is used to design monohybrid materials with novel electronic properties.

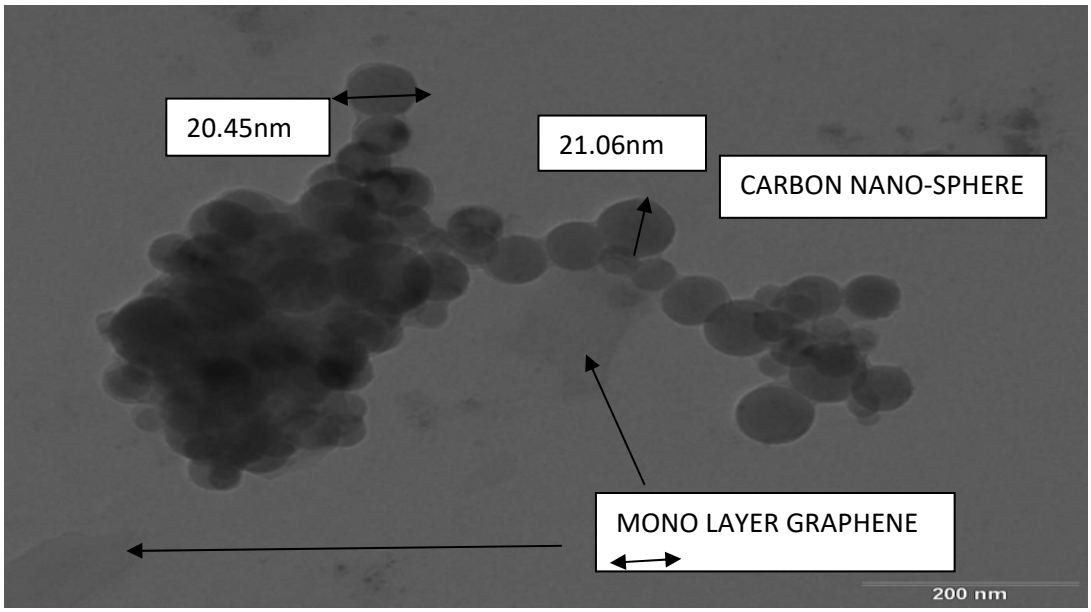
The different methodogy has been divided into the three chapters**.**

CHAPTER-1

Microwave- sonic exfoliation of citric acid treated graphite to Carbon nanosphere and few layer graphene.

INTRODUCTION AND OBJECTIVES:

This Chapter enlighten the Environmental friendly method adopting microwave and ultrasonication approach for direct exfoliation of graphite to monolayer, few layer or multilayer graphene by using **Citric Acid as organic exfoliant**. Inspite of hazardous and more toxic chemical this method utilized simple and easily available citric acid as exfoliant. In this experiment we have used 2.2 GHz domestic microwave energy and low power sonication bath operated at frequency 20KHz. The graphite has been dispersed in different solvents resulting dark black colored dispersion. The larger flakes have been isolated by ultracentrifuge method and the resulting dispersion analyzed by different instrumentation techniques. The final product has been analyzed by FTIR, UV-Visible spectroscopy, XRD and TEM.



The following instrumentations have been used for analysis.

FTIR : IRSpirit FT-IR spectrophotometer by Shimadzu Scientific Instruments Inc. at Department of chemistry, St. Xavier's College, Ahmedabad

UV-Visible spectrometer:

UV1800 UV-Vis spectrophotometer by Shimadzu Scientific Instruments Inc. at Department of chemistry, St.Xavier's College, Ahmedabad

XRD: XRD Diffractometer (powder) PANalytical's X'pert Pro XRD with X'Celerator solid-state detector.The XRD spectra was taken by Cu-Kα radiation taken at SAIF, Chandigadh

TEM: Transmission Electron Microscopy- FEI Tecnai T20 with accelerating voltage of 200kV with LaB_6 filament gun. The sample was analysed at SICARD, V.V.Nagar, Anand.

The above analysis of the graphite dispersion in chapter-1 by adopted methodology supports the few layered graphene sheets and CNS(Carbon Nano Sphere).

CHAPTER-2

Microwave-sonic exfoliation of urea treated graphite to few layer graphene.

INTRODUCTION AND OBJECTIVES:

This Chapter highlights the Environmental friendly method adopting microwave and ultrasonication approach for direct exfoliation of graphite to monolayer, few layer or multilayer graphene by using **Urea as organic exfoliant**. The different weight percentage of urea has been studied as an efficient exfoliant. The urea treated graphite was microwave irradiated at different time interval. Inspite of hazardous and more toxic chemical this method utilized simple and easily available Urea as green exfoliant. In this methodology first Graphite powder is churn into mortar and pastel above room temperature with urea latter it is irradiated in domestic microwave at 2.45 GHz frequency. It is then sonicated in low power sonication bath operated at frequency 20KHz. The urea treated graphite has been dispersed in different solvents resulting dark black colored dispersion. The larger flakes have been isolated by ultracentrifuge method and the resulting dispersion analyzed by different instrumentation techniques. The final product has been analyzed by FTIR, UV- Visible spectroscopy, XRD, SEM , TEM and RAMAN.

Urea treated Graphite powder

MW-irradiated graphite

Here we demonstrated green solvent-free microwave approach using urea as exfoliating agent. The microwave irradiation of urea treated graphite decomposed into H_2O vapor, CO_2 and NH_3 generate the strong pressure which weakening and breaking the the van der Waals forces and π-interactions between stacked graphitic layer. It is then dispersed by mild sonication to the graphene sheets with fewer defects.

Few layered Graphene dispersion in solvent.

The microwave irradiated product is dispersed by ultrasonication and analyzed by different instrumentation technique.

FTIR : IRSpirit FT-IR spectrophotometer by Shimadzu Scientific Instruments Inc. at Department of chemistry, St.Xavier's College, Ahmedabad

UV-Visible spectrometer:

UV1800 UV-Vis spectrophotometer by Shimadzu Scientific Instruments Inc. at Department of chemistry, St. Xavier's College, Ahmedabad

XRD: XRD Diffractometer (powde). The XRD spectra was taken by Cu-Kα radiation at SAIF, Chandigadh.

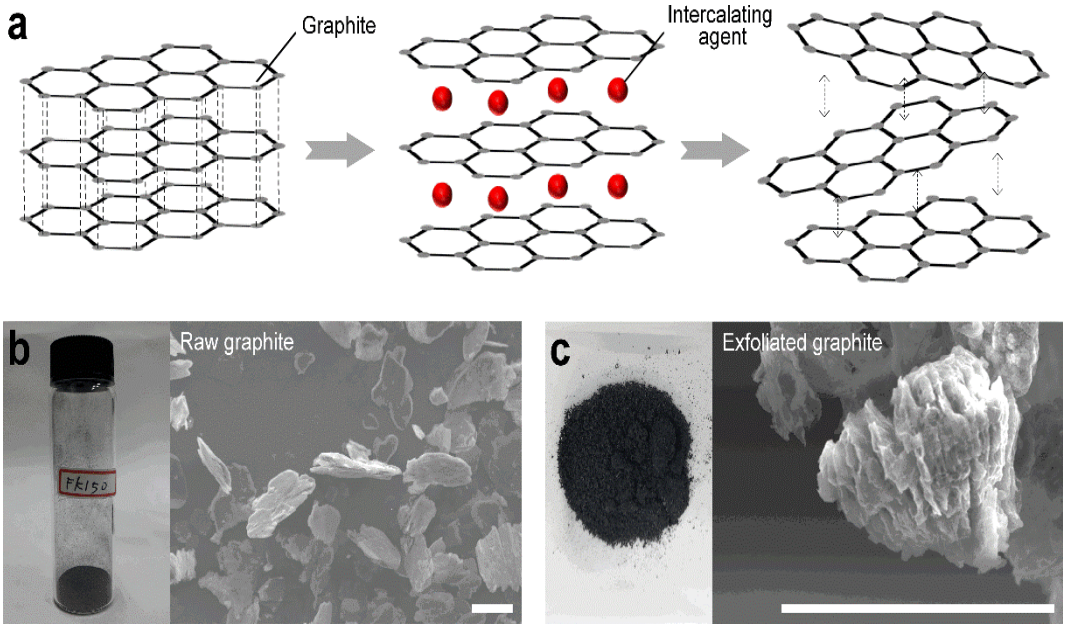
TEM: Transmission Electron Microscopy sample was analysed at SICARD, V.V.Nagar, Anand.

CHAPTER-3

Scalable production of reduced graphene oxide(rGO) of less defect using microwave-sonic exfoliation and improvised hummers method.

INTRODUCTION AND OBJECTIVES:

This Chapter explored improvised hummers methods for controlled oxidation of graphite to produce less defect graphite oxide by using different weight ratio of Graphite KMnO4 and H2SO4. The mildly oxidized graphite is reduced by ethylene glycol followed by microwave irradiation in domestic microwave oven at 2.45GHz frequency produce dark black powder of exfoliated reduced graphite oxide(XRGO) with large expansion volume. It is then dispersed in solvents by using low power sonication bath. The resulting dispersion analyzed by different instrumentation techniques. The final product has been analyzed by FTIR, UV-Visible spectroscopy, XRD and SEM-EDS and RAMAN.



Here we reported mild oxidation of graphite to XGO (exfoliated graphite oxide) to isolate graphitic sheet with less defect by mixing together different weight ratio of graphite, KMnO4, and H2SO4 at different time interval. The intercalated graphite oxide is then microwave irradiated in domestic microwave at2.45 GHz frequency for different time interval, results a large volume expansion, accompanied by 'violent fuming' was observed. The final exfoliated power (XRGO) was analyzed by FTIR, XRD and SEM.

It is then dispersed in different solvents by sonication to the uniform black color dispersion which is characterized by different instrumentation technique.

Sonication

XRGO **dispersion**

CONCLUSION: Here we have reported simple yet green promising and ecofriendly route for the scalable and cost-effective production of processable graphene materials which could be used as promising applications such as photocatalyst, sensor, supercapacitors, solar-energy conversion devices and lithium-ion batteries, electrode materials and energy storage devices of future technology.

The final products were analyzed by FTIR, Uv-Visible, XRD, SEM and TEM analysis.

FTIR : IRSpirit FT-IR spectrophotometer by Shimadzu Scientific Instruments Inc. at Department of chemistry, St.Xavier's College, Ahmedabad.

UV-Visible spectrometer:

UV1800 UV-Vis spectrophotometer by Shimadzu Scientific Instruments Inc. at Department of chemistry, St. Xavier's College, Ahmedabad

XRD: XRD Diffractometer (powder). The XRD spectra was taken by Cu-K_α radiation at SAIF, Chandigadh.

TEM: Transmission Electron Microscopy sample was analyzed at SICARD, V.V.Nagar, Anand.

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