ELECTROCHEMICAL EXFOLIATION OF GRAPHENE AND ITS CHARACTERIZATION

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2015

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CERTIFICATE

This is to certify that the thesis entitled "**ELECTROCHEMICAL EXFOLIATION OF GRAPHENE AND ITS CHARACTERISATION"** submitted by **Nitish Kumar Patra (111MM0374) and Paramananda Chhatria (111MM0359)** in partial fulfillment of the requirements for the award of **Bachelor of Technology degree** in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela, is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge the matter embodied in this thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date : 5th May 2015

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Place : Rourkela

Date : 5th May 2015

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Abstract

A green approach is reported for the production of few layered graphenes (FLGs) via electrochemical route utilising the benefits of anodic exfoliation process, wherein electrochemical intercalation of nitrate ions into pyrolytic graphite resulted in electrochemical exfoliation of nitrate ions-intercalated graphite electrode. The role of applied potential in intercalation and concentrations of nitric acid are well defining factors in controlling the number of layers in FLGs. The success of this approach was confirmed by FTIR, wherein smaller particles of intercalated graphite led to broader peaks due to increased interaction with light wave. The SEM images showed several layers of graphene stacked together and slightly twisted at edges. An increased exfoliation in intercalated graphite was revealed by XRD patterns. Desirable conductive properties of the FLGs synthesised makes it a viable option for utility as conductive ink.

Keywords : **Pyrolytic Graphite, Exfoliation, Intercalation, Few layered graphene, Graphene Oxide**

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INTRODUCTION

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Introduction

1.Introduction

1.1 BACKGROUND

Graphene is a monolayer of sp^2 bonded carbon atoms resembling a honeycomb or chicken wire. Measuring out at just one atom thick graphene is a flat sheet of carbon. Dating back to 2004, pioneering work by Andre Geim and Konstantin S. Novoselov of University of Manchester, UK led to yielding of individual sheets of graphene. The methods used by Andre Geim and Konstantin S. Novoselov of University of Manchester, UK to exfoliate graphene comprised of a simple method of sticking scotch tape to peel off the graphene flakes of the chunk of graphite. The successive steps comprised a continuation of the process for a dozen of times which followed sticking another tape to the earlier used piece of tape to separate as many layers of graphene from it. When the last piece of the tape was stuck to silicon wafer and was peeled off, some of the layers remaining on the wafer were found out to be one atom thick which led to the amazing discovery of graphene, the material that was about to revolutionize the entire material science. The recent decade or so has recorded an upsurge in the popularity of graphene in research field inasmuchas it possess some significant properties of high current density, high thermal conductivity, optical transmittance, super hydrophobicity, chemical inertness and ballistic transport. Potential futuristic applications for graphene exists in the field of transistors, solar cells, flexible displays as sensors or as a superconductive membrane in battery. So far many methods have been developed to produce graphene, viz, micromechanical cleavage, the process that utilised a simple method of separating graphitic layers by utilisation of scotch tape; epitaxial growth via ultra high vacuum graphitisation, which consisted of growing a thin graphene film on a crystalline substrate; chemical synthesis through oxidation of graphite and dispersing the flakes by sonication followed by its reduction back to graphene; chemical vapour deposition (CVD) growth of graphene either on a substrate or free of substrate, whereby a solid material is deposited from vapour by a chemical reaction occurring in the vicinity of a heated substrate, capable of preparing high quality and large area graphene; solvothermal synthesis combined with pyrolysis and liquid phase exfoliation of graphite.

Electrochemical tehniques are alternatively used to produce graphene flakes because they are simple, economic, non-destructive, environment friendly, operates at ambient temperature and pressure and provides thickness control by mere adjustment of electrode potential[1,2].

In this work, the benefits of "electrochemically anodic exfoliation" and excellent properties of the protic nitric acid (HNO_3) electrolyte were combined to investigate direct exfoliation of graphite to few layer graphene (FLG) sheets.

Depending upon the polarity of the applied DC bias, anions or cations from the electrolytic bath tends to intercalate the stratified graphite. Subsequently monolayer or few layer graphene sheets are generated as a result of delamination of the graphite due to the inhibition of the π-bonding between carbon-carbon layers of graphite.

Cations such as lithium ions, tetraalkyl ammonium ions, lithium-propylene carbonate ionic complexes and N-butyl-methylpyrrolidium ions and anions such as sulphate ions, perchlorate ions, nitrate ions, polystyrene sulfonate ions, tetrafluoroborate ions, dodecyl sulphate ions and hexafluoro phosphate ions have been expansively explored. Voluminous gas evolution makes the anodic process of exfoliation more effective giving it an edge over the cathodic process that utilises a negative DC bias. Albeit oxygenation of the graphene sheets were observed, electrochemical exfoliation of pyrolytic graphite in the electrolytic bath of nitric acid was successfully employed to generate few layer graphene sheets.

1.2 OBJECTIVES

- Study the effectiveness of the anodic process of electrochemical exfoliation in intercalating graphene from pyrolytic graphite .
- Analysis of the obtained graphene flakes to understand the nature of
    - Influence of various functional groups on the synthesised graphene sheets by Fourier transform infrared spectroscopy (FTIR), carried out in the range of 4000 to 400 cm^{-1}.
    - Shape and structure of the obtained graphene sheets by doing a morphological analysis to it under Scanning electron microscope (SEM).
    - Effect of surface functionalization on interlamellar spacing of the graphene sheets from X-ray diffraction (XRD) patterns, using a monochromatic Cu Kα radiation ($\lambda = 0.154$ nm) in the range of 2θ from 10 - 70°.
    - Conductive properties of graphene analysed by two probe method.

CHAPTER 2

LITERATURE REVIEW

2. Literature review

2.1 WHAT IS GRAPHENE ?

Graphene is a two dimensional carbon allotrope. It is a single layer of carbon in a hexagonal lattice, with carbon-carbon distance of 0.142 nm, exhibiting planar structure [3].

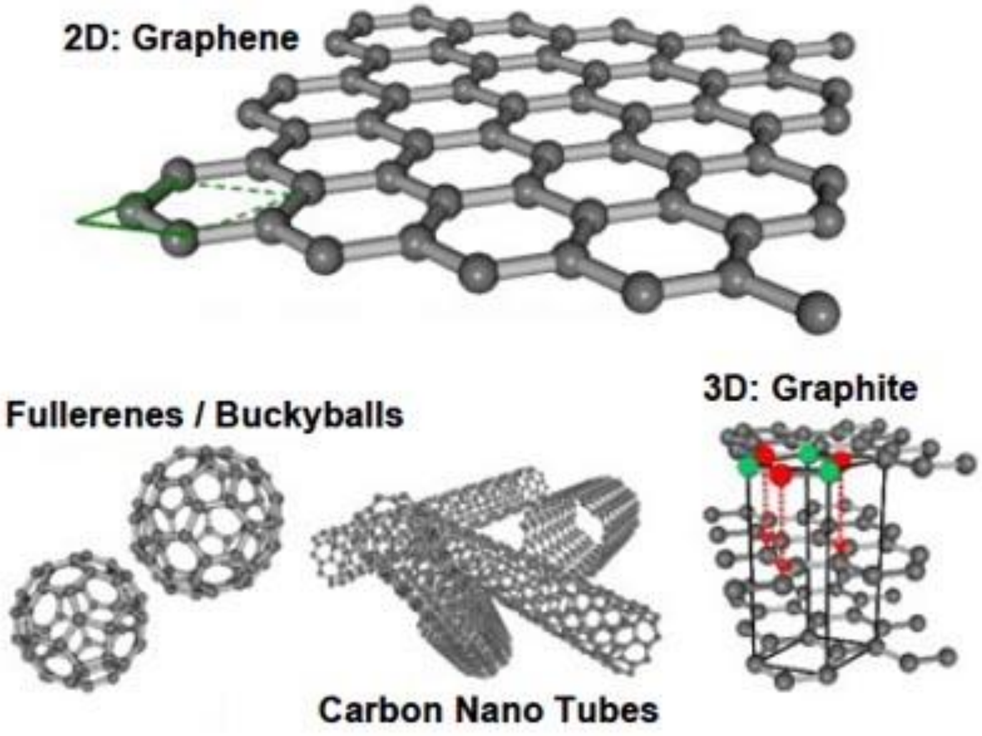


Figure 1 : **2D structure of graphene. Graphene can be rolled on to form Fullerenes, folded up to form nanotubes and stacked upon to form 3D graphite.**

- It is the thinnest compound at one atom thick.
- It is the lightest material weighing at around 0.77 milligrams.
- It is the strongest material, stronger enough than steel yet quite flexible in nature.
- It has better heat conductivity than diamond[4].
- It has better electrical conductivity in nature.
- It exhibits unique levels of light absorption and potential utility in spin transport.

Those amazing properties of graphene enables its utility in improving the performance and efficiency of current materials and substances. It lays a possible futuristic scope of creating even more amazing compounds to suit a wider range of applications when used in conjunction with other two dimensional crystals.

Abundance of carbon in universe makes graphene ecologically friendly and a sustainable solution for intangible applications.

2.2 PROPERTIES OF GRAPHENE

Hitherto thermal instability upon separation incapacitated the existence of two dimensional materials. However the small and strong carbon to carbon bonds in graphene prevent thermal fluctuations from destabilising it.

Electronic Properties

Graphene is a semimetal with no band gap, exhibiting very high electrical conductivity where both electrons and holes effectively acts as charge carriers.

- Carbon atoms have a total of six electrons with two in the inner shell and four in the outer shell. Compared to carbon atom where four outer electrons are available for chemical bonding in graphene, each atom is connected to three other carbon atoms on the two dimensional plane, leaving one electron freely available in the third dimension for electronic conduction. These highly mobile electrons are called **pi (π) electrons [5]** and are located above and below the graphene sheet. The overlapping of these pi orbitals tends to enhance the carbon to carbon bonds in graphene. Fundamentally, the bonding and anti bonding of the valence and conduction bands dictates the electronic properties in graphene.

- Dirac point in graphene, electrons and holes have zero effective mass. This occurs because the energy-movement relation is linear for low energies near the six individual corners of the Brillouin zone. The electrons and holes are known as the **Dirac fermions** and the six corners of the Brillouin zones are known as **Dirac points** **[5]**. Zero density of states at the Dirac points results in low electronic conductivity. However doping of the the Fermi level with electrons and holes can engineer a material with better electrical conductivity[6].

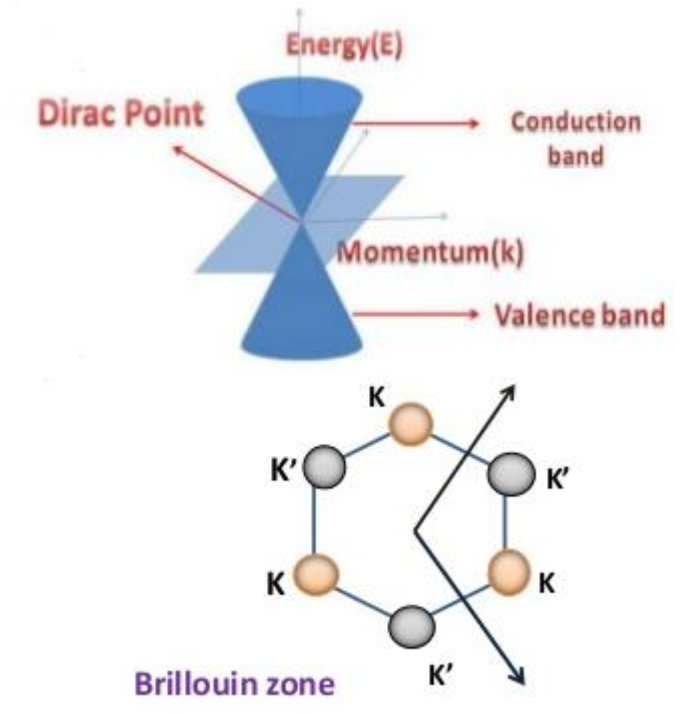


Figure 2 **: Bonding and antibonding of the valence and conduction bands in the Brillouin zones**

- The electronic mobility of graphene is very high, with theoretical potential limits of 200,000 $cm^2V^{-1}s^{-1}$. Graphene elctrons are very much like photons in their mobility due to their lack of mass. These charge carriers are able to travel sub-micrometer distances without scattering : a phenomenon termed as **ballistic transport** [3,5].

Mechanical Properties

- Graphene is the strongest material ever discovered, with an ultimate tensile strength of 130,000,000,000 Pascals.
- It is also very light at 0.77 milligrams per square meter.
- Graphene exhibits a young's modulus of 0.5 TPa.

Optical Properties

In graphene electrons act as massless charge carriers with high mobility thus allowing graphene to absorb relatively a large amount of white light approximately to about 2.3% . Increasing the number of graphene layers will only increase its light absorption capacity.

2.3 USES OF GRAPHENE

Energy Storage

Incorporation of graphene as anode can enhance the capabilities of lithium ion batteries[7,8] to offer much higher storage capacities with much better longevity and charge rate. Low energy applications such as smart phones and portable computing devices can utilise the graphene based supercapacitors[9] enabling them to charge very quickly and assisting them in storage of large amount of electricity.

Graphene enhanced lithium ion batteries could be used in much higher energy usage applications such as electrically powered vehicles, or they can be used as lithium ion batteries in laptops, smartphones and tablet at significantly lower levels of size and weight.

Photovoltaic cells

A possible combination of low absorption of light and high electron mobility enables graphene to be used as an alternative to expensive silicon or Indium tin oxide (ITO) in the manufacture of photovoltaic cells[10,11]. When graphene absorbs a photon it actually generates multiple electrons thereby saving a great amount of heat loss in comparison to silicon, which produces a photon for every electron produced while turning light into electricity. Graphene is quite efficient, being able to work on all wavelengths compared to ability of silicon to generate electricity from certain wavelength bands of light. Graphene being flexible and thin, photovoltaic cells engineered from graphene could be used in clothing to help recharge mobile phones and also can be used in retro-fitted photovoltaic window screens[12].

Optical Electronics

Graphene is an almost completely transparent material and is able to optically transmit 97.7% of light. It is also highly conductive, and so it would work very well in optoelectronic applications such as LCD touchscreens for smartphones, tablet, computer and television.

Composite Material

Graphene is strong, stiff and very light. Graphene can be integrated into platics such as epoxy[13] to create a material that can replace the steel in the structure of aircraft, improving fuel efficiency and reducing weight. Its better electrical conductivity enables graphene to be used to coat aircraft surface material to prevent electrical damage resulting from thunder bolts. Graphene coating can measure strain rate and thus its sensitivity to changes in the stress levels is advantageous to protect aircraft wings from excessive stress. These characteristics can also help in the development of applications such as body armour for military personnel and vehicles that utilises the high strength of graphene.

Biological Engineering

With graphene offering a large surface area, high electrical conductivity, thinness and strength, it digs deep to prove its mettle in fast and efficient bioelectric sensory devices[14,15] and also displays ability to monitor glucose levels, haemoglobin levels, cholesterol and DNA sequencing. Engineered toxic graphene can be used as an antibiotic or for anticancer treatment. Graphene can also be ued in tissue generation due to its molecular build up and biocompatibility.

Ultrafiltration

Even relatively small than helium molecules, graphene is impervious to all liquid and gas allowing water to pass through it, thus could be used as ultrafiltration medium acting as barrier between two substances.

Being one atom thick graphene can be beneficially deployed as a barrier to electronically measure strain and pressure between two substances.

Graphene is much stronger and less brittle than aluminium oxide allowing it to be developed for the usage of water filtration systems, desalination system and efficient and economically more viable biofuel creation.

2.4 SYNTHESIS OF GRAPHENE

Basically there are two different approaches to preparing graphene.

- Graphene can be detached from an already existing graphite surface, the so called exfoliation process.
- Graphene layer can be grown directly on a substrate surface.

2.4.1 TOP DOWN APPROACH

Mechanical Exfoliation

This process is also known as “scotch tape method” and is the first of many process to be used for the discovery of graphene.

Multi-layer graphene are obtained by peeling off a graphite source using a tape. Multi-layer graphene can be cleaved into few graphene layer flakes by repeated peeling.

It results in production of very high quality graphene with no defects.

Limitation:

- Reliability of the mechanical exfoliation process is quite low regarding production of similar structured graphene.
- This process is not feasible for industrialisation.

Chemical Exfoliation

It simply involves synthesising graphite oxide, dispersing the flakes by sonication to form graphene oxides and reducing it back to graphene[16].

By the oxidation of graphite using strong oxidising agents, oxygenated functionalities are introduced in the graphite structure aiding in intercalating and rendering the surface hydrophilic thus enabling graphite oxide to be exfoliated in water using sonication, ultimately producing single or few layer graphene, known as **graphene oxide (GO),** which is a system of few layers to monolayer.

Properties of graphene oxide

- The presence of oxygenated functionalities makes graphene oxide easily dispersable in water and other organic solvents. This is an important property in terms of improving the electrical and mechanical properties when used with ceramic or polymer matrices.
- Graphene oxide is an electrical insulator.
- Functionalization of graphene oxide can fundamentally change graphene oxide's properties thus enabling the chemically modified graphene much more adaptable to a numerous applications.
- Chemical reduction of graphene oxide fabricates the path for mass production of graphene.

Limitation:

- Though it is a low temperature process that makes it easier to fabricate graphene on various types of substrates at ambient temperature however, homogeneity and uniformity of large area graphene is not satisfactory.
- The incomplete reduction of graphene oxide leads to degradation of electrical property.

2.4.2 BOTTOM UP APPROACH

Epitaxial Growth

Epitaxial growth involves growth of a single crystal film on top of a crystalline substrate[17].

- The growth of graphene starts at several location on the crystal simultaneously and these graphene islands grow together.

- Complexity of the process is effectively low and allows for graphene growth on a perfect single cystal.
- Size of the graphene layer can be limited by the size of crystal used.

Limitation:

- Graphene synthesised is inhomogeneous in nature due to defects or grain boundaries.

Chemical Vapour Deposition (CVD)

It is one of the most commonly used process for synthesising graphene.

In this process generally, a substrate is exposed to gaseous compounds. These compounds decompose on the surface in order to grow a thin film, whereas the by products evaporate.

It is advantageous for large area device fabrication and favourable for complementary metal-oxide semiconductor technology[18].

Limitation:

- Purity of the graphene produced by this method is not very high making it unsuitable for laboratory research.

2.5 ELECTROCHEMICAL EXFOLIATION OF GRAPHENE

Most of the above mentioned processes for graphene synthesis has been well explored barring electrochemical exfoliation process. Most of them are time consuming process and the yield is quite low.

Electrochemical exfoliation is a greener process, comparatively cheaper, capable of mass production of few layer graphene (FLG) by mere control of potential operating at ambient conditions of temperature and pressure.

- Using electrochemical method (Liu et al., 2008) peeled FLG off graphite at anode in ionic liquids. This solution based method makes graphene amenable to be processed into the form of film, on most substrates including flexible type.

  In his experiment, the author reported about development of a simple, fast and green electrochemical method for the synthesis of graphene nanosheets (GNS) having high structural homogeneity and excellent electrical conductivity with one treatment step and with the assistance of an ionic liquid (IL) and water.

In a typical synthesis, 10 ml 1-octyl-3-methyl-imidazolium hexafluorophosphate and 10 ml water was used as electrolyte. A static potential of 15 V was applied between the two graphite rods. After corrosion for 6 hours at room temperature, a black precipitate of GNS was obtained at the bottom of the reactor.

- (Ching Yuan Su et al., 2011) carried out electrochemical exfoliation of graphite in a 0.5 M H_2SO_4 solution using graphite as anode and platinum as cathode. High quality graphene but with lower yield was obtained.

  In his study, the author performed electrochemical exfoliation of graphite in sulphuric acid to obtain high quality and large area thin graphene sheets. He used Pt wire as grounded electrode and 4.8 g of 98% H_2SO_4 diluted in 100 ml of deionised water (DI) as electrolyte. A static bias of +1 V was first applied to the graphite for 5-10 min, followed by ramping of the bias to +10 V for another 1 min. In order to reduce the oxidation of graphite by H_2SO_4, KOH was also added to the electrolyte. Meanwhile the author also optimised the exfoliation conditions by applying a potential of +2.5 V for 1 min and then applying high bias, alternating between potential of +10 V and -10 V until desired amounts of exfoliated sheets were obtained.

- (Parvez et al., 2013) used electrochemical exfoliation method to obtain comparatively large graphene sheets by tuning the acidity of H_2SO_4 to 1.0 M solution.

  In the experimental setup natural graphite flakes, platinum wires and 0.1 M H_2SO_4 solutions were used as working electrodes, counter electrodes and electrolytes, respectively. In the experiment, a positive potential of +10 V was applied to a graphite electrode for a duration of 2 min to complete the exfoliation process.

- Most recent work by (Sumanta et al., 2015) entails using the method of electrochemical exfoliation to fabricate thin graphene with lateral dimension of 11 to 26 µm comprising of 4 to 6 stacked layers. His work was indicative of increment in lateral dimension of graphene by a variation of intercalating potential.

  In his experiment, the author synthesised thin layered graphene nanosheets following a simple electrochemical route with varying intercalate concentrations. In the experiment setup, a pyrolytic graphite sheet of thickness 3 mm was employed as both the working electrode and counter electrode and a simple protic H_2SO_4 was dissolved in double distilled water to form electrolyte at various concentrations of 0.1M, 0.3M, 0.5M and 1M. The working electrode was initially given a cathodic pretreatment at 10 V followed by initiation of anodic exfoliation at a lower bias of 0-5 V with ramping step of 1 V for 15 min. Subsequently, exfoliation was commenced at a higher bias of 10 V for about 30 min until required amount of stratified material was procured.

CHAPTER 3

EXPERIMENTAL DETAILS

3. Experimental Details

3.1 SAMPLE PREPARATION

- Two pyrolytic graphite sheets of 6×1×0.3 cm were used as both cathode and anode.
- Graphite sheets were properly washed with acetone before being employed for experimentation.
- Graphite sheet to be used as anode was wrapped up in adhesive tapes exposing an area of 2 cm^2. The exposed area of the sheet was given a genteel peel off by the adhesive tape to get rid of any residue from its surface, making sure the availability of pores to speed up the reaction process, followed by acetone wash-up.
- HNO_3 of 0.5M, 1M, 1.5M, 2M, 2.5M solutions were used as electrolyte.

3.2 EXPERIMENTAL SET UP

- An electrochemical cell was developed by the use of graphitic sheets as cathode and anode, successively with electrolyte solutions of 0.5M, 1M, 1.5M, 2M, 2.5M HNO_3.
- Initiating the experiment from a minimum potential, the experiment was continued with an increment of 0.5V at an interval of 180 seconds until completion of exfoliation.
- Changes in current levels were noted for respective applied potential and subsequently the erratic changes to the exfoliation process were observed.

3.3 EXFOLIATION PROCESS

In this experiment, electrochemical exfoliation of pyrolytic graphite sheets was done in aqueous nitric acid solution to obtain few layered graphene sheets (FLGs). A pyrolytic graphite (Absury Graphite Mills, AR 12) was employed as both the working and counter electrode in a voltage regulated DC bias system (Aplab, Model no. 7103). The anodic exfoliation was commenced at a potential of 1V followed by a subsequent increase of 0.5V at regular intervals of 180 seconds. Exfoliation was carried for an overall duration of 4380 seconds in general, till procurement of fully stratified graphene layers.

During hydrolysis reaction, hydrogen gets adsorbed on the lattice of graphite leading to release of hydrogen gas which later on accounts for expansion of graphite surfaces and removal of any residue.

$C_{lattice} + H^+ \rightarrow C_{lattice}H_{adsorbed}$

$C_{lattice}H_{adsorbed} + H_2O + e^- \rightarrow C_{lattice}(\text{expanded}) + H_2\uparrow + OH^-$

At higher applied potential, the pre-expanded graphite sheet at the anode gets intercalated, subjected primarily to the action of NO_3^- and OH^- . As a result of the intercalation the graphite intercalate compounds are subjugated by oxidation, hydroxylation and carboxylation with subsequent release of CO_2 and O_2 gas.

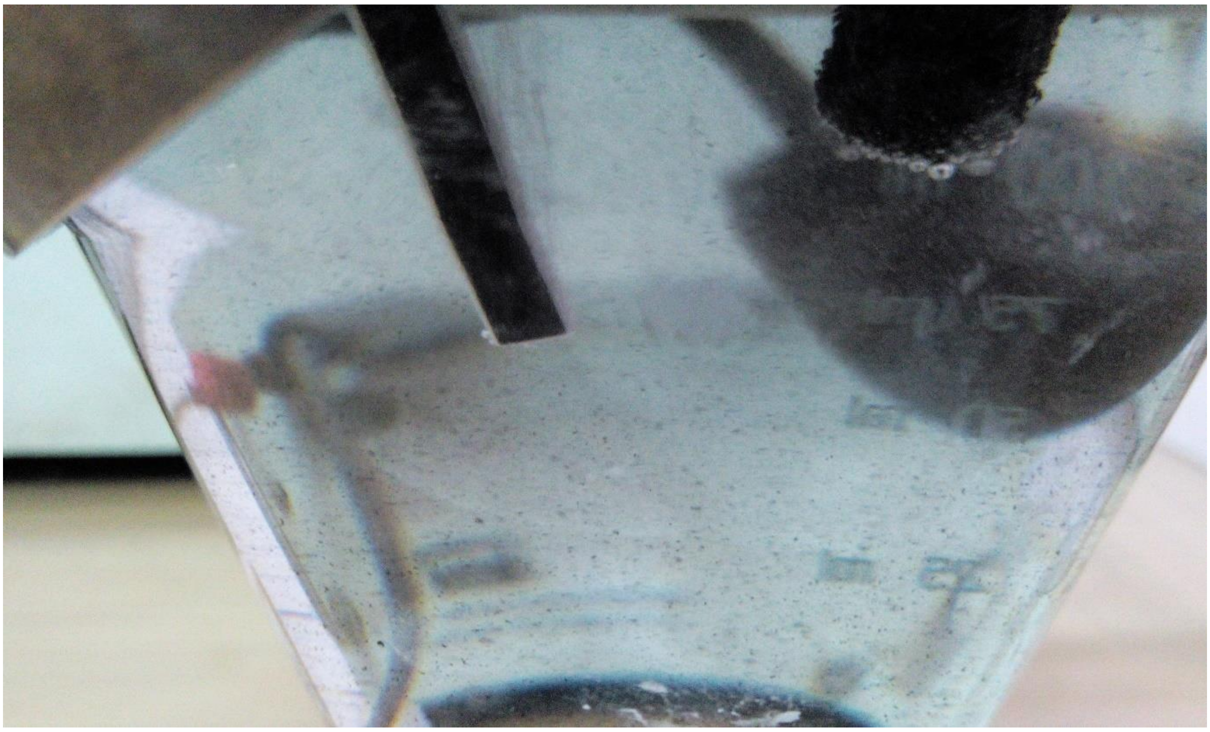


Figure 3 **: Formation of the hydrogen bubbles in the cathode is indicative of the initiation of exfoliation process .**

$2HNO_3 \rightarrow H_2O + NO_3^- + NO_2^+$

$\mathbf{C_{n\ lattice}(expanded) + A + H_2O \rightarrow AC_{(n-1)lattice}(exfoliated) + CO_2\uparrow + O_2\uparrow}$

● NO_3^-	● H^+
‖ Graphite layers	‖ Intercalated and exfoliated graphite layers

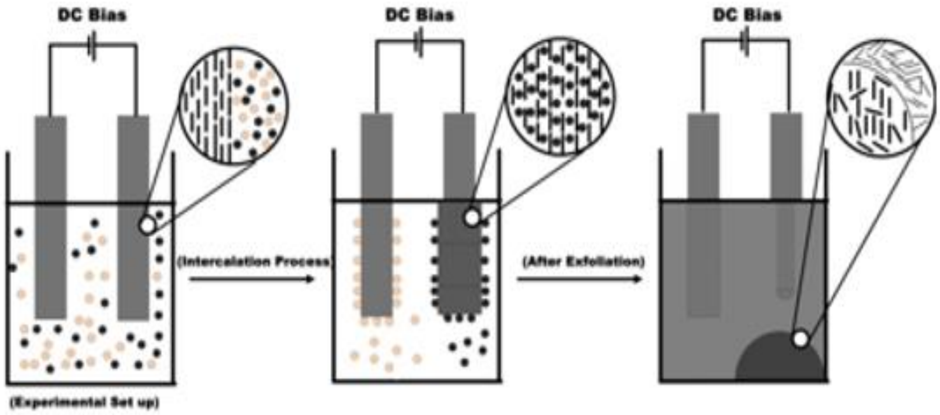


Figure 4 **: Schematic diagram of the exfoliation process**

Following completion of exfoliation process, the obtained graphene solutions were repeatedly washed for about five to six times over a period of ten days to dispose of any residual nitric acid and graphitic flakes from its bulk. Hitherto the liquid graphene solution was subjected to sonication for duration of 30 minutes to disintegrate the graphitic flakes followed by a centrifugation at 3000 rpm for another 30 minutes. Prior to characterisation of graphene, the liquid solution was finally oven dried at a temperature of 80°C for about 2 to 3 hours.

3.4 CONDUCTIVE ANALYSIS

- Few layered graphene powder exfoliated at HNO_3 concentration of 2M was separated into three separate quantities of 0.01, 0.02 and 0.03 g.
- Those separated quantities of FLGs were dispersed in 15 ml of dimethyl formamide (DMF).
- The obtained solution was sonicated for 300 seconds at an amplitude of 20.

- Two copper sheets of area 2.5 × 2 cm^2 were used for forming electrodes for the conductive analysis.
- An area of 2 cm^2 of these copper sheets were exposed, wrapping up the rest with adhesive tapes.
- An electrolytic cell was formed using these copper sheets in a small beaker of 10 ml, dipped in the electrolyte of the obtained solution of FLG and DMF.

CHAPTER 4

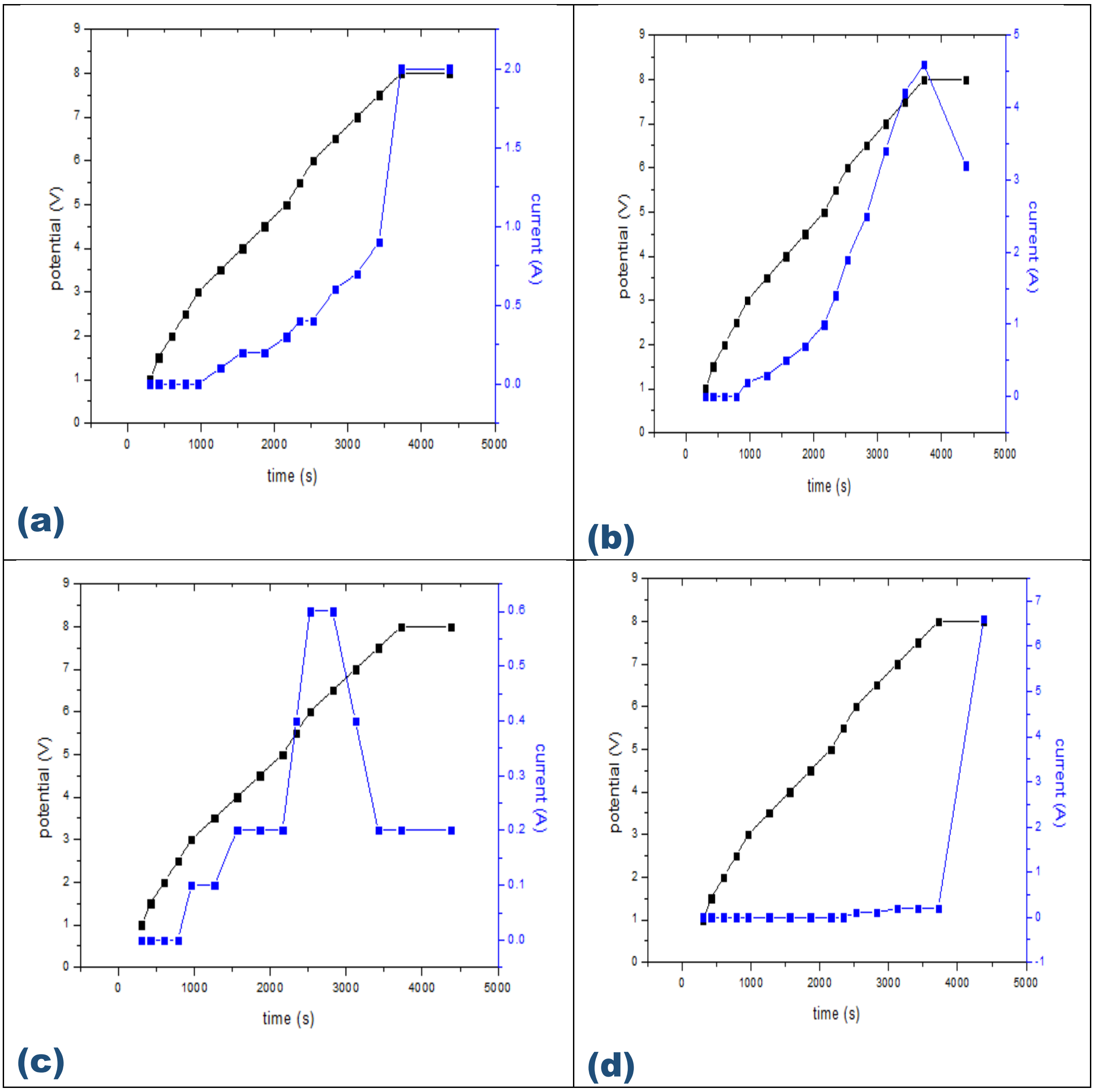
RESULTS AND DISCUSSION

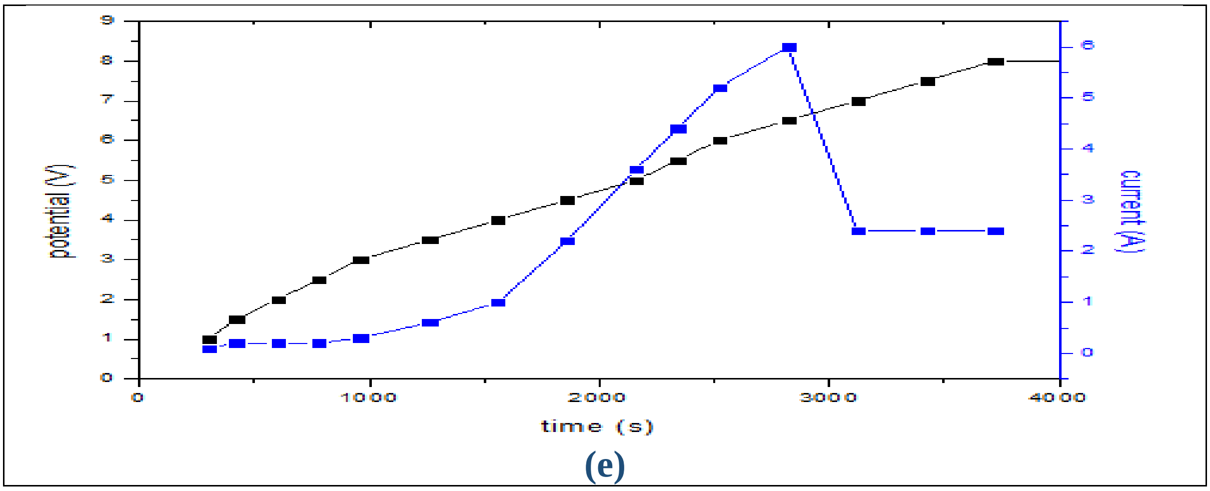
CHAPTER 4

Results and Discussion

4. Results and Discussion

4.1 EFFECT OF INTERCALATION POTENTIAL ON EXFOLIATION PROCESS



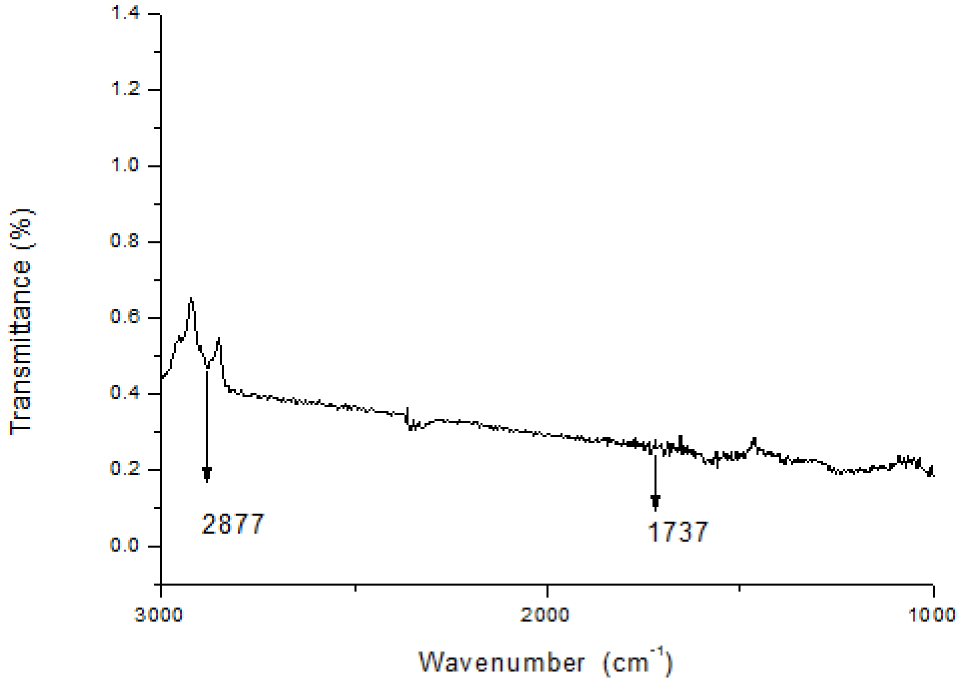


(e)

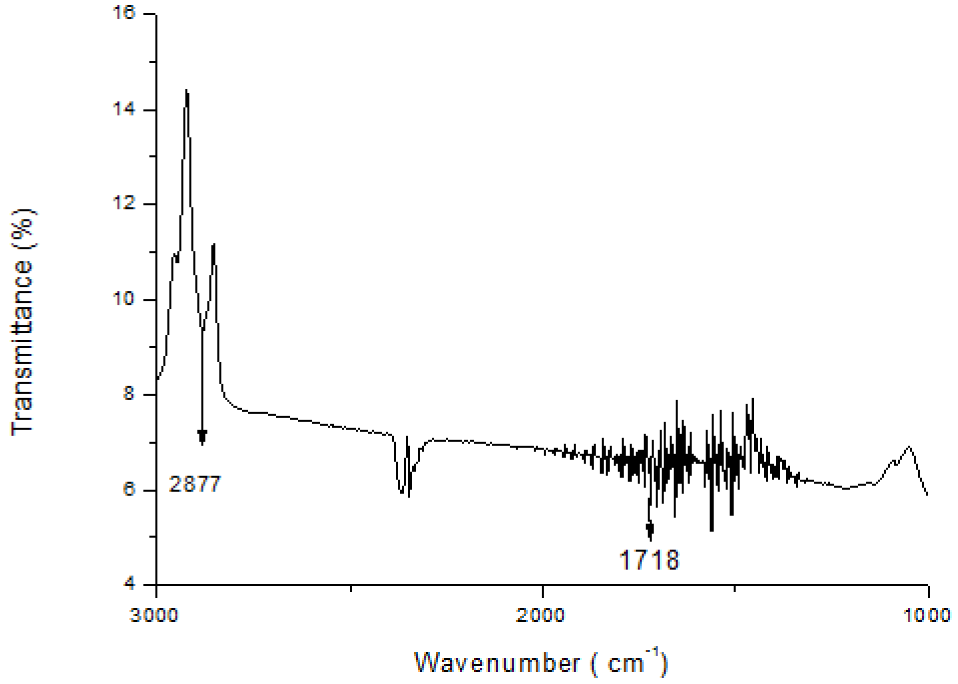
Figure 5 **: Variation of current with respect to applied potential at specific point of time for electrolyte concentrations of (a) 0.5M (b) 1M (c) 1.5M (d) 2M (e) 2.5M**

Exfoliation process initiates with the formation of hydrogen bubbles at the cathode. Exfoliation starts only at a specific potential sufficient enough to dissociate nitric acid into nitrate ions thus enabling intercalation. Higher concentration of the electrolyte results in faster dissociation of nitric acid hence, results in faster exfoliation rate as compared to solutions of lower concentrations. An increase in current generally marks intercalation of $NO3^-$ ions into graphite expanding it for exfoliation of newer graphitic flakes. The drop in current is generally due to withering away of the exfoliation process.

4.2 FTIR Analysis



(a)



(b)

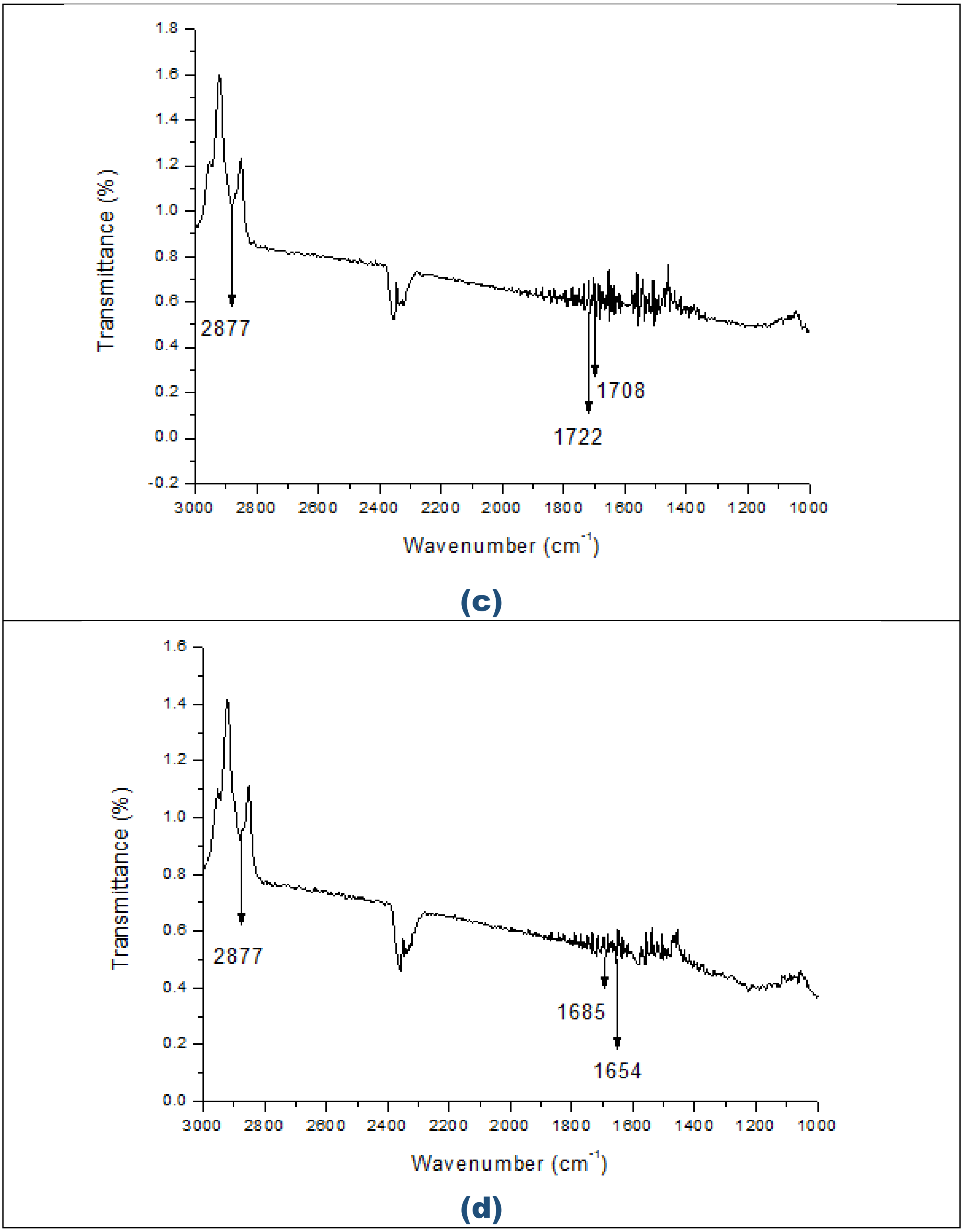


Figure 6 **: FTIR Spectra of FLGs powder exfoliated at HNO^3 concentrations of (a) 1M (b) 1.5M (c) 2M (d) 2.5M**

FTIR spectra of the exfoliated graphene powders obtained at concentrations of 1M, 1.5M, 2M and 2.5M confirms oxygenation and carboxylation of the obtained graphene. To the delight of the experiment, the samples are devoid of any non bonded NO_3^- ions as reported by IR spectra.

Table 1 **: IR Spectra chart showing the types of bonds and functional groups present in FLGs obtained at HNO^3 concentrations of (a) 1M (b) 1.5M (c) 2M (d) 2.5M**

Concentration of HNO_3 at which graphene powders are obtained (M)	Frequency (cm^{-1})	Bond	Functional group
1	2877	O-H stretch	Carboxylic acids
	1737	C=O stretch	Carboxylic acids
1.5	2877	O-H stretch	Carboxylic acids
	1718	C=O stretch	Esters and saturated aliphatic
2	2877	O-H stretch	Carboxylic acids
	1722	C=O stretch	Aldehydes and saturated aliphatic
	1708	C=O stretch	α β unsaturated aldehydes, ketones
2.5	2877	O-H stretch	Carboxylic acids
	1685	C=O stretch	α β unsaturated aldehydes, ketones
	1654	C=C stretch	Alkenes

4.3 XRD Analysis

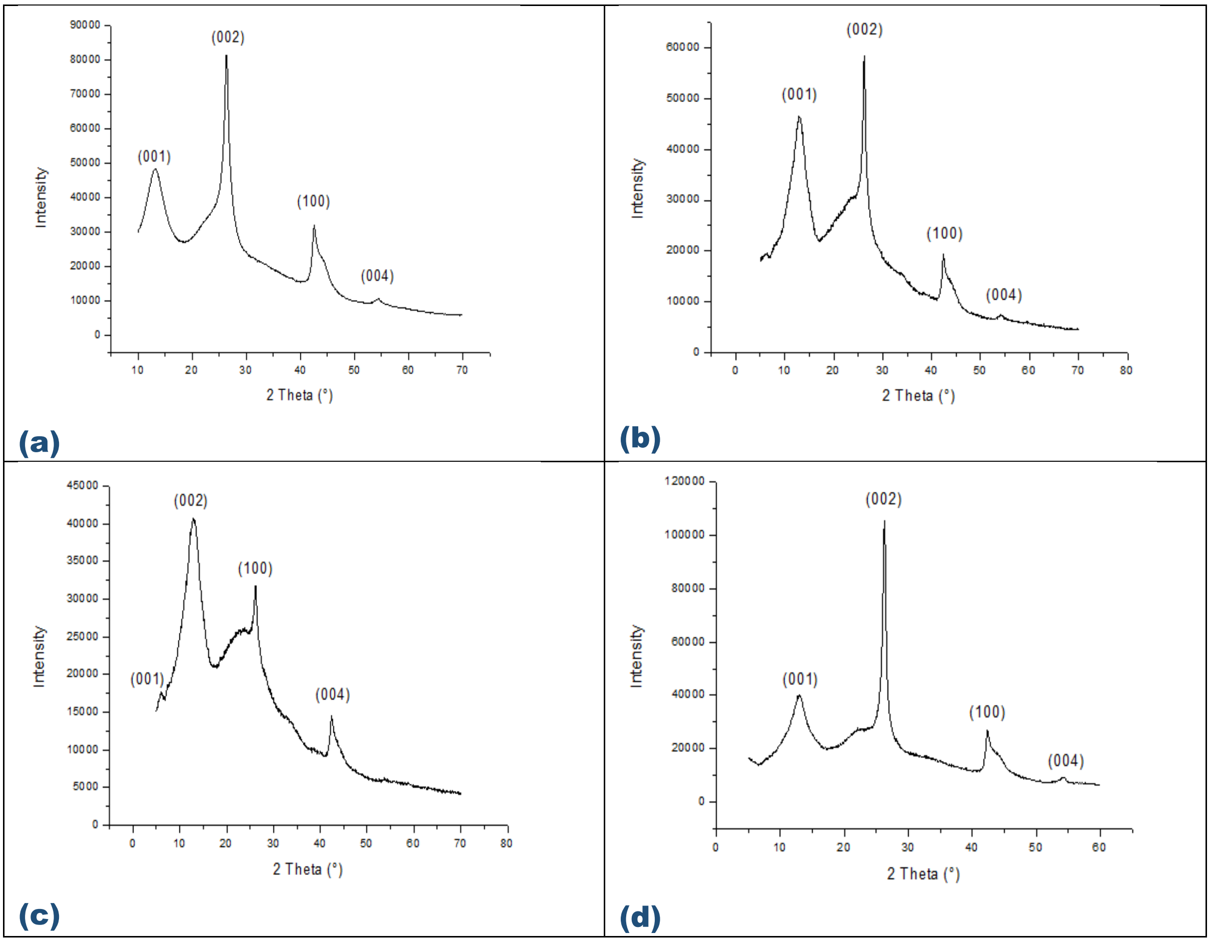


***Figure 7*: XRD pattern of the FLGs powder exfoliated at HNO^3 concentrations of (a) 1M (b) 1.5M (c) 2M (d) 2.5M**

XRD analysis was commenced upon to reveal any structural changes related to the interplanar expansion of the graphitic sheet.

The XRD pattern is indicative of four intensive peaks, more or less, at 12.9°, 26.5°, 42.4° and 54.3° corresponding to (001), (002), (100) and (004) crystal planes.

The sharp intense peak obtained at 2θ value about 26.5° is a confirmation regarding formation of graphene as (002) crystal plane happens to be the basal plane of graphene.

Subsequent peak broadening at about 42.4°, 54.3° corresponding to (100) and (004) crystal planes gives a clear indication of the increase in interlayer spacing within graphitic structures, confirming the presence of few layered graphene.

Though exfoliation of pyrolytic graphite yielded few layered graphenes, some of them might have reverted back to form graphene oxide (GO) due to ample availability of oxygen as marked by (001) peak at 2θ value of 12.98°.

4.4 SEM Analysis

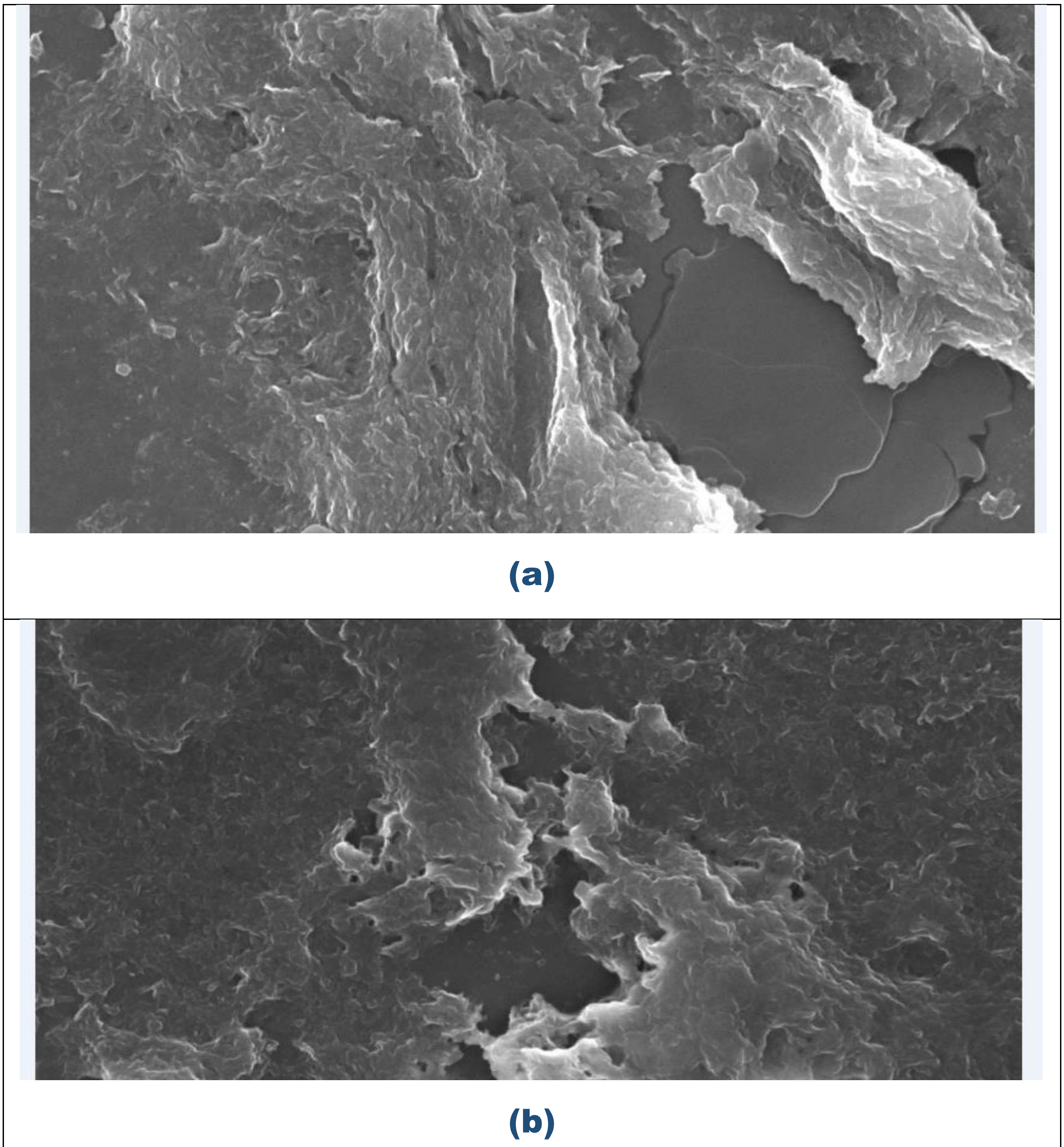


Figure 8 **: SEM images of FLGs exfoliated at HNO_3 concentrations of (a) 2M (b) 2.5M**

Figure 8(a) and 8(b) are the SEM images of the graphene obtained upon dispersing the exfoliated graphite powder from HNO_3 concentrations of 2M and 2.5M in dimethyl formamide (DMF).

The images indicate few layers of graphene with distinctive clarity. These clear images are a substantial confirmation of formation of FLGs. However extensive sonication has led to corrugation of the graphene layers as can be seen from the folded edges of the layers.

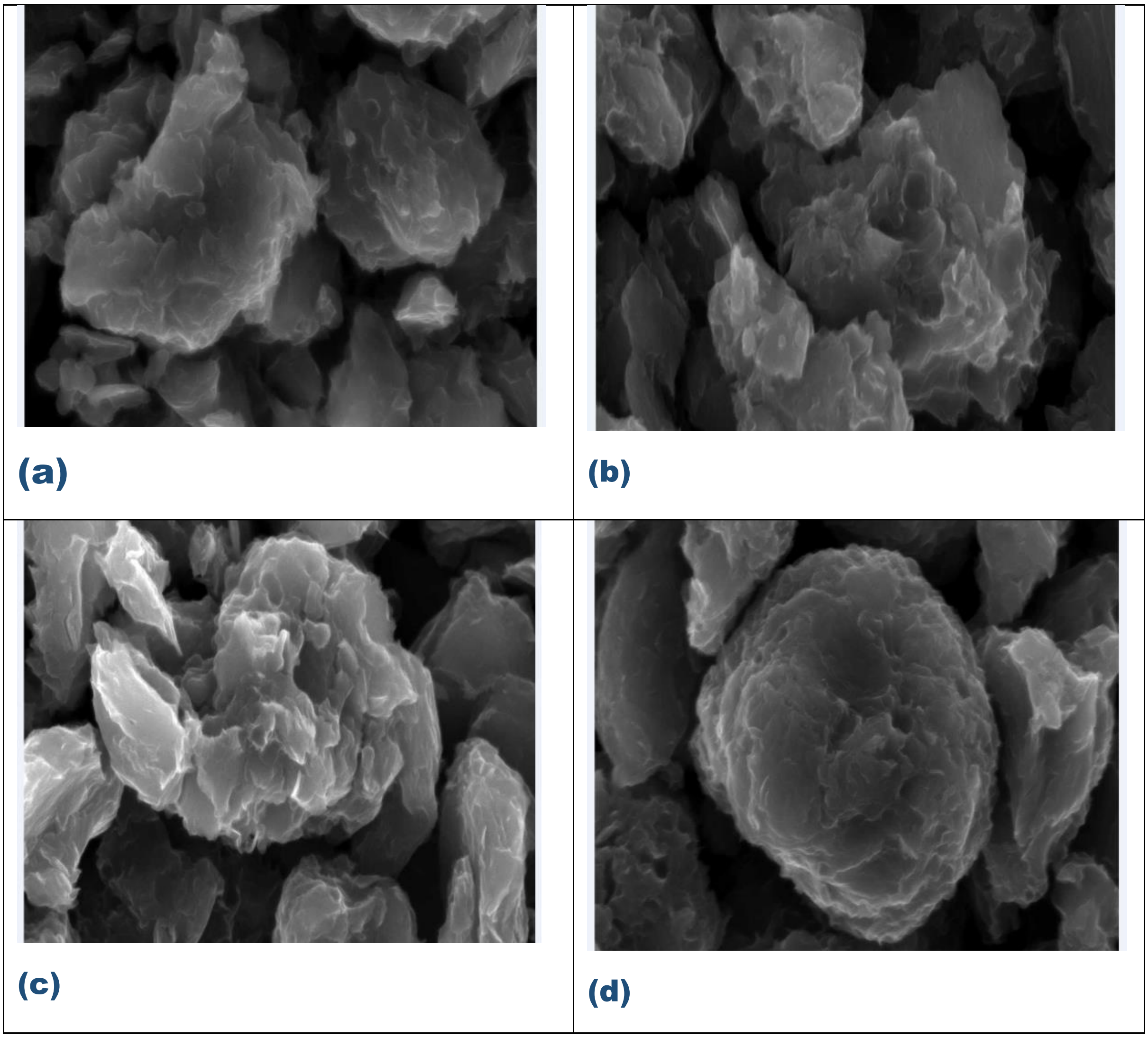


Figure 9 **: SEM images of the FLGs powder exfoliated at HNO_3 concentrations of (a) 1M (b) 1.5M (c) 2M (d) 2.5M**

Figure 9(a), 9(b), 9(c) and 9(d) are the SEM images of the graphitic powder obtained upon exfoliating pyrolytic graphite in HNO_3 solution of 1M, 1.5M, 2M, 2.5M. It can be clearly seen of thin transparent and stacked on each other within a small chunk of graphite talc.

4.5 CONDUCTIVITY Test

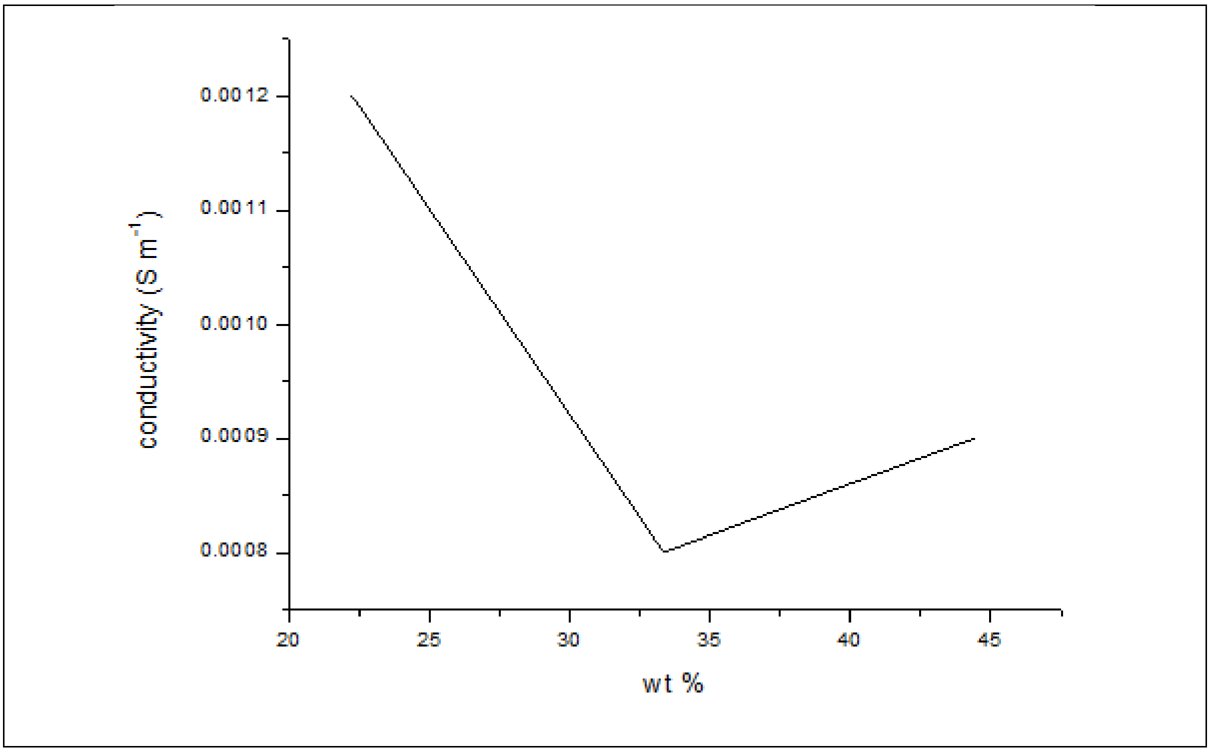


Figure 10 **: Conductivity test result of the exfoliated few layered graphene (FLG) obtained at HNO_3 concentration of 2.5 M**

As expected the conductive analysis has resulted in a decreasing trend of the plot with increasing weight percentage[19]. At lower weight percentage presence of few layers of graphene offers lesser resistance to ionic flow, hence improving the conductivity. As the weight percentage increases the stacking of graphene layers increases to offer a higher resistance thus deteriorating the performance of graphene.

5. Conclusion

The very effective combination of the beneficial properties of nitric acid and anodic process of exfoliation yielded successful results to the "exfoliation process of pyrolytic graphite". The rate of intercalation is perceptibly affected by the HNO_3 concentrations and applied potential. An increase in HNO_3 concentration ensures ample availability of nitrate ions (NO_3^-) for effective intercalation. The process of exfoliation is triggered by a faster ionic movements in the solution at increased potential.

The exfoliated powder product obtained upon exfoliating nitric acid at different concentrations of 0.5M, 1M, 1.5M, 2M, 2.5M gave sufficient ammunition to prove the final product to be few layered graphenes (FLGs) based on its characterisation.

- The FTIR analysis performed in the range of 4000 to 400 cm^{-1} Shimadzu IR Prestige-21 instrument showed peaks at 2877, 1737, 1718, 1722, 1708, 1685 and 1654 cm^{-1} indicating the graphene samples having undergone oxygenation, carboxylation and hydroxylation during the exfoliation process.
- The SEM images showed several layers of graphene stacked together and slight corrugation due to sonication as compared to graphitic images where several platelets combined to form agglomerates.
- The XRD pattern obtained in the range of 2θ from 10 to 70° by X'Pert Pan analytical model : DY 1656, using a monochromatic Cu Kα radiation revealed a sharp intensive peak at (002) crystal plane, the basal plane of graphene. Oxygenation of graphene yielded a peak at (001) relating to that of graphene oxide (GO). The successive broadening of peaks at (100) and (004) gives sufficient confirmation to the strain lumbered on the graphitic layers by ample NO_3^- ions to generate FLGs.
- Good electrical conductivity of graphene was confirmed by the results yielded upon conductive analysis performed by two probe method. However error generated due manual handling resulted in an inconvenient reading of reduced resistance at higher weight percentage in contradiction to the converse of a more likeable result where increased resistance with weight percentage resulting in reduced conductivity is expected.

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