

**PREPARATION OF GRAPHENE SHEETS**

**BY**

**MICROWAVE IRRADIATION**

**Dissertation submitted in partial fulfilment of the**

**requirements for the degree of**

**MASTER OF SCIENCE**

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**CERTIFICATE**

This is to certify that, the work in the report entitled “**PREPARATION OF GRAPHENE SHEETS BY MICROWAVE IRRADIATION**” by **Anchal Paramguru**, in partial fulfillment of Master of Science degree in **PHYSICS** at the National Institute of Technology, Rourkela (Deemed University); is an authentic work carried out by her under my supervision and guidance. The work is satisfactory to the best my knowledge.

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## **DECLARATION**

I hereby declare that the project work entitled “**Preparation of graphene sheets by microwave irradiation**” submitted to NIT, Rourkela, is a record of an original work done by me under the guidance of **Dr. Pitamber Mahanandia**, Faculty Member of NIT, Rourkela and this project work has not performed earlier for the award of any Degree or diploma/ associate ship/fellowship and similar project if any.

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## **ABSTRACT**

Due to its unique structural, physical properties (viz: higher mobility, electrical and thermal conductivity, higher mechanical strength, optical transmittance etc.) and chemical properties like easy functionalization and dispersion etc. the interest towards Graphene and its compounds going on increasing day to day. Here we are reporting the synthesis of Graphene using an efficient and simple method under microwave irradiation. Natural graphite and expected graphene were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Raman spectroscopy. In microwave irradiated expansion, high quality graphene was prepared. . This method is facile, inexpensive, and produces usable results. Extensive characterizations showed that the as-prepared materials consisted of creased, few-layer thick and electronically conductive graphitic sheets.

**Keywords:** Graphite, Graphene, Microwave irradiation, Electrical, optical, Thermal, mechanical

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# Chapter 1

## Introduction

### 1.1 DIFFERENT FORMS OF CARBON

Carbon is the most attractive element in the periodic table. It is the base for all life on Earth. Carbon exists in numerous different forms. The most common form of carbon is graphite, which consists of arranged carbon sheets with a hexagonal structure. Under high pressure a metastable form of carbon called diamond is formed.

A new form of molecular carbon is so called fullerenes. A quasi-one-dimensional form of carbon called carbon nanotubes have been known for several decades. These can be formed from graphene sheets which are rolled up to form tubes and their ends are half spherical in the same way as the fullerenes. The electronic and mechanical properties of single walled nanotubes have many similarities with graphene.

Graphite consists of hexagonal carbon sheets that are stacked on top of each other but it was considered that a single sheet could not be produced in isolated form such that electrical measurements could be performed. Therefore it came as a surprise to the physics community when in October 2004, Konstantin Novoselov, Andre Geim and their collaborators showed that such a single layer could be isolated and transferred to another substrate and that electrical characterization could be done on a few such layers. In July 2005, they published electrical measurements on a single layer. The single layer of carbon is called graphene.

Graphene like structures were already known of since the 1960, but there were experimental difficulties in isolating single layers in such a way that electrical measurements could be performed on them, and there were doubts that this was practically possible.

Everyone who has used an ordinary pencil has possibly produced graphene-like structures without knowing it. A pencil contains graphite and when it is moved on a piece of paper, the graphite is sliced into thin layers that end up on the paper and make up the text or drawing that we are trying to produce. A small fraction of these thin layers will contain only a few layers or even a single layer of graphite, i.e. called graphene.

## 1.2 ABOUT GRAPHENE

Graphene is a single layer of carbon crammed in a hexagonal lattice, with a carbon-carbon distance of 0.142 nm. It is the first actually two-dimensional crystalline material. The electronic structure of graphene is different from usual three-dimensional materials. This two dimensional(2D)graphene sheet shows tremendous physical properties such as large theoretical surface area ( $2630 \text{ m}^2 \text{ g}^{-1}$ ),high intrinsic mobility( $200000 \text{ cm}^2 \text{ v}^{-1} \text{ s}^{-1}$ ),high young's modulus( $\sim 1.0 \text{ TPa}$ ), high thermal conductivity( $\sim 5000 \text{ Wm}^{-1} \text{ k}^{-1}$ ),high current carrying capacity( $\sim 10^9 \text{ A/cm}^2$ ),optical transmittance( $\sim 97.7\%$ ).Graphene is practically transparent. In the optical region it absorbs only 2.3% of the light. This number is given by  $\pi\alpha$ , where  $\alpha$  is the fine structure constant that crowds the strength of the electromagnetic force. In contrast to low temperature 2D systems centered on semiconductors, graphene maintains its 2D properties at room temperature. It is significantly stronger than steel, very stretchable and can be used as a flexible conductor. The unique electrical, physical and optical properties of graphene promise a variety of applications.

## 1.3 PROPERTIES OF GRAPHENE

The unique electronic, thermal and mechanical properties of graphene make it a very favorable candidate for a wide range of applications in nanoscience and nanotechnology. The adaptable properties of graphene are very well documented in the exponentially growing scientific literature. Some of its interesting properties and its technological implications are given below.

## 1.4 ELECTRONIC PROPERTIES

Graphene has giant potential for electronics for its extraordinarily high mobility of its charge carriers at room temperature. When Si-based technology is approaching its fundamental limits, graphene seems to be an ideal candidate to take over from silicon. Graphene is semi-metallic with no band gap, which severely limits its applications in electronics due to its high trickle current in many applications. The electronic band gap plays a central role in modern device physics and technology and panels the presentation of semiconductor devices. It is a property inherent to semiconductors and insulators which significantly govern their transport and optical properties. It has been possible to open and adjust the band gap of graphene bilayers by applying an electric field or by doping. The

structural operation may include optical properties which in turn get assimilated into it, resulting in its potential for opto-electronic applications.

### **1.5 OPTICAL PROPERTIES**

Quantum size effects display when the  $\pi$  electrons in graphene are confined laterally that is in graphene segments or graphene nanoribbons(GNR).An energy gap releases when carriers are confined to a quasi-one dimensional system like graphene Nanoribbons. GNR shows optical properties which are penetrating to their width, family, crystallographic orientation and edge dissolution similar to the CNTs. The energy gap of lithographically patterned GNR structures has been found to scale contrariwise with the ribbon width, which exhibits the possibility to engineer the band gap of graphene nanostructures by lithographic processes. An different route to induce the formation of a band gap is through the hydrogenation of graphene. The alteration of the carbon bonds associated with the hydrogenation conserves the crystalline order of the lattice but leads to rehybridization of the carbon atoms from a planar  $sp^2$  to a distorted  $sp^3$  state. Recent experimental studies have established reversible hydrogenation through heating.

### **1.6 NON-COVALENT BINDING PROPERTIES**

The weak, intermolecular, $\pi$ - $\pi$  interactions play a decisive role in the crystal packing of organic molecules containing pungent rings, the intercalation of certain drug molecules into DNA, the binding attractions of host-guest complexes, as well as the three-dimensional structures of biological systems, including proteins and nucleic acids, and their molecular organization and appreciation processes. Graphene sheets can be stacked into bilayers and multilayers by virtue of  $\pi$ - $\pi$  interactions between the neighboring sheets. The electronic properties of graphene multilayers fluctuate with the stacking order and rapidly change with the number of layers approaching the 3D limit of graphite.

### **1.7 FUTURE APPLICATIONS**

Graphene has a number of properties which makes it interesting for some different applications. It is an finally thin, mechanically very strong, transparent and malleable conductor. Its conductivity can be reformed over a large range either by chemical doping or by an electric field. The mobility of graphene is very high which makes the material very stimulating for electronic high frequency applications. Since graphene is a translucent conductor it can be used in applications such as touch screens, light panels and solar cells,

where it can substitute the quite fragile and exclusive Indium-Tin-Oxide (ITO). Flexible electronics and gas sensors are additional potential applications. The quantum Hall effect in graphene could also possibly add to an even more accurate resistance standard in metrology. New types of composite materials based on graphene with great strength and low weight could also become fascinating for use in satellites and aircraft.

Based on properties and discernment of graphene, enormous effect has been put forth for the synthesis of graphene for hitching its potential application in science and technology. However, obtaining graphene sheets is a challenge. Graphene obtained by other methods, including mechanical exfoliation, epitaxial growth and chemical vapour deposition is of high quality but limited. The graphene produced by above mentioned methods are high quality but are not suitable for large scale production. Single or few layers graphene have also been prepared by modified Hummers' method. In this method oxidation of graphite into graphene oxide is done by chemically. By using strong aqueous oxidizing agents such as fuming nitric acid/potassium chlorate or sulphuric acid/potassium permanganate, oxidation of graphite into graphene oxide can be done. Due to the presence of oxygen functional groups GO is electrically insulating and thus cannot be used without further dispensation as a conductive nanomaterial. Therefore it is very much vital to recover the graphene by removing oxygen functional groups by reducing in hydrazine, dimethyl hydrazine, sodium borohydride followed by hydrazine, hydroquinone, and UV-irradiation.

The above mentioned methods are monotonous and time consuming which follows with many steps. Moreover the superiority of the graphene (single or multilayer graphenes) depends upon processing parameter. Therefore it is highly essential to prepare single or few layers graphene by a simple method. The simple technique should not time consuming with a very few steps. On this regard taking above mentioned complications, I plan to prepare single or few layers graphene by microwave processing. This technique will be simple and expected graphene materials will be better in quality. Therefore, I believe this method will be quite efficient to prepare graphene in large scale. The prepared materials will be characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Raman spectroscopy etc.

## CHAPTER 2

### 2.1 REVIEW ON PREPARATION OF GRAPHENE SHEETS BY MICROWAVE IRRADIATION

Graphene has attracted marvelous attention for its significant electronic and thermal conductivity, large specific surface area, high mobility of charge carriers, excellent chemical stability and mechanical strength due to its unique structure made of  $sp^2$  carbon atoms tightly packed into a honeycomb lattice. For the sake of practical application, it is critical to find adaptable methods that can produce graphene profusely and efficiently at low cost. Until now, several strategies, such as micromechanical cleavage, epitaxial growth, chemical vapor deposition, and exfoliation of graphite oxide (GO) have been tracked to synthesize graphene sheets. Among these methods, exfoliation of GO is the most promising method for low-cost and ascendable production, and has been researched intensively. Thermal expansion of GO represents one of the most attractive approaches because of its straight forwardness, high efficiency, and high degree of exfoliation. However, this process is energy-consuming and must be carried out at high temperature. Microwaves, an different energy input source, have been widely used because of their internal and volumetric heating of materials, in the field of organic synthesis, environmental remediation, preparation of catalysts and activated carbon. A variety of nanostructures with different compositions have also been fabricated via the energy efficient microwave irradiation (MWI) approach. In this process, microwave energy is converted into heat by using a microwave absorbent. For this reason, it is necessary to select a proper microwave absorbent to efficiently convert microwave energy into heat. MWI has demonstrated the ability to efficaciously produce graphene from GO, where the main attention has been focused on the production efficiency. However, the interaction of microwaves with GO and graphene, which is very important for the further development of this method. In the present work, I investigate the response of oxidized graphite with varying degrees of oxidation under MWI. Graphene is demonstrated to behave as an excellent microwave absorbent. By dispersing tiny amounts of graphene into a GO matrix, a local heating stimulated by graphene under MWI creates an avalanche-like deoxygenating reaction of GO, thus giving augmentation to graphene, which shows a high specific surface area and good electrochemical performance.

## **2.2 AIM OF THE PROJECT**

The main objective of this project work is to prepare and characterize graphene sheets by microwave irradiation. Graphene prepared by microwave irradiation was found to be better than other methods like CVD, electrochemical synthesis.

## **CHAPTER 3**

### **EXPERIMENTAL PROCEDURE**

Before the sample preparation, the crucible was washed to avoid contamination of the sample using acetone. After drying of the crucible 500 mg graphite powder (GFG-50) was taken in a crucible. Then the powder was grinded for 3-4 hours using an Agate mortar. Then graphite powder was treated in microwave furnace at the heating rate of 20<sup>o</sup>c/min. When the temperature was raised to 500<sup>o</sup>c at around 30 minutes the furnace was switched off. After cooling crucible was removed and the sample was taken for characterization.

## **CHAPTER 4**

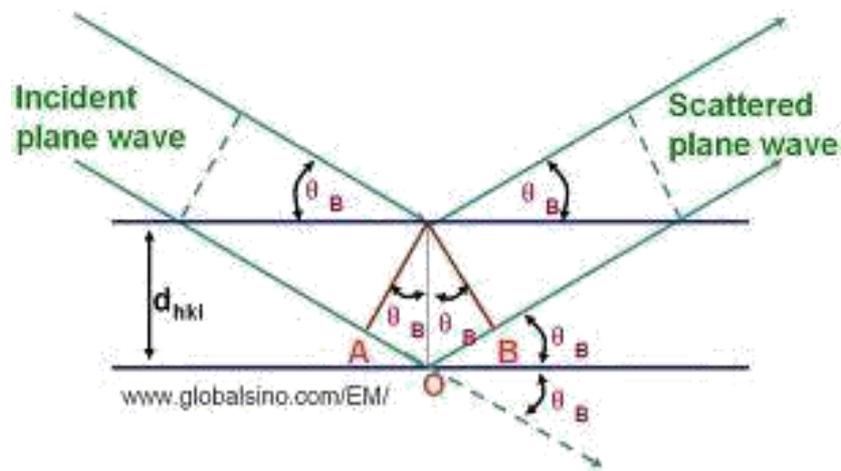
### **CHARACTERIZATION**

#### **4.1 X-Ray Diffraction (XRD)**

- When X-rays interact with a single particle, it scatters the incident beam uniformly in all directions.
- When X-rays interact with a solid material the scattered beams can add together in a few directions and buttress each other to yield diffraction. The regularity of the material is responsible for the diffraction of the beams.
- Diffraction can occur when any electromagnetic radiation interacts with a periodic structure. The repeat distance of the periodic structure must be about the same wavelength of the radiation.
- X-rays have wavelengths on the order of a few angstroms (1 Angstrom = 0.1 nm). This is the typical inter-atomic distance in crystalline solids, making X-rays the correct order of magnitude for diffraction of atoms of crystalline materials.

#### **Bragg's Law and Diffraction**

The relationship describing the angle at which a beam of X-rays of a particular wavelength diffracts from a crystalline surface was discovered by Sir William H. Bragg and Sir W. Lawrence Bragg and is known as Bragg's Law:



Diffraction from atomic planes

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

$\lambda$  = wavelength of the x-ray

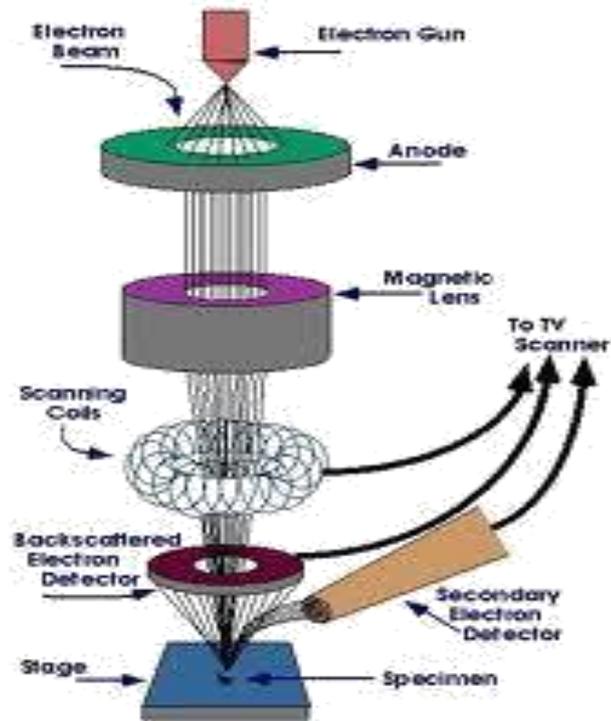
$\theta$  = scattering angle

$n$  = integer representing the order of the diffraction peak.  $d$

= inter-plane distance of (i.e. atoms, ions, molecules)

## 4.2 Scanning Electron Microscopy (SEM)

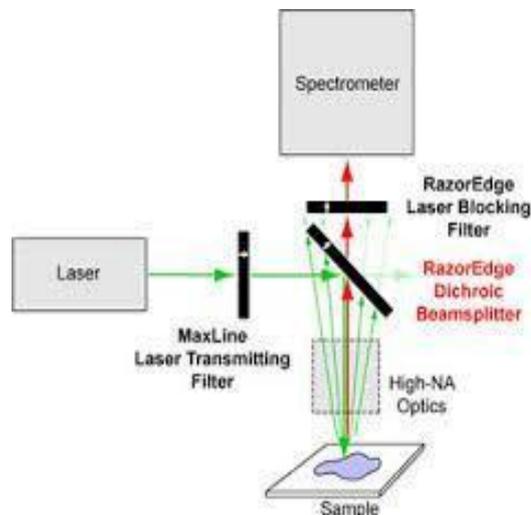
Scanning electron microscopy is used to study the microstructure and geographies of the sample. It scans the surface of the sample to build a 3-D image of the specimen with the help of electron beam. A typical SEM can magnify up to nanometer scale. The basic principle of SEM involves the interaction of the electron beam generated from x-ray tube and the sample surface. This interaction generates a variety of signals. These signals include secondary electron, backscattered electron, X-rays, photons, heat and even transmitted electrons. Backscattered electrons and secondary electrons are used for the imaging of the sample. Secondary electrons are used to study the topography and morphology of the sample whereas the back scattered electrons help to clarify the contrast in the composition of multiphase samples. SEM most commonly comes in combination with EDAX. SEM has a wide range of applications ranging from the ceramic industry to the material lab. Through SEM observations can be done in macro and submicron ranges. It can be used in the forensic lab to investigate the gun shot residues. This is possible due to its ability of combining imaging with elemental analysis.



SCHMATIC DIAGRAM OF SEM

### 4.3 Raman spectroscopy

When light is scattered from a molecule or crystal, most photons are elastically scattered. The scattered photons have the same energy and wavelength as the incident photons. However, a small fraction of light is scattered at optical frequencies different from the frequency of the incident photons. The process leading to this inelastic scatter is termed the Raman effect. Raman scattering can occur with a change in vibrational, rotational or electronic energy of a molecule. If the scattering is elastic, the process is called Rayleigh scattering. If it's not elastic, the process is called Raman scattering.

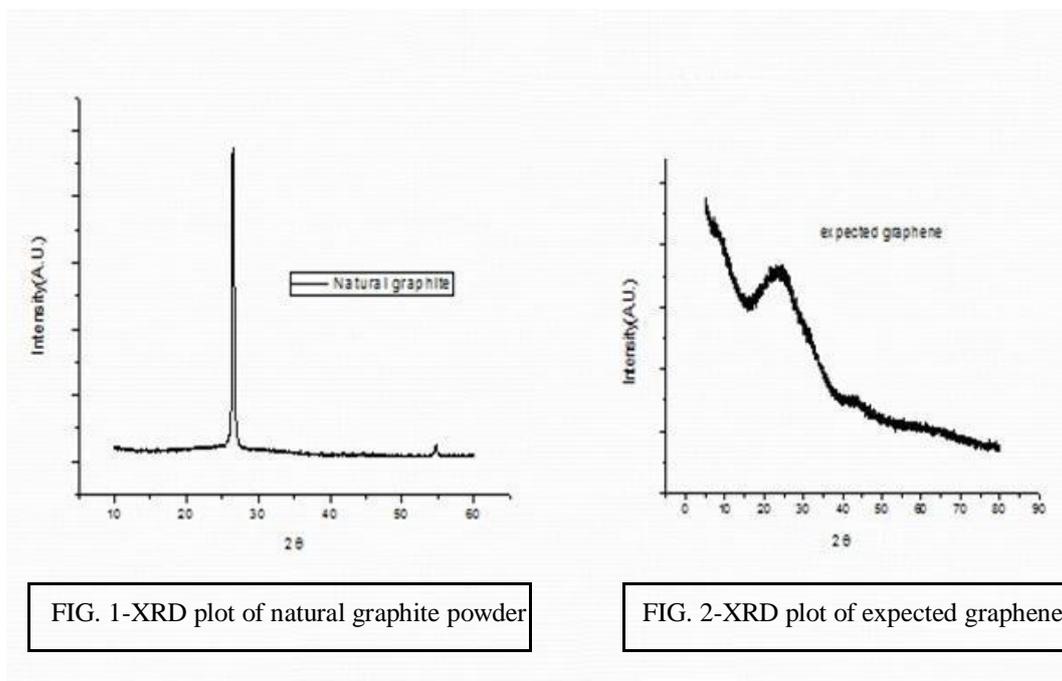


SCHMATIC DIAGRAM OF RAMAN SPECTROSCOPY

# CHAPTER 5

## EXPERIMENTAL RESULTS AND DISCUSSION

### 5.1 X-ray Diffraction Data



From the above XRD plot of natural graphite and expected graphene, it is shown that the XRD peak shifts towards left and becomes broad as compared to natural graphite. The broadening may be due to the nano-size effect of the sample.

## 5. 2 SEM

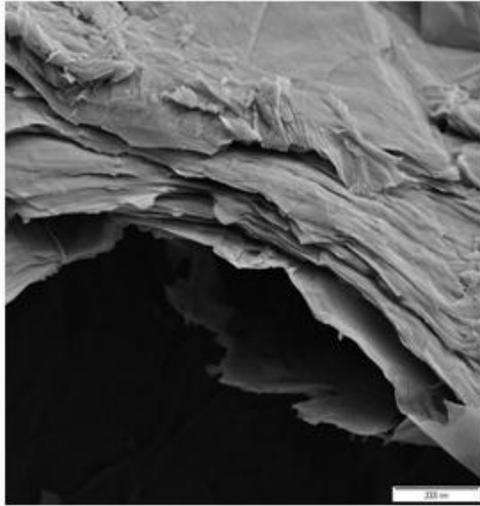


FIG.3-SEM image of Natural graphite

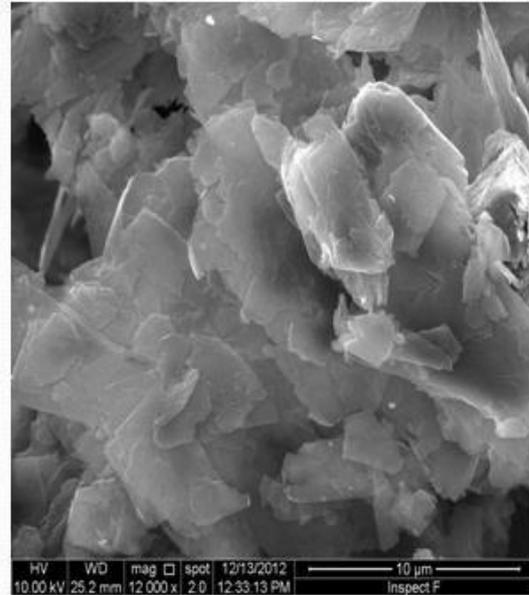


FIG.4-SEM image of Expected graphene

The SEM image of Natural graphite and Expected graphene are shown above. The SEM image of natural graphite is like layer structure and in case of Expected graphene some persons are peeled off.

### 5.3 RAMAN SPECTROSCOPY

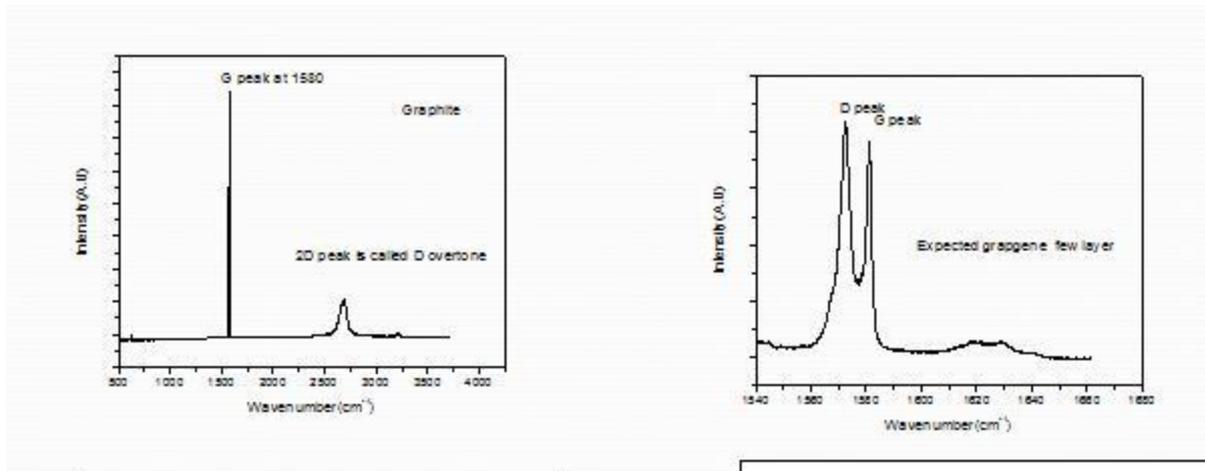


FIG.5-Raman spectroscopy of Natural graphite

FIG. 6-Raman spectroscopy of Expected graphene

As we see from the Raman data plotted above there are two peaks corresponding to different wavenumber/ wavelength in case of Natural Graphite powder. Among these two peaks one corresponds to the G-peak and the other the so called 2D-peak. However in The Raman spectroscopy of Expected graphene, there are two peaks; but in this case one is disordered peak (D peak) while the other is Graphite peak (G peak). The presence of the G-peak here gives the confirmation about the presence of Carbon in the sample while the d-peak about the formation of Graphene.

## **CHAPTER-6**

### **CONCLUSION**

Microwave heating was used for the preparation of graphene from graphite powder. Graphene addition could generate an avalanche-like deoxygenation reaction under microwave irradiation to achieve the synthesis of graphene from GO. The material produced using this method was successfully used as an electrode in supercapacitors. The understanding of the structure-dependent collaboration of carbon-based materials with microwaves may facilitate the design and synthesis of novel graphene-based composites using this energy efficient method. Based on microwave irradiated expansion, high quality graphene was prepared. This method is facile, inexpensive, and produces usable results.

Ultrathin, uniform graphene films were fabricated at room temperature by a vacuum filtration method. However, micron-size pieces are present that cannot overlap piece by piece, resulting in high sheet resistances from unconnected boundaries.

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