IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Vol. 8, Issue 5, May 2021

DOI: 10.17148/IARJSET.2021.85115

SYNTHESIS OF GRAPHENE USING LIQUID PHASE EXFOLIATION TECHNIQUE

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Abstract: Nanomaterials have gained prominence in technological improvements because of their high-quality physical, chemical and biological properties with superior overall performance over their bulk materials. The foremost effect of nano-substances has been in the fields of mechanical, electronics, energy and medicine. Nanoparticles are substantially used to enhance the strength, stiffness and durability of composites. Carbon nanomaterials have attracted vast interests because of the promising benefits of mechanical flexibility which includes excessive strength, stiffness, durability, excessive conductivity, adjustable energy degrees and long-time period stability. Graphene, two-dimensional fabric has been taken into consideration as a promising material because of its extra-everyday optical, digital and mechanical homes. Graphene, a 'wonder material' is the world's thinnest, most powerful and stiffest material. It is an high-quality conductor of warmth and electricity. There are many techniques of synthesizing graphene like mechanical exfoliation, chemical vapour deposition (CVD) and epitaxial growth of graphene on sic. But every technique has its personal disadvantages.In this project, Graphene became synthesized through Liquid Phase Exfoliation (LPE) technique the usage of Graphite because the number one material. The synthesis of Graphene by this system is simple and value effective. The Graphite powder is delivered to solvent and subjected to sonication and centrifugation. The samples have been then characterised the usage of Scanning Electron Microscope (SEM), FTIR spectroscopy and X-Ray Diffraction for the confirmation of Graphene particles organized through this technique.

.Keywords: Graphite, Graphene, Liquid Phase Exfoliation (LPE), chemical vapour deposition (CVD)

I. INTRODUCTION

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a large and interdisciplinary region of research and improvement activity that has been developing explosively worldwide in the past few years. It has the ability for revolutionizing the approaches in which substances and products are created and the variety and nature of functionalities that may be accessed. It is already having a extensive industrial impact, which will assuredly growth in the future. Nanoscale substances are described as a set of materials where as a minimum one measurement is much less than about one hundred nanometres. A nanometre is one millionth of a millimetre about 100,000 instances smaller than the diameter of a human hair. Nanomaterials are of interest due to the fact at this scale precise optical, magnetic, electrical, and different residences emerge. These emergent properties have the ability for great affects in electronics, medicine, and different fields.

II. METHODOLOGY

2.1 GRAPHITE

The most common allotropic form of carbon is graphite which is an abundant natural mineral and together with diamond has been known since antiquity. Graphite consists carbon atomic layers which are stacked together by weak van der Waals forces. The single layers of carbon atoms tightly packed into a two-dimensional (2D) honeycomb crystal lattice is called graphene. Graphite is built up from many stacked layers of graphene planes each slightly offset from the plane below. This is called a lamellar structure and the simplest stacking scheme. This is why layers of graphite can be easily sheared off. Graphite exhibits a remarkable behavior with respect to thermal and electrical conductivity. Graphite is also highly valued in industry applications as a dry lubricant for the same reasons. Other uses of graphite include conductive fillers, battery electrodes and in nuclear fission reactors.

In this project, Graphite powder is taken as the primary material for the synthesis of Graphene by means of Liquid Phase Exfoliation technique.

2.2 SOLVENT

N-Methyl-2-pyyrolidone (NMP) is an organic compound consisting of 5- membered lactam. It is a colorless liquid, although impure samples can appear yellow. It is miscible with water and with most common organic solvents.

It also belongs to the class of dipolar solvents such as Dimethyl formamide and Dimethyl sulfoxide. It is used in the petrochemical and plastics industries as a solvent, exploiting its non-volatility and ability to dissolve diverse materials.

NMP is produced industrially by a typical ester-to-amide conversion, by treating Butyrolactone with Methylamine. Alternative routes include the partial Hydrogenation of N-Methyl succinimide and the reaction of Acrylonitrile with methylamine followed by Hydrolysis.

NMP is used to recover certain Hydrocarbons generated in the processing of Petrochemical, such as the recovery of 1,3-butadiene and Acetylene. It is used to absorb Hydrogen sulfide from Sour gas and hydro desulfurization facilities. Its good solvency properties have led to NMP's use to dissolve a wide range of Polymer. Specifically, it is used as a solvent for surface treatment of Textile, resins, and metal coated plastics or as a Paint stripper. It is also used as a solvent in the commercial preparation of Poly (p-phenylene sulfide). In the pharmaceutical industry, N-methyl-2-pyrrolidone is used in the formulation for drugs by both oral and transdermal delivery routes. It is also used heavily in Lithium-ion battery fabrication, as a solvent for electrode preparation, though there is much effort to replace it with solvents of less environmental concern, like water.

2.3. SAMPLE CHARACTERISATION TECHNIQUES

2.3.1. ELECTRON MICROSCOPY

When imaging an object, the radiation used to observe it must have a wavelength comparable to that of the object. Electrons accelerated at 10 kV or 200 kV have a wavelength of 12.3 pm or 2.5 pm respectively, making them ideal for interacting with2D nanosheets and thus will contain information about any interaction and ultimately the sample. Scanning electron microscopy (SEM) of the powders was used to identify the layered strata in the powder and if there was an impurity phase. SEM of the filtered dispersions allowed for film morphology, density and uniformity to be determined.

2.3.1.1. SCANNING ELECTRON MICROSCOPY

A scanning electron microscope uses a focused beam of accelerated electrons (~5 Kv) to probe the sample, while current carrying coils are used to raster scan the beam across the sample. As the beam interacts with the sample, kinetic energy is transferred and the incident electrons are decelerated. This energy is then dissipated as a variety of beam-sample interactions which are monitored by a variety of detectors inside the chamber. All SEM measurements were made using a Zeiss Ultra Plus SEM. The electron beam generator is a thermal field emission tungsten tip, with a sintered reservoir of zirconium oxide in the shank.

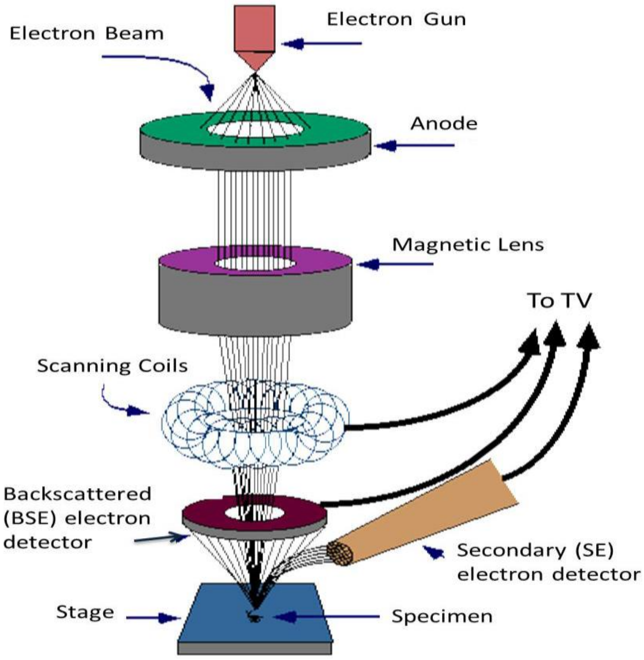

Figure 1 Schematic diagram of Scanning Electron Microscope

Three detectors were used to monitor these interactions, the secondary electron (SE) detector, the back scattered electron detector (BSE) and the in-lens detector. Each detector is positioned at a discrete location to collect electrons from a different interaction volume. The SE detector collects electrons produced by inelastic scattering events

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International Advanced Research Journal in Science, Engineering and Technology
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that have low energy and a short mean free path, hence contain good topography information. The BSE detector collects higher energy, elastically scattered electrons from deeper within the interaction volume. These energies of the scattered electrons can be used to identify chemical compositions in multiphase samples. The In-lens detector was also sometimes used. This detector is efficient at collecting scattered electrons from low acceleration voltages, and is placed directly in the beams path, close to the sample, allowing for better surface analysis.

2.3.1.2. FTIR SPECTROSCOPY

A FTIR spectrometer is an effective technique for the characterization of graphene. It is based on the interaction of infrared radiation with graphene sample at different frequencies. It measures the frequencies at which graphene sample absorbs the IR radiation along with their intensities. This method is used to detect various functional groups present in graphene sample. As different functional groups absorb light at specific frequencies so this method can be used for determining the chemical structure from the frequencies recorded in FTIR. Fourier transform infrared (FTIR) spectroscopy is used to get information on the molecular structure of the sample.

The FTIR spectroscopy range can be divided into three types, near infrared (NIR) which is from 12800 to 4000 cm^{-1}, the mid infrared (MIR) range is from 4000 to 200 cm^{-1} and the far infrared (FIR) range is from 50 to 1000 cm^{-1}. The most common range is from 4000 to 400cm^{-1}. It is because the molecular vibrations of most of the compounds lie in this range. FTIR spectroscopy method also has the advantage that it can be used for analyzing the samples in liquid, gas, or solid form.

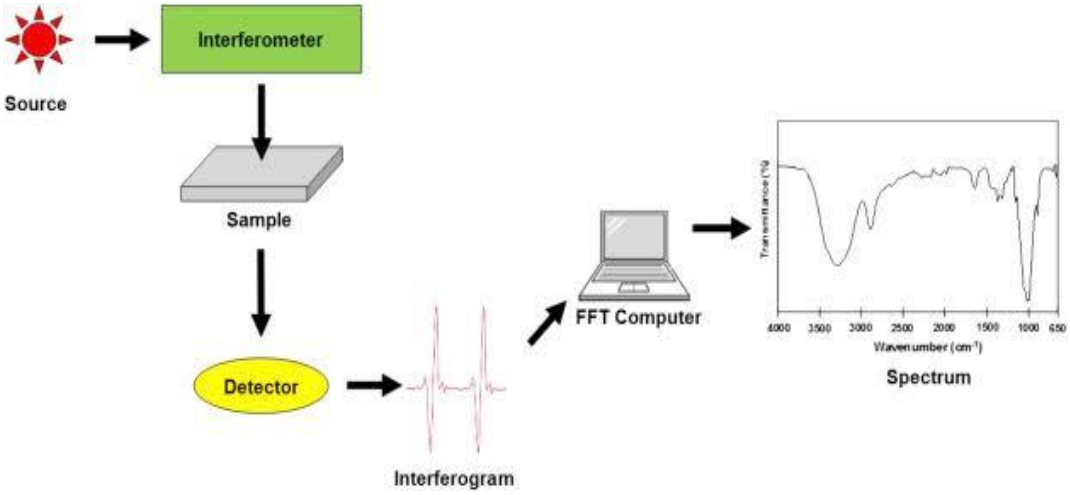

Figure 2 Schematic diagram of FTIR spectroscopy

The FTIR spectrometer records absorption/transmission spectrum with high accuracy and resolution. The FTIR spectroscopy depends upon the absorption of specific frequencies by different molecular bonds present in the sample.

2.3.1.3. X-RAY DIFFRACTOMETER

X-ray diffraction (XRD) is a characterization technique used to characterize the powdered form of the nano particle. This technique helps in the identification of structural morphology of the crystalline materials. This technique can be used for the identification of phase and crystal planes of a variety of metals, minerals, organic and inorganic compounds. The schematic diagram of the X-ray diffractometer is shown in the figure

X-ray diffraction technique can be used for finding the inter-planar spacing in the nano material by using Bragg's law which is given by:

$$n\lambda = 2d\sin\Theta$$

Where, d = inter-planer distance, Θ = diffraction angle,
λ = X-rays wavelength, n = diffraction order

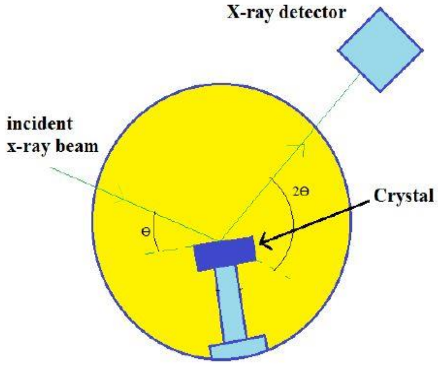

Figure 3 Schematic diagram of X-Ray Diffraction

For the characterization using XRD technique material is analyzed in the powdered form under X-rays beam. As each particle in the powder is the tiny crystal oriented randomly to different planes of orientations such as (100) plane or (110) plane. Each and every particle in the powder will give pattern pertaining to different planes of reflections. So, different peaks will be observed in the XRD pattern corresponding to different planes. X-ray diffraction (XRD) is the graphene characterization technique for obtaining crystalline structural information. As the X-rays are made to fall on the graphene sample, x-rays are scattered from different lattice planes of the sample. As a result, the scattered intensity rays are plotted which results in the XRD pattern. XRD pattern is the signature of any particular material which is unique. XRD is an important characterization technique used to determine the crystal phase structure. After the X-ray beam hits the sample to be analyzed, the incident and scattered angle of the beam is recorded. Each sample is made up of atoms arranged in a particular arrangement in the unit cell. This particular arrangement gives the variation of intensities of the diffraction peaks in XRD pattern. The XRD pattern can be used to find the crystal structure, its chemical composition and some of the properties of material. The XRD is the characterization techniques used in research and industries in areas of material science and pharmaceuticals.

III. EXPERIMENTAL DETAILS

3.1. LIQUID PHASE EXFOLIATION

The exfoliation of graphite in the liquid environments can be effectively done by exploiting ultrasonication to extract individual layers. The liquid phase exfoliation process normally includes three stages.

1. Dissolve graphite in a solvent,
2. Exfoliation, and
3. Purification

Liquid phase exfoliation is a method to exfoliate graphite into liquid solution. It is a feasible way to obtain colloidal suspension of graphene layers in the solution. The quality and quantity of graphene layers are higher than those produced from graphite oxide due to the absence of oxygen functionalities which disturb the properties like electrical conductivity and carrier mobility of graphene layers. This method is more efficient when the applied force to the graphene can overcome the graphene–graphene interlayer vander Waal interaction force. The exfoliation is better when the surface energy of the solvent is close to the graphene. By the mechanical force, which is sufficiently greater than Vander Waals force, we can separate graphene layers.

The mechanical force is achieved by either sonication or centrifugation. The long-term sonication prompts to undesirable fragmentation into exfoliated graphene layers which brings about small size graphene layers. Generally, sonication is a process to transfer the sound energies to fragment the particles. It has been found that the surface energies play important role when graphite surface is immersed in the liquid. Liquid phase exfoliation is one of the effective and straightforward method to decrease the strength of the Vander Waals attractions.

Meanwhile in ultra-sonication, the growth and the breakdown of the micrometre-sized bubbles because of pressure fluctuations, work over the bulk material and induce exfoliation.

3.2. DISPERSION PREPARATION

3.2.1. ULTRASONICATION

Sonication is a shorthand term that is commonly used to refer to the application of ultrasonic energy to either a sample or in some cases a piece of equipment as a method of cleaning. Ultrasonic is a broad term which refers sound

DOI: 10.17148/IARJSET.2021.85115

waves with a frequency far above that which human ears are sensitive to, typically greater than 16 kHz. These high frequency transverse waves have many applications such as medical imaging (i.e. ultrasound diagnostic imaging), navigation and industrial scale mixing. As mentioned previously this is commonly used for cleaning and ultrasonic baths are commercially available to clean jewellery. The applied energy in these baths is enough to remove material from the surface of objects and it is a device in the same vein as these that was used to separate the layers of graphite in suitable solvents to form graphene.

On applying sonic energy to a liquid sample, the solvent molecules there in begin to oscillate about their mean positions at the frequency of the applied sonic energy. This sound wave goes through compression and rarefaction cycles with solvent molecules being forced towards one another and apart respectively. For ultrasonic cycles this can exceed the critical molecular distance necessary to hold the liquid intact and so a cavity is formed which will grow during the rarefaction cycle. These bubbles subsequently contract or collapse entirely once the rarefaction cycle ceases releasing large amounts of energy in the form of a shock wave. These shock waves generate large local shear stresses, large enough to delaminate the vander Waals bound layered materials used in this work.

The process must be carefully monitored however as large amounts of heat are generated during sonication. This is largely due to energy losses to the acoustic wave due to viscous frictional losses as well as thermal conduction from areas of high pressure to low pressure areas. This means, particularly for higher power sonication, that cooling must be employed either through circulating cooled water about the sample or, in the case of sonic baths, circulating cooled water through the bath itself.

3.2.1.1. SONICATION EQUIPMENT

The equipment used in this work employs piezoelectric transducers to convert high frequency electrical energy into high-frequency sonic energy. In the case of the sonic bath, a number of transducers supply energy to a steel tank filled with water. Liquid samples are then held in this tank in vials or beakers and the sonic energy supplied to the tank passes from the tank to the water in the vessel and is then transmitted into the sample. Care must be taken to ensure the liquid level in the sonic bath does not fall below the marked operating levels. In the case of a sonic tip, the transducers supply the energy to a titanium probe that is directly immersed in the sample allowing more direct control of the energy input into the sample. Samples sonicated in this manner must be secured such that the tip does not come into contact with the sample holder and that the tip is placed centrally in the sample a few millimetres from the bottom to ensure consistency.

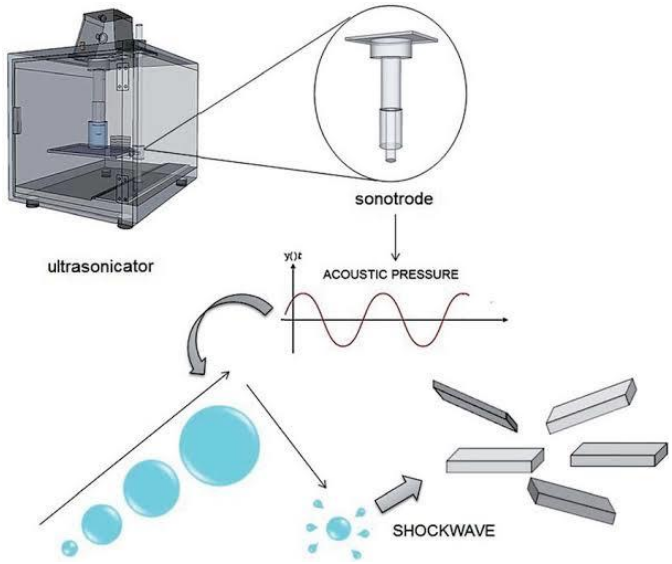

Figure 4 Schematic diagram of Ultrasonication equipment

3.2.2. CENTRIFUGATION

Dispersions produced using sonication will still contain large quantities of large, unexfoliated material, unstable dispersed material. In order to study and characterise the produced nano sheets they must first be separated from the bulk material and unstable phases. The earth's gravitational field causes materials above $1mm^3$ to sediment rapidly. However, for materials below this size, centrifugation of materials in suspension can speed up this process by creating a centrifugal force on the nano sheets in dispersion. During centrifugation the unexfoliated material is forced against the wall of the via land collects at the bottom. This will happen naturally over time as the larger particles settle to the bottom of the container and the unstable particles flocculate and follow. Centrifugation drives the large unstable particles to the bottom of the sample vial and the remaining stable dispersion (the supernatant) can then be decanted from the top to be kept and characterised.

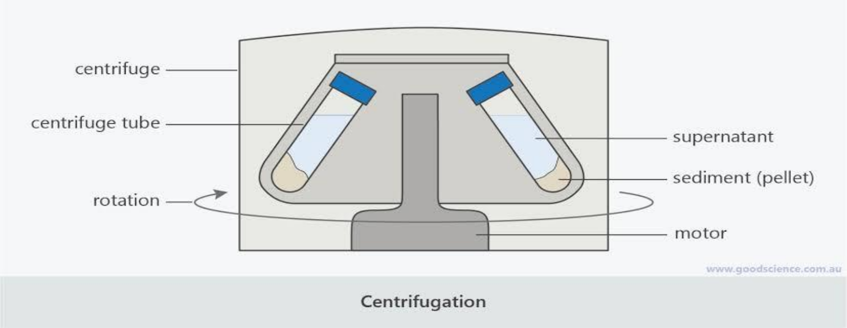

Figure 5 Schematic diagram of Ultracentrifugation equipment

A centrifuge operates by rotating the samples in a sample holder about a fixed axis at a known rotation rate, typically given in RPM, for a known period of time. However, the effective force applied to samples is dependent on more than simply the rotation rate and so to allow comparisons to other devices the centrifuge rate can be converted to relative centrifugal force (RCF) which is quoted relative to gravity. This can be calculated from

$$RCF = r\omega^2/g$$

where g is the gravitational force, r is the radius of the rotor and the angular rotation
$\omega = 2pN$ where N is the rotation rate in rotations per second. Centrifugation will separate particles on the basis of mass. While centrifugation is used in order to yield a stable dispersion, particles may continue to drop out even after a centrifugation step. This can be due to an insufficient centrifugation or it could be indicative of an unstable dispersion in which particles are aggregating and falling out of suspension.

3.3 LIQUID PHASE EXFOLIATION OF GRAPHENE

In this process, the graphite powder was dispersed in NMP solvent (Beaker,40 mL solvent) at a concentration of 5 mg/mL.The mixture was sonicated in a probe sonicator for 90 minutes at 50 – 60^0C. The sonication tool has a fixed frequency output of 20 kHz. The sonication time is controlled via a timer. The resultant dispersion was centrifuged using an ultracentrifuge at 3000 rpm for 30 min. After centrifugation, decantation was carried out by pipetting off the top half of the dispersion. The graphene particles settle down with respect to time and it was collected it by means of filtration. The sample was then subjected to characterization for confirmation of graphene particles.

3.4. CHARACTERIZATION OF SAMPLES

The collected samples are subjected to characterization for the confirmation of Graphene particles. The characterization of the liquid phase exfoliated graphene is performed using scanning electron microscopy (SEM). The micro structural analysis was done by scanning electron microscope technique. The SEM instrument used for characterization was model Hitachi, S3400N (Karunya University, Coimbatore).

FTIR spectra were recorded with a Perkin Elmer Frontier FTIR spectrophotometer (Karunya University, Coimbatore). Spectra was recorded at room temperature, in the wave number range of 4000–500 cm−1, with an incident laser power of 1 mW and a minimum resolution of 4 cm^{-1}. Prior to the measurements, the powder samples were mixed and ground with KBr, and the mixtures were then pressed into a round transparent pellet in a pellet forming die. XRD is an important characterisation technique for characterization of intercalation and exfoliation in composites made up of layered materials. the X-ray powder diffraction patterns were recorded on a BRUKER-AXS diffractometer (Karunya University, Coimbatore) using Cu Kαradiation ($\lambda = 0.154$ nm).

IV.RESULTS AND DISCUSSION

4.1. CHARACTERIZATION RESULTS OF SAMPLES

4.1.1. SCANNING ELECTRON MICROSCOPE ANALYSIS

SEM image gives the morphology of the graphene sheets from which the lateral size of the graphene nano sheets can also be observed. In SEM the electrons hit the graphene specimen and produces secondary electrons which are emitted from the sample and collected to create the SEM images. The intensity of the secondary electrons depends upon morphology of the graphene nano sheets. It is observed that the size of the graphene nano sheets varies from nm to few µm.

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SEM uses the electron beam which is focused on the surface of the sample and by scanning back and forth over the surface, the topography of a sample is revealed by the reflected or ejected electrons from the sample. The interaction between the main electron beam and the back scattered electrons at each scan line gives rise to an image on (CRT) cathode ray tube screen. The SEM image can be analysed for getting the morphological information at different resolutions.

It depicts their presentative SEM image of GN sheets, which confirms the formation of free standing 2D graphene sheets which are not perfectly flat but illustrates roughened surfaces and out of plane deformations with crumpled/wrinkled paper like appearance. These features are characteristic of Graphene sheets and confirm the formation of Graphene sheets.

4.1.2. FTIR SPECTROSCOPIC ANALYSIS

The characteristic FTIR spectrum of Graphene nano sheets are shown. Generally, Graphene contains epoxide and hydroxyl functional groups on both sides of its basal plane and carboxyl at the edge sites.

The most characteristic features in the IR spectrum of Graphene are the strong broad-band centred at ~3400 cm^{-1}, corresponding to the O–H stretching vibrations, the peaks at around 2924 and 2851 cm^{-1} are attributed to sp^2 and sp^3 C-H stretching bands, produced at defects sites of the graphene network. The peak at ~1723 cm^{-1} arising from the C=O stretching of the carboxylic acid groups, the band at 1606 cm^{-1} assigned to the aromatic C-C stretching and the C–OH stretching at 1225 cm^{-1}.

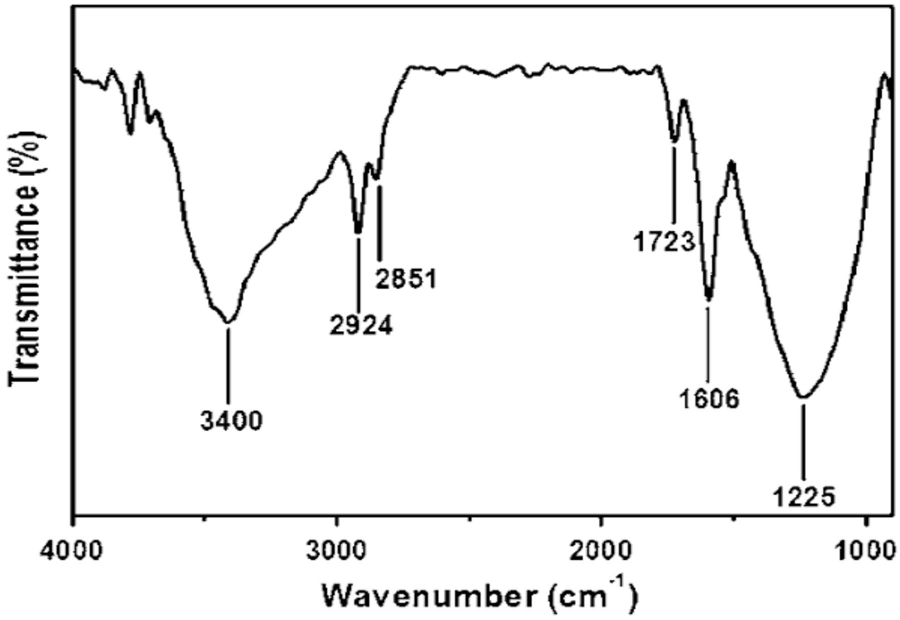

Figure 6 FTIR Spectroscopy of Graphene samples

4.1.3 X-RAY DIFFRACTION ANALYSIS

XRD is an important characterisation technique for characterization of intercalation and exfoliation in composites made up of layered materials. X-ray diffraction (XRD) is the graphene characterization technique for obtaining crystalline structural information.

As the X-rays are made to fall on the graphene sample, x-rays are scattered from different lattice planes of the sample. As a result, the scattered intensity rays are plotted which results in the XRD pattern. XRD pattern is the signature of any particular material which is unique. In case of graphite the XRD peak is observed near 26.5 degrees which shifts in case of graphene XRD due to increase in the inter planar spacing in graphene as shown. Graphite contains a very distinct and sharp peak which transforms into a broad shaped peak in graphene due to addition of the functional groups. Graphite loses its crystallinity and converts into a semi-crystalline and hydrophilic structure on oxidation.

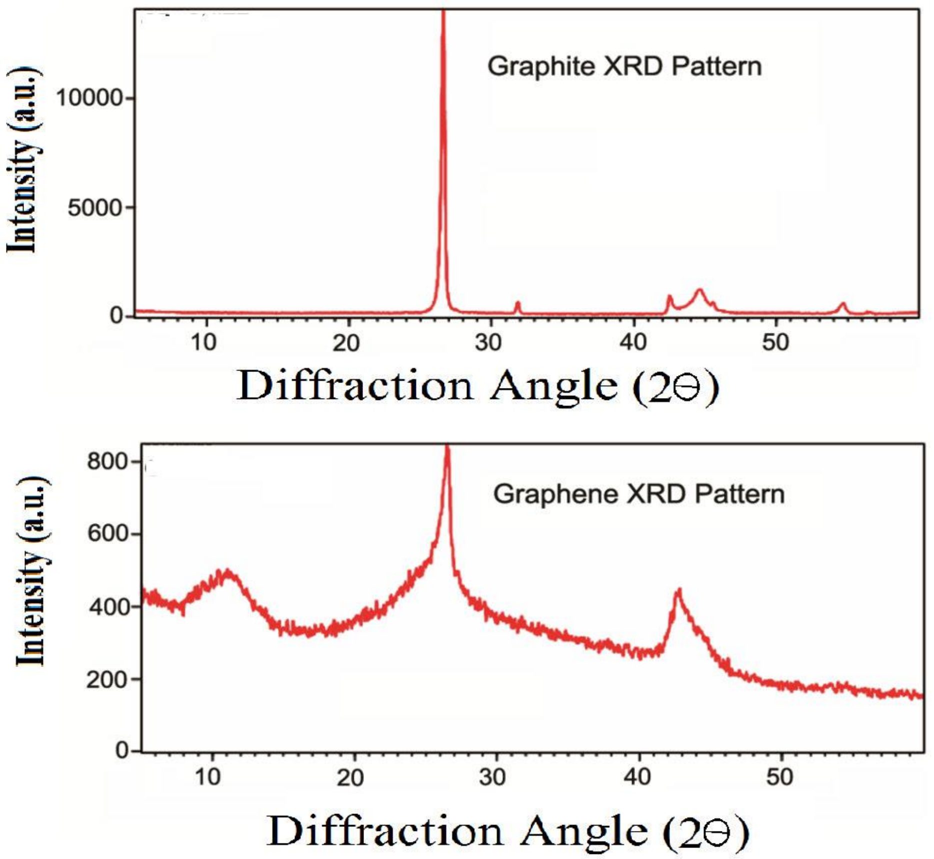

Figure 7 XRD pattern of Graphite and Graphene

V. CONCLUSION

Graphene is a super material that could be used in various multipurpose applications. Graphene could be synthesized by various methods; each method has its own disadvantage. To overcome the problem, Liquid Phase Exfoliation was proposed in this project and the following results were obtained.

- Graphite was reduced to produce high quality Graphene by Liquid Phase Exfoliation successfully.
- Bulk synthesis of graphene nanoplatelets could be carried out using refractory grade graphite as the starting material.
- Scanning Electron Microscopy showed fluffy morphology and few layers of graphene sheets.
- The FTIR spectroscopy has the sp^2 bands showing the formation of Graphene sheets.
- XRD pattern of Graphene shows a broad shaped peak at 26.5^0 confirming the graphene nanosheets.
- All these characterisation techniques confirmed the formation of few layered Graphene sheets.
- Graphene prepared by mechanical exfoliation method and has the disadvantages of low yield and poor throughput and hence cannot be scaled up for mass production of graphene.
- Other techniques of graphene synthesis such as chemical vapor deposition (CVD) and epitaxial growth on SiC substrate are complex, costly, require sophisticated equipments and high temperature and low pressure conditions.
- Hummer's method of graphene preparation is also not suitable because of the use of strong chemicals such as HNO3, H2SO4, KMnO4, hydrazine, NaBH4 etc. which are not safe for the environment.
- The Liquid Phase Exfoliation of graphite into graphene is a facile, easy, environment friendly and economical method to produce high quality defect free graphene nanosheets. The method can be performed using the equipment easily available in the laboratories.
- The molecule of the solvent helps to overcome the wanderwaals force of attraction between individual graphene layers of graphite. It helps in preparation of stable graphene, which are used for making thin films and graphene composite materials.

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