

CARBON QUANTUM DOTS ASSISTED  
GRAPHENE EXFOLIATION DERIVED  
ACTIVATED CARBON

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CARBON QUANTUM DOTS ASSISTED GRAPHENE  
EXFOLIATION DERIVED ACTIVATED CARBON

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Thesis submitted in fulfillment of the requirements  
for the award of the degree of  
Bachelor of Applied Science (Honours) Material  
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DECEMBER 2016

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## **DEDICATION**

*I dedicate this thesis to my beloved family for their unconditional love, support and encouragement. My supervisor, Dr. Izan Izwan and Miss Nurul Khairiyyah for their generous guidance, knowledge and time. Lastly, for Nur Ainina and Nur Rasyidah for always being there through thick and thin.*

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## ABSTRACT

Graphene is deemed as the strongest and toughest material since its discovery in 2004 by Andre Geim and Konstantin Novoselov as it offers exceptional potential in electronic, thermal and mechanical properties for various application in future. Graphene can be derived from any materials that have presence of carbon in its structure and can be exfoliated in various ways including wet chemicals route. However, chemical reduction of graphene from any carbon sources is highly toxic and harmful to human's health and environment. In this study, an environmental friendly approach to exfoliate graphene is proposed where graphene is derived from activated carbon (AC) and water as solvent through liquid phase exfoliation method. The exfoliation is assisted by sonication process where the induced microbubbles due to cavitation will collapse and release a tremendous amount of energy to exfoliate graphene from AC. Since water has high surface tension, carbon quantum dots (CQDs) is added to reduce the surface tension to the optimum range and as an exfoliation agent. The CQDs is synthesized from citric acid and urea by microwave irradiation. Dialysis process of CQDs solution is done to remove large and unreacted particles to obtained fine particle size of CQDs. The morphology of exfoliated graphene and CQDs is confirmed by FESEM analysis. The functional groups for exfoliated graphene and CQDs are determined by FT-IR (ATR) spectroscopy analysis. The concentration of exfoliated graphene obtained is calculated by linear regression equation obtained from a standard curve of graphene where 0.01177 mg/mL is produced from 24 mg of activated carbon.



## ABSTRAK

Graphene dianggap sebagai bahan yang paling kuat sejak penemuannya pada tahun 2004 oleh Andre Geim dan Konstantin Novoselov kerana ia menawarkan potensi yang luar biasa dari segi ciri-ciri elektronik, haba dan mekanikal untuk pelbagai kegunaan pada masa hadapan. Graphene boleh diperolehi dari mana-mana sumber yang mempunyai kehadiran karbon dalam strukturnya dan boleh menjalani proses pengelupasan dalam pelbagai cara termasuk kaedah kimia. Walau bagaimanapun, pengelupasan graphene daripada mana-mana sumber karbon menggunakan kimia adalah sangat bertoksik dan berbahaya serta memberikan kesan kepada kesihatan manusia dan alam sekitar. Dalam kajian ini, pendekatan mesra alam untuk pengelupasan graphene telah dicadangkan di mana pengelupasan graphene daripada karbon aktif (AC) dan menggunakan air sebagai pelarut melalui kaedah fasa cecair pengelupasan (LPE). Proses pengelupasan ini dibantu oleh proses sonikasi di mana buih-buih mikro disebabkan oleh peronggaan (cavitation) akan pecah dan melepaskan tenaga yang sangat besar untuk mengelupas graphene daripada AC. Oleh kerana air mempunyai ketegangan permukaan air yang tinggi, titik karbon kuantum (CQDs) telah ditambah ke dalam air untuk mengurangkan ketegangan permukaan air hingga menghampiri julat optimum dan juga bertindak sebagai agen pengelupasan. Titik karbon kuantum (CQDs) disintesis daripada asid sitrik dan urea melalui penyinaran gelombang mikro (microwave irradiation). Titik karbon kuantum kemudiannya melalui proses dialisis di mana ia bertujuan untuk mengeluarkan zarah besar dan tidak aktif untuk mendapatkan zarah halus titik karbon kuantum. Morfologi graphene yang telah mengelupas dan titik kuantum karbon dikaji dan disahkan menggunakan analisis FESEM. Kumpulan berfungsi (FTIR) untuk graphene yang telah mengelupas dan titik kuantum karbon disahkan oleh FT-IR-ATR analisis. Kuantiti graphene yang mengelupas dikira menggunakan persamaan regresi linear yang diperolegi melalui lengkungan standard graphene di mana sebanyak 0.01177 mg/mL berjaya dihasilkan daripada 24 mg AC.

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## LIST OF SYMBOLS

|                             |   |   |
|-----------------------------|---|---|
| ~                           | - | approximately   |
| $\text{cm}^2/\text{Vs}$     | - | electron mobility                                     |
| $\text{W/mK}$               | - | heat conductivity                                     |
| $\Omega^{-1}\text{cm}^{-1}$ | - | electrical conductivity                               |
| $\text{mJ/m}^2$             | - | surface tension                                       |
| C-C                         | - | carbon single bond                                    |
| C=C                         | - | carbon double bond                                    |
| %                           | - | percentage  |
| wt%                         | - | weight percentage                                     |
| g                           | - | gram  |
| mmol                        | - | milimol   |
| W                           | - | Watt  |
| $\mu\text{m}$               | - | micro metre   |
| mL                          | - | mili litre  |
| A                           | - | absorbance unit                                       |
| $\alpha$                    | - | constant value of $2460 \text{ Lg}^{-1}\text{m}^{-1}$ |
| l                           | - | length  |
| $\lambda$                   | - | wavelength  |
| $^{\circ}\text{C}$          | - | degree celcius  |
| $\text{\AA}$                | - | angstrom ( $10^{-10}$ )                               |
| h                           | - | hour  |
| $t$                         | - | time  |

## LIST OF ABBREVIATIONS

|       |   |   |
|-------|---|---|
| AC    | - | activated carbon                            |
| CQDs  | - | carbon quantum dots                         |
| CVD   | - | chemical vapour deposition                  |
| DI    | - | deionized water                             |
| DMF   | - | Dimethylformamide                           |
| FESEM | - | field emission scanning electron microscope |
| FT-IR | - | fourier transform infrared spectroscopy     |
| GICs  | - | graphite intercalation compounds            |
| GO    | - | graphene oxide                              |
| KOH   | - | potassium hydroxide                         |
| LPE   | - | liquid phase exfoliation                    |
| NMP   | - | N-methyl-2-pyrrolidone                      |
| NMP   | - | N-methyl-2-pyrrolidone                      |
| rpm   | - | rotation per minute                         |
| UHV   | - | ultra-high vacuum                           |

# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND PROBLEM

Graphene is a single layer of stacked graphite which is an allotrope of carbon in 2-dimensional (2D) plane where the  $sp^2$  hybridised carbon atoms are arranged in a honeycomb lattice. Graphene has garnered a lot of attention and intense interest due to its excellent physical properties and because its surface and edges can be modified chemically (Du *et al*, 2013). It is the thinnest material on earth where the size is about one atom thick. Graphene owns excellent electronic ( $\sim 15000 \text{ cm}^2/\text{Vs}$ ), mechanical ( $\sim 1000 \text{ GPa}$ ) and optical properties where it can conduct heat ( $\sim 5000 \text{ W/mK}$ ) and electricity ( $\sim 0.96 \times 10^6 \text{ } \Omega^{-1}\text{cm}^{-1}$ ) efficiently. Thus, graphene is foreseen as a promising material for various application such as nano-electronics, energy storage and conversion, drug delivery, sensor and catalysis (Liu *et al*, 2013).

Many synthesis methods have been developed in order to produce a quality, defect-free graphene in large quantities and with a lower production cost. Chemical reduction of graphene oxide (GO) is used widely as one of the common methods to exfoliate graphene. However, GO is intrinsically defective and electrically insulating due to the aggressive oxidation process that causing many defects in the  $sp^2$  carbon lattice. Thus, disrupts the band structure and degrade the unique electronic properties of graphene (Wei and Sun, 2015). This method also raises environmental issue as strong oxidizing (eg:  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NHO}_3$ ) and reducing (eg: hydrazine,  $\text{NaBH}_4$ ) reagents are used. There is an urge to develop a green method by following environmentally friendly approach.



In order to cope with the issue, liquid phase exfoliation (LPE) is seen as the best option. This method has garnered a lot of attention from researchers due to its simple method preparation to produce graphene by dispersing graphite in the ionic liquid, surfactant solution and organic solvent. Based on a report by (Guardia *et al*, 2011), a wide range of non-ionic surfactants is useful to exfoliate and disperse graphene at significant concentrations. (Khan *et al*, 2010) prepared stable graphene by dispersing in N-methyl-2-pyrrolidone (NMP) at high concentration. (Lotya *et al*, 2009) proposed that LPE is a non-oxidative method and does not require high temperature processes or chemical post treatments. Furthermore, to ensure a successful graphene exfoliation LPE should be compatible with safe, user-friendly, low boiling-point solvents, preferably water. But, the process consumed a large amount of time (~400 h) and too much of excess energy from sonication bath does not help in obtaining large areas of graphene layer (Zhu *et al*, 2013). Therefore, in order to produce defect-free graphene layer with high efficiency of electrical performances, types of dispersion solution used and time of sonication is taken into consideration. Moreover, ionic liquid and NMP solvents is considered as expensive and hazardous even though the surface tension of the solvents match with graphene which is around 40 mJ/m<sup>2</sup> but the boiling points is very high (NMP 203°C, o-DCB 181°C, DMF 154°C) (Ciesielski and Samorì, 2014).

In most LPE synthesis, graphite was used as the starting material. Theoretically, graphite is a stacked of graphene consists of sp<sup>2</sup> hybridised carbon atoms which bonds to formed hexagonal crystal lattice. The LPE will allow formation of individual graphene sheet or few layer graphene. In this research, activated carbon is used instead of graphite as starting material. Activated carbon is a crude form of graphite obtained by incinerating of plant biomass where sp<sup>2</sup> and sp<sup>3</sup> hybridised carbon atoms may exist. Due to the presence of sp<sup>3</sup> hybridised carbon atoms in activated carbon structure, dangling carbon atoms exist between layers of graphene. This is because in sp<sup>3</sup> hybridisation, carbon is bonded by four other carbon atoms by a single bond ( C-C ) instead of three carbon atoms in sp<sup>2</sup> due to the presence of double bond ( C=C ). These carbon atoms are held by a covalent bond. In order to produce graphene of sp<sup>2</sup> hybridised carbon atoms, the dangling carbon atoms between layers of graphene need to be removed. A large amount of energy is required to break covalent bond between carbon atoms. This can be achieved using sonication process. During sonication, cavitation will induced formation

of micro-bubbles and upon collapsing of this bubbles it will release a tremendous amount of energy. Thus, the dangling carbon atoms can be removed and leaves each atom a free electron or we call it delocalized sea of electrons ( $\pi$  bonds). This behaviour enables a graphene layers to conduct electric. Recently, many efforts have been done to develop eco-friendly method in exfoliating graphene in scalable size for industrial purpose aiming to lower down the production cost. Activated carbon is ought to be the solution and some research have been done by using rice husks (Wang *et al*, 2016), tea leaves (*Melaleuca alternifolia*) (Jacob *et al*, 2015), camphor leaves (*Cinnamomum Camphora*) (Shams *et al*, 2015) and alfafa plant (Qu *et al*, 2013). In this research, palm kernel shell (PKS) is used due to massive palm oil plantation that exists in Malaysia. Palm oil plantation is expected to produced approximately 100 million tons/year of biomass waste where 8% from it is palm kernel shell (Misnon *et al*, 2015). Palm kernel shell is a dry solid waste that yielded after palm oil extraction; the hardest portion that shows ease handling for carbon activation process. Due to the enormity of PKS, recycling them for value added products is highly desirable (Misnon *et al*, 2015). Activated carbon has gained great interest due to its larger surface area and highly porous morphology.

In this research, the main target is to synthesis graphene by utilizing carbon quantum dots in water as solvent and sonication process where sonication probe device is used instead of sonication bath.

## **1.2 PROBLEM STATEMENT**

Since the discovery of graphene in 2004 by Andre Geim and Konstantin Novoselov at Manchester University, many methods of graphite exfoliation have been developed to increase mass production of graphene for industrial purposes. Exfoliation is achieved by overcoming the van der Waals forces between the neighbouring graphene layers. There are various method involving graphene exfoliation include oxidation of graphite and chemical vapour deposition.

Oxidation of graphite to produce GO is done by introducing oxygen containing functional group such as aldehyde, ester, hydroxyl, carbonyl and carboxylic acid to graphite to reduce interlayer interaction between graphene. The functional groups will be bonded to the graphitic layer and form a very stable dispersion in water. However, GO are an electric insulator due to the presence of defects in  $sp^2$  plane and it has to be reduced thermally, chemically or by irradiation to restore the electrical conductivity (Zurutuza and Marinelli, 2014).

Chemical vapour deposition (CVD) is done on metallic substrates to produce graphene film. The CVD is one of the relevant manufacturing methods that is used widely in industry because it can produce large-area films that can be transferred onto a variety of substrates (Zurutuza and Marinelli, 2014). However, CVD has one major problem where the precursor use is highly toxic and the by-product from CVD is hazardous because it uses toxic chemicals to cultivate graphene as a monolayer by exposing platinum, nickel, titanium carbide to ethylene or benzene at high temperature. It is also a very expensive and complex process.

On the other hand, LPE is seen as a promising method; using water as solvent is the ultimate condition on several environmental issues. However, the surface tension of water is very high ( $\sim 72.8 \text{ mJ/m}^2$ ). In order to make it suitable for graphene exfoliation, the surface tension of water has to be lowered to match graphene's surface tension ( $\sim 40 \text{ mJ/m}^2$ ). This will be tackled by introducing CQD. The CQD will lower the surface tension of water by matching it with graphite and taking the weak interaction ( $\pi$ - $\pi$  conjugation, hydrophobic force and Coulomb attraction) with graphite surface (Xu *et al.*, 2015). It has been reported that the lower the difference of surface energies between solvents and 2D materials are the better the LPE process should take place (Shen *et al.*, 2015). It was revealed that the matching of surface tension between graphene and solvents also had a strong effect on the stabilization of the suspensions after the exfoliation step in the LPE process (Shen *et al.*, 2015). Thus, in this research, we will investigate how CQD usage and time of sonication affect the LPE yield and production of graphene quality.

### **1.3 OBJECTIVES OF STUDY**

The objectives of this research are:

- i. To develop an environmentally friendly approach in exfoliating graphene by using water as solvent and activated carbon obtain from plant biomass.
- ii. To investigate properties of carbon quantum dots on yield of graphene production.
- iii. To develop condition to increase exfoliation rate of graphene from palm kernel shell activated carbon (AC) by liquid phase exfoliation methods.
- iv. To study the structural, morphological and physical properties of graphene as a function of exfoliation rate.

### **1.4 SCOPE OF STUDY**

Graphene is synthesis by dispersing AC in water as solvent to exfoliate graphene from AC. The high surface tension of water is lowered to match with graphite by using CQDs as it will take the weak interaction of graphite surface. Dispersion of AC in suitable solvent whose surface tension is similar with graphite is necessary for a successful exfoliation. The LPE assisted with sonication is ought to increase the production of graphene yield. During sonication process, growth and collapse of micro-bubbles due to cavitation and shear force will act on graphite thus induce exfoliation.

The obtained graphene will be further characterized and analysed using Field Emission Scanning Electron Microscope (FESEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Ultraviolet Visible Spectroscopy (UV-Vis).

## **CHAPTER 2**

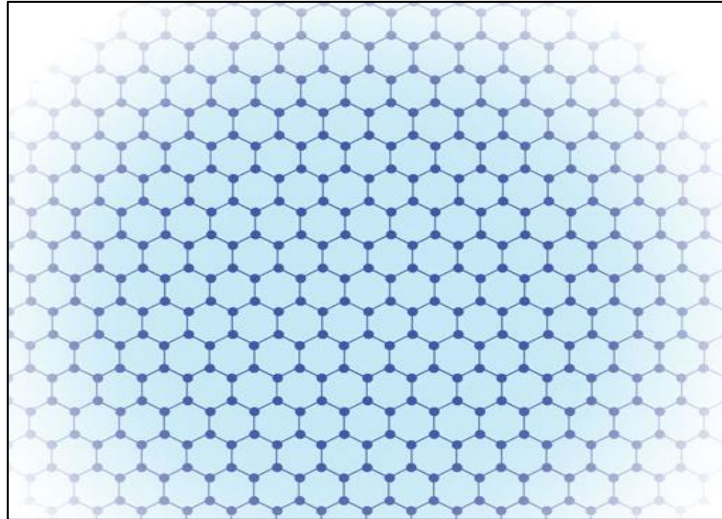
### **LITERATURE REVIEW**

#### **2.1 INTRODUCTION**

This chapter will provide a brief discussion on synthesis of graphene by liquid phase exfoliation technique (LPE) assisted by sonication. It will cover on history of graphene, properties of graphene, past and recent research development on graphite exfoliation by LPE technique. This chapter will also cover on recent research report which enhancement of the mass production of graphene for commercialisation industrial purpose in terms of solvents used and sonication process and improvement of graphite exfoliation from one method to another.

#### **2.2 HISTORY OF GRAPHENE**

Graphene was discovered by Andre Geim and Konstantin Novoselov at Manchester University in 2004 by using a Scotch Tape method where a tape is applied to a piece of graphite and ripped off, pulling together flakes of graphite with it. This process is repeated many times until a graphene of atom thick is obtained. Graphene is a single layer of stacked graphite where carbon bonded together to form a hexagonal honeycomb lattice (Figure 2.1). It is so thin that it is considered as 2-dimensional. In a complex term, it is one of the carbon allotrope in the structure of  $sp^2$  plane bonded with a molecule bond length of  $1.42\text{\AA}$  (Shams *et al*, 2015).

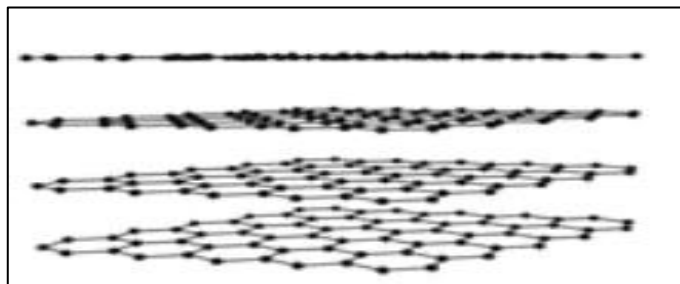


*Figure 2.1.* Honeycomb lattice structure of graphene. Carbon atoms are shown in blue dots

Source: Reproduced from (Fuhrer, 2010)

### 2.3 PROPERTIES OF GRAPHENE

Many layer of graphene made up a graphite and between each layer of graphene, it is held together by an electrostatic force called van der Waals forces (Figure 2.2). Although van der Waals forces are relatively weak to let the graphene sheets to slip past each other, but the attraction forces is strong enough making it impossible to separate graphene into its individual layer. Carbon atoms are bonded together by covalent bond with a molecule bond length of  $1.42 \text{ \AA}$  and inter planar spacing of graphene is  $3.35 \text{ \AA}$  (Shams *et al*, 2015).

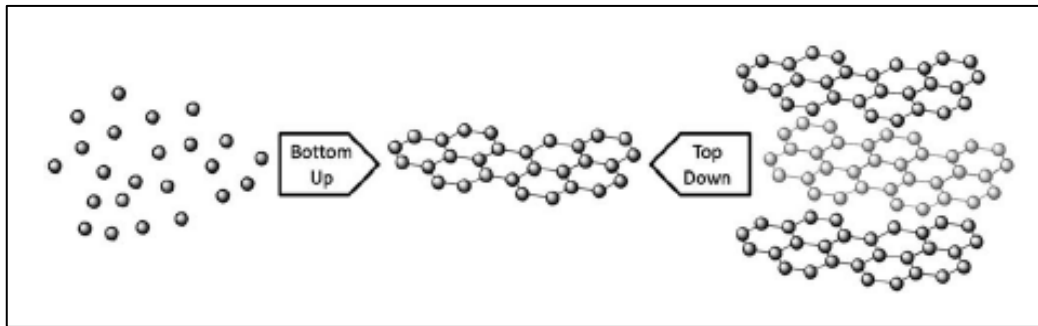


*Figure 2.2.* Layers of graphene held together by van der Waals forces

Source: Reproduced from (Li and Shi, 2012)

## 2.4 METHODS OF GRAPHENE SYNTHESIS

Since graphene is successfully exfoliated in 2004 by Novoselov and Geim by using Scotch tape method, it has pricked interests from many researchers to develop new method in graphene synthesis over the last decade. Thus, several methods have been reported. There are two types of synthesis approach: top-down and bottom-up approaches (Figure 2.3). Exfoliation of graphene by overcoming the van der Waals forces to increase the surface area is referred as top-down approach while bottom-up approach focussing on carbon molecules as building blocks (Shams *et al*, 2015)



*Figure 2.3.* Schematic diagram of top-down and bottom-up approaches in synthesis of graphene

Source: Reproduced from (Edwards and Coleman, 2012)

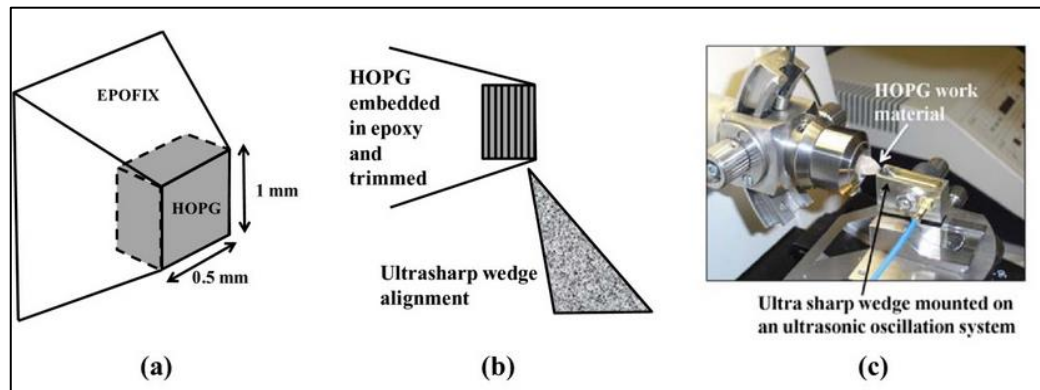
### 2.4.1 Top-down Approach

Top-down approach consists of several methods that have been employed such as micromechanical cleavage, electrochemical exfoliation, exfoliation of graphite intercalation compounds (GICs) and exfoliation of graphite oxide.

#### 2.4.1.1 Mechanical Exfoliation

One of the early method used to experimentally exfoliate graphene is mechanical exfoliation which utilize adhesive tape to separate graphene layers. However, this method does not fit for industrial purpose as the method consumes a large amount of time and graphene produced is small in quantity. There is another approach

introduced by (Jayasena et al, 2011) which scraping off graphene by using diamond wedge from highly ordered pyrolytic graphite (HOPG) aided by sonication (Jayasena et al, 2011) (Figure 2.4).



*Figure 2.4.* Schematic diagram of graphene synthesis by mechanical exfoliation using diamond wedge of HOPG

Source: Reproduced from (Jayasena et al, 2011)

#### **2.4.1.2 Electrochemical Exfoliation**

Electrochemical exfoliation uses electrolyte to collect exfoliated graphene. Common electrolytes used are surfactants and sulphuric acid ( $H_2SO_4$ ) neutralized by potassium hydroxide (KOH) solutions. Surfactants are ought to prevent re-agglomeration of graphene by interacting hydrophobic group with  $\pi$ -orbital of graphene while the hydrophilic group stabilize the sheets in water. But, surfactants are hard to remove and affect electric and electrochemical properties of graphene (Edwards and Coleman, 2012). Sulphuric acid is a good electrolyte to exfoliate graphene due to the intercalation of  $SO_4^{2-}$  ions. However KOH is needed to reduce high level of oxidation of sulphuric acid. The drawbacks of this method are production of non-uniformed thickness of graphene layer.



### 2.4.1.3 Exfoliation of Graphite Intercalation Compounds (GICs)

Graphene can also be exfoliated by inserting chemical species in between layers of graphene to produce graphite intercalation compounds (GICs) (Figure 2.5). Inter-planar spacing between graphene increases due to the addition of chemical species thus changes the properties of graphene. The properties of graphene changes because as inter-planar distance of graphene increases the electronic coupling between graphene layers is affected.

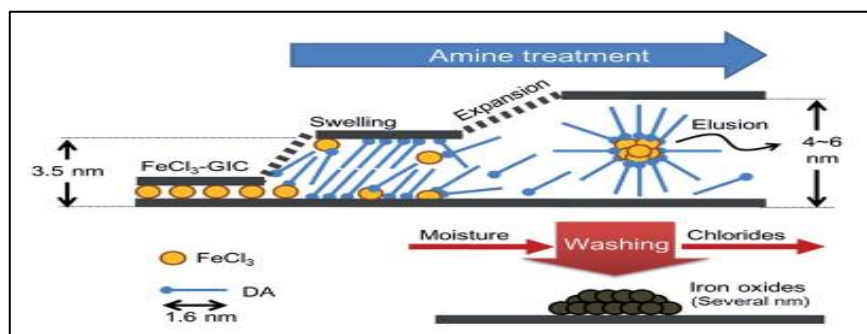


Figure 2.5. Schematic diagram of FeCl<sub>3</sub>-GICs of amine treatment and formation of iron-oxide domains

Source: (Ujihara *et al.*, 2014)

Table 2.1

*Different methods of graphene synthesis in top-down approach*

| <b>Method</b>               | <b>Precursor</b> | <b>Chemical used</b>   | <b>Yield %</b> | <b>Inter-planar spacing (nm)</b> | <b>I<sub>D</sub> / I<sub>G</sub></b> | <b>References</b>              |
|-----------------------------|------------------|--|----------------|----------------------------------|--------------------------------------|--------------------------------|
| Mechanical exfoliation      | HOPG             | -  | >50%           | -                                | -                                    | (Jayasena <i>et al</i> , 2011) |
| Electrochemical exfoliation | Graphite rod     | Deionized water, NaCl, DMSO, thionin acetate salt  | -              | 1.246                            | -                                    | (Zhou <i>et al</i> , 2013)     |
| GICs exfoliation            | Graphite flakes  | Anhydrous iron chloride (FeCl <sub>3</sub> ), Triethylamine (TEA), Trihexylamine (THA), Hexylamine (HA), dodecylamine (DA) | -              | DA: 1.59                         | HA: 0.83<br>DA: 0.77                 | (Ujihara <i>et al</i> , 2014)  |

Table 2.2

*Morphological studies of graphene by various types of exfoliation method*

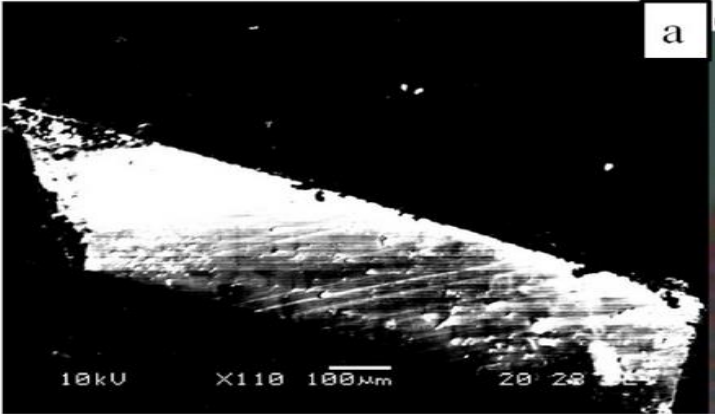
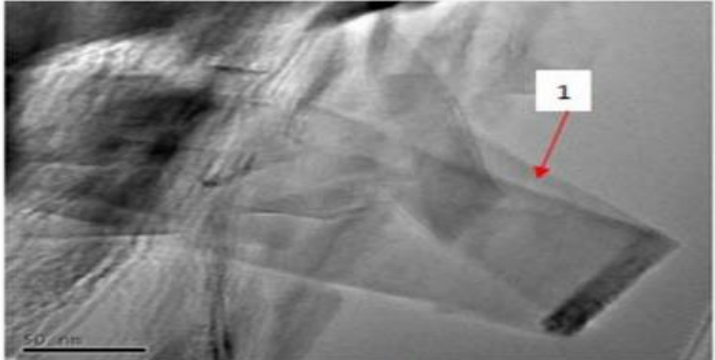
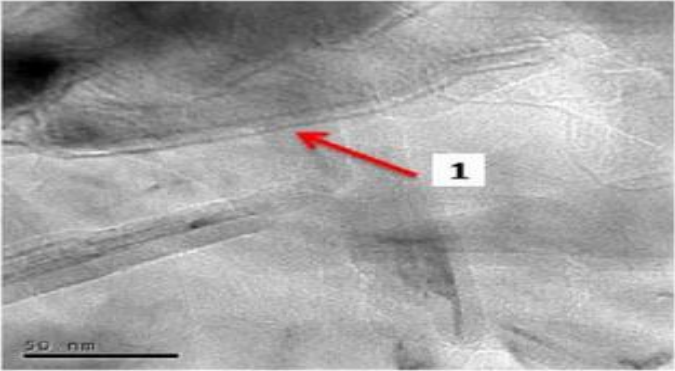
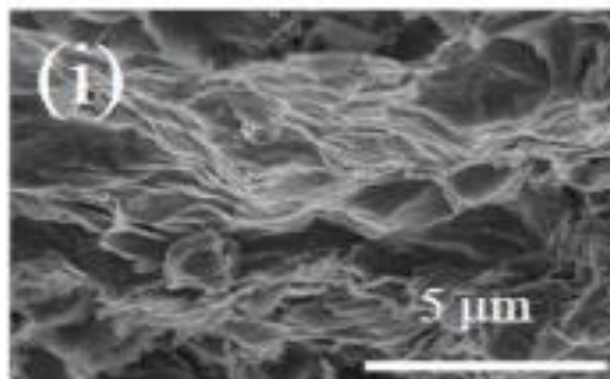
| Method                    | Structural Characterization  | Reference                    |
|---------------------------|--|------------------------------|
| Mechanical<br>Exfoliation |  <p data-bbox="525 949 679 981">SEM image</p>  <p data-bbox="525 1391 1294 1476">TEM image without ultrasonic oscillation – Graphene sheet with rolled edge</p>  <p data-bbox="525 1901 1294 1986">TEM image with ultrasonic oscillation – Edge of graphene sheet.</p> | (Jayasena<br>et al,<br>2011) |

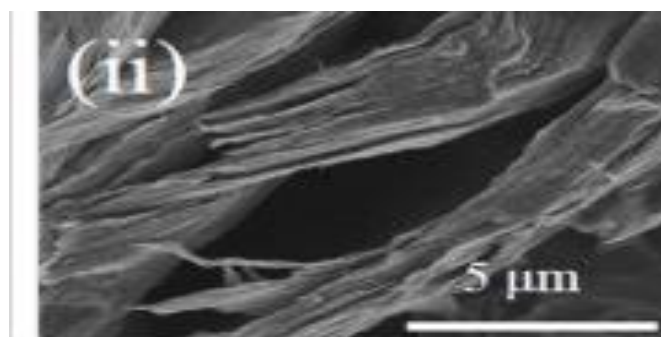
Table 2.2  
*Continued*

Electrochemic  
al exfoliation

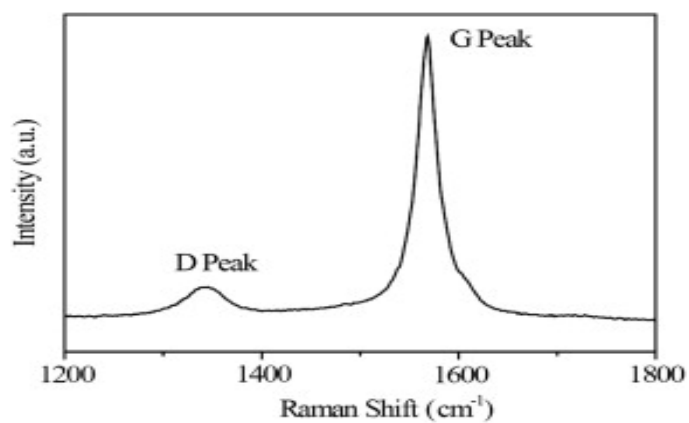


(Zhou *et al.*, 2013)

SEM image – natural graphite



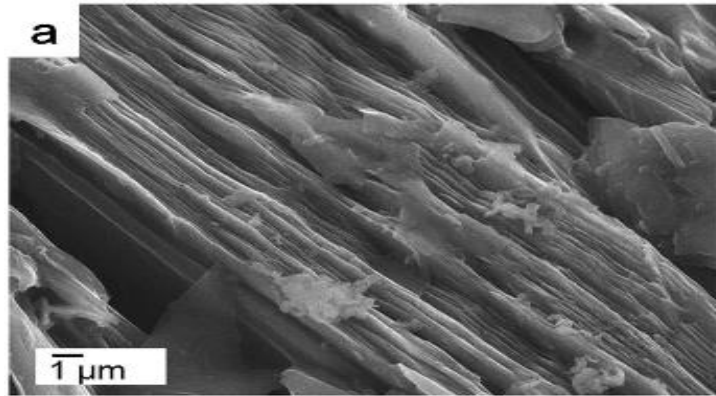
SEM image – electrochemically exfoliated graphite



Raman spectrum – few layers of graphene (FLG) prepared by electrochemical exfoliation of graphite cathode.

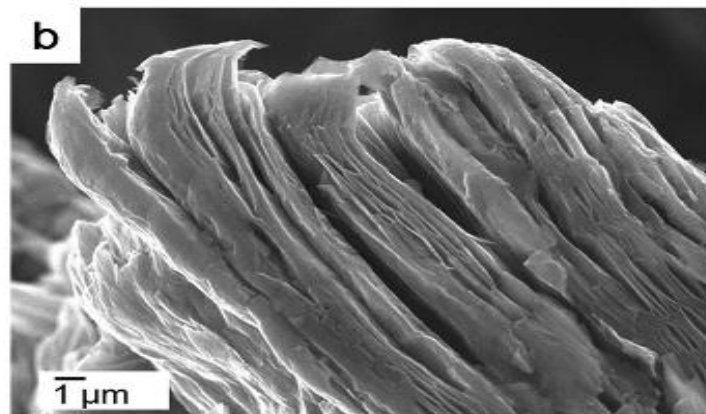
Table 2.2  
*Continued*

GICs  
exfoliation

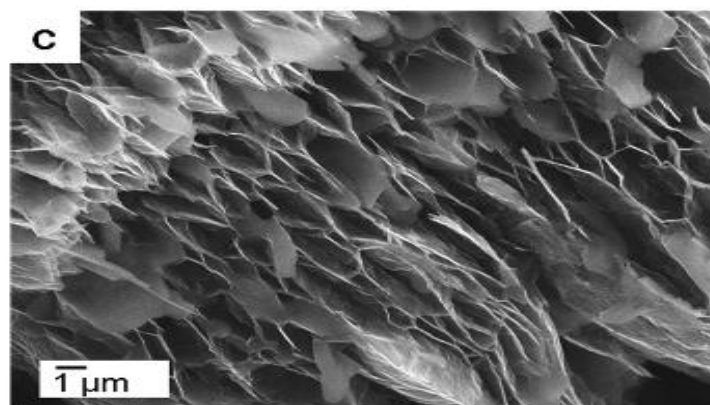


(Ujihara *et al*,  
2014)

SEM image - FeCl<sub>3</sub>-GICs



SEM image – FeCl<sub>3</sub>-GICs after treated with HA



SEM image - FeCl<sub>3</sub>-GICs after treated with DA

## **2.4.2 Bottom-up Approach**

Bottom-up approach consists of several methods that have been employed such as epitaxial growth on silicon carbide and chemical vapour deposition (CVD).

### **2.4.2.1 Epitaxial growth on silicon carbide (SiC)**

Graphene can be grown epitaxially on silicon carbide substrate at a very high temperature ( $\sim 1100^{\circ}\text{C}$ ) and usually performed in ultra-high vacuum (UHV) condition (Shams *et al*, 2015, Edwards and Coleman, 2012). Even though epitaxial graphene grown on silicon carbide displayed extremely large, temperature independent mobility but it tend to have weak anti-localization (Shams *et al*, 2015). The surface area where graphene is grown plays an important role as it influence the thickness, mobility and density carrier of graphene (Shams *et al*, 2015). However, this method is highly cost as silicon carbide substrate is expensive and yield production of graphene through this method is relatively low due to that this method is deemed as not suitable for industrial manufacturing purpose (Shams *et al*, 2015).

### **2.4.2.2 Chemical vapour deposition (CVD)**

There are two types of deposition recorded on this method: growth on metal and substrate free (Edwards and Coleman, 2012). The CVD by growing graphene film on transition metal substrate is done by pyrolysis of carbon compound (Eg: benzene, ethanol) at a very high temperature ( $\sim 1000^{\circ}\text{C}$ ). A wide range of metal group is used as transition metal. However, the optimum condition to grow graphene varies with each metal as a lot factors is taken into consideration such as pressure and temperature. Thus, it was resulted in different quality of graphene as end product. Drawbacks of growing graphene on transition metal substrate is due to its harsh growing condition needed where UHV is done with a very high temperature and to improve this condition it required a complicated process. CVD is also used to synthesis graphene nano sheets. While the advantage of using substrate free synthesis, it is not necessary to purchase or prepared the specific substrate and that the removal of graphene from the substrate is not required.

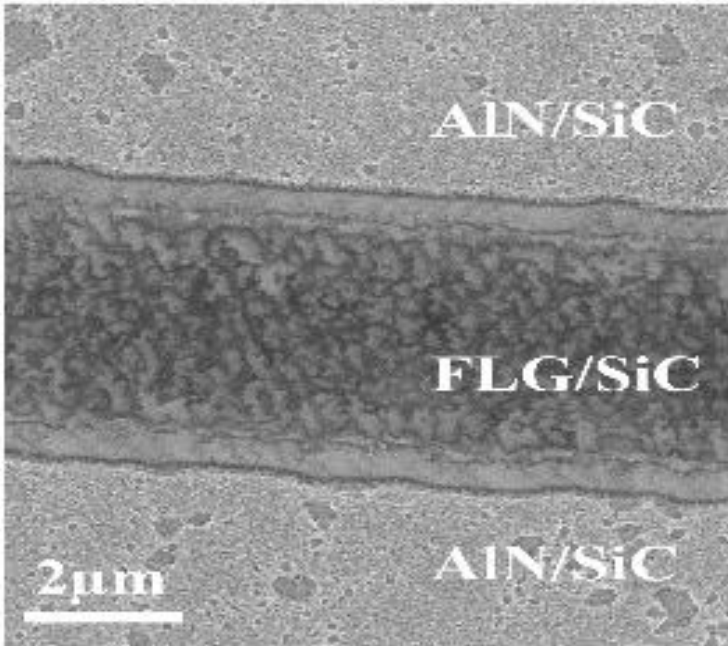
Table 2.3

*Methods of graphene exfoliation in Bottom-up approach*

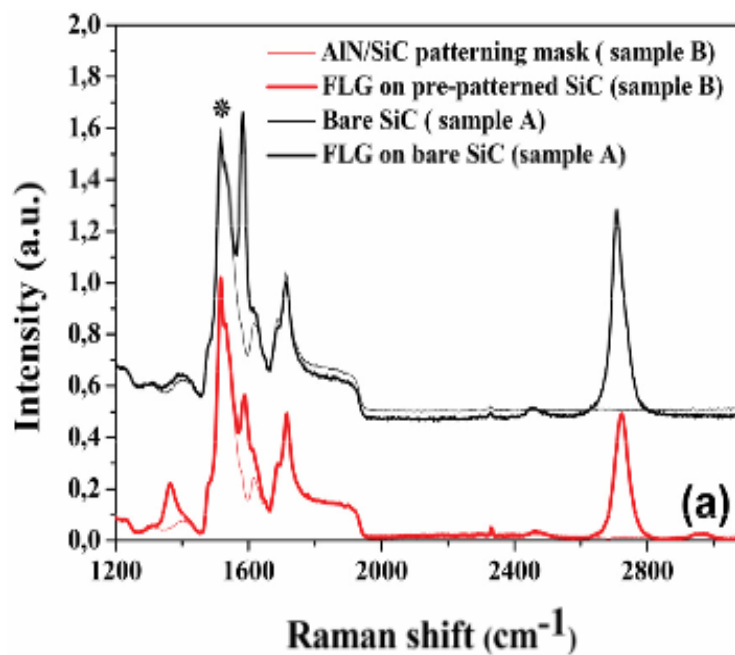
| <b>Method</b>                             | <b>Precursor</b>              | <b>Chemical<br/>used</b>                        | <b>Yield<br/>%</b> | <b>Inter-<br/>planar<br/>spacing<br/>(nm)</b> | <b>I<sub>D</sub> / I<sub>G</sub></b> | <b>References</b>             |
|---|-------------------------------|---|--------------------|---|--------------------------------------|-------------------------------|
| Epitaxial<br>growth on SiC                | 6H-SiC                        | Tetra Methyl<br>Ammonium<br>Hydroxide<br>(TMAH) | -                  | -   | A : 0.859<br>B : 0.865               | (Nicolas<br>Camara,<br>2008)  |
| Chemical<br>vapour<br>deposition<br>(CVD) | Ethanol/<br>Pentane<br>liquid | Iron Chloride                                   | -                  | -   | 0.23                                 | (Dong <i>et al</i> ,<br>2011) |

Table 2.4

*Morphological studies of graphene by various types of exfoliation method*

| Method                  | Structural Characterization   | Reference              |
|-------------------------|---|------------------------|
| Epitaxial growth on SiC |  | (Nicolas Camara, 2008) |

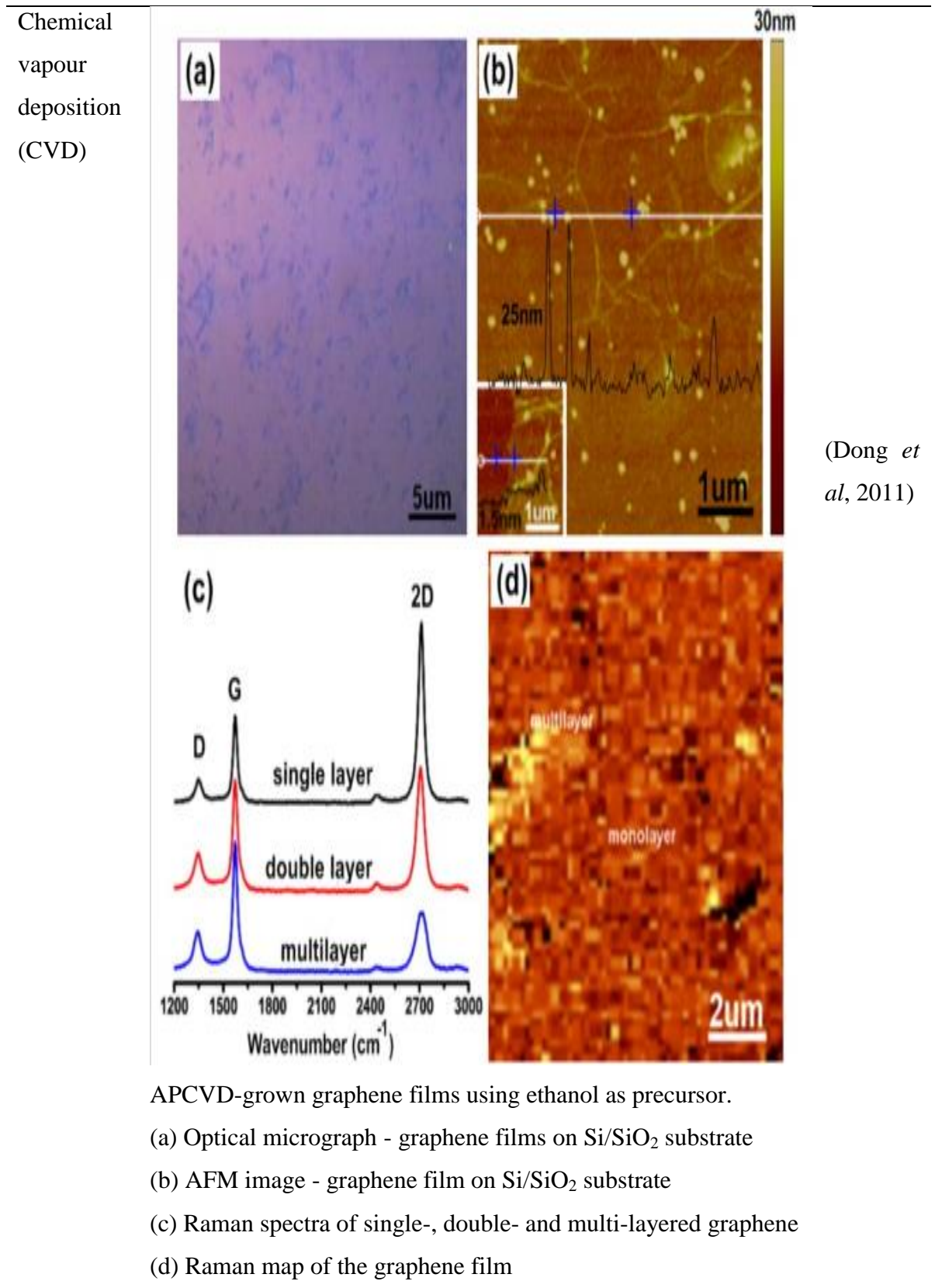
SEM image - FLG grown on SiC by using a patterned AlN mask.



Raman Spectroscopy - FLG grown on bare SiC and FLG grown on “AlN patterned” SiC.



Table 2.4  
Continued



## 2.5 Liquid Phase Exfoliation (LPE)

The LPE method is widely used in exfoliation of graphene due to its simplicity in procedure. The typical procedures of LPE involve dispersion of graphite in solvent and undergo sonication process where quality of resulted graphene may vary depend on the solvent used, time of sonication and rotation per minute (rpm) during centrifugation process. For a successful exfoliation to occur, van der Waals attraction between layers of graphene in stacked graphite must be overcome by using solvent whose surface tension is match with graphene. Therefore, a good solvent is characterized by its surface tension ranging from 40-50 mJ/m<sup>2</sup> due to graphene surface tension of ~40 mJ/m<sup>2</sup> (Xianjun Liu *et al*, 2015). The N-methyl-2-pyrrolidinone (NMP) is the first solvent used that successfully exfoliate graphene through LPE where graphene is dispersed at concentrations of up to 0.01 mg/mL and the monolayer yield was around 1 wt% (Hernandez *et al*, 2008). Different solvents have been used throughout the past decade in order to improvise the yield production of graphene. Table 2.5 shown LPE process done using different solvent as exfoliator resulted in different percentage of yield production and ratio of I<sub>D</sub> / I<sub>G</sub>.

Table 2.5

*LPE process with different solvents used*

| Method                                  | Solvent  | Yield       | Flakes size | I <sub>D</sub> / I <sub>G</sub> | Reference                    |
|---|--|-------------|-------------|---------------------------------|------------------------------|
| Liquid<br>Phase<br>Exfoliation<br>(LPE) | Water  | 0.4 mg/mL   | -           | 0.53                            | (Xu <i>et al</i> ,<br>2015)  |
|   | NMP with addition of<br>naphthalene                                | 0.15 mg/mL  | -           | -                               | (Xu <i>et al</i> ,<br>2014)  |
|   | N,N-<br>dimethylformamide<br>(DMF) with addition of<br>water (9:1) | -           | ~2 μm       | 1.57                            | (Zhu <i>et al</i> ,<br>2013) |
|   | Oley amine and toluene   | 0.128 mg/mL | -           | 0.11                            | (Dang and<br>Kim, 2015)      |

Table 2.6

*LPE process using activated carbon precursor*

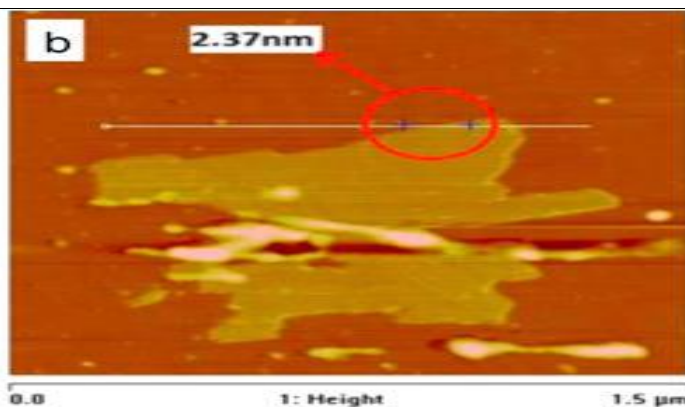
| Precursor                               | Yield     | Flakes thickness | $I_D / I_G$ | Reference                      |
|---|-----------|------------------|-------------|--------------------------------|
| Camphor leaves<br>(Cinnamomum Camphora) | 0.8 mg/mL | ~2.37 nm         | 0.99        | (Shams <i>et al</i> ,<br>2015) |

Table 2.7

*Morphological studies of graphene by LPE using activated carbon precursor*

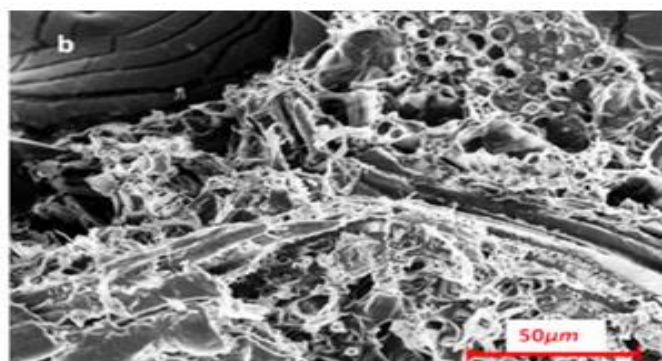
| Precursor | Structural Characterization | Reference |
|-----------|-----------------------------|-----------|
|-----------|-----------------------------|-----------|

Camphor leaves  
(Cinnamomum Camphora)



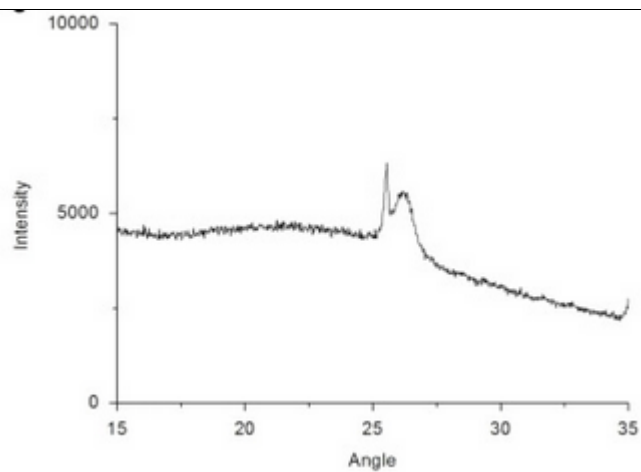
(Shams *et al*,  
2015)

AFM images showing thickness of few layered graphene (FLG) synthesized from leaves



FE-SEM image showing cross-sectional area and porosity characteristics of graphene synthesized from leaves

Table 2.7  
*Continued*



XRD results of FLG synthesized from leaves

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Table 2.8

*Morphological studies of graphene by LPE using different solvent*

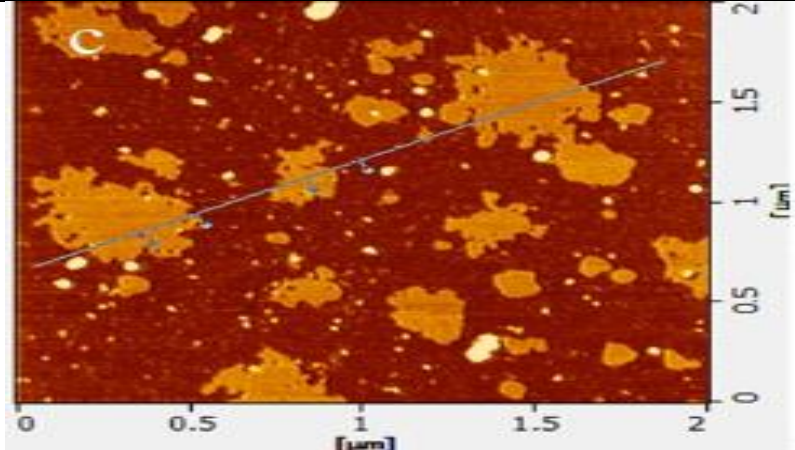
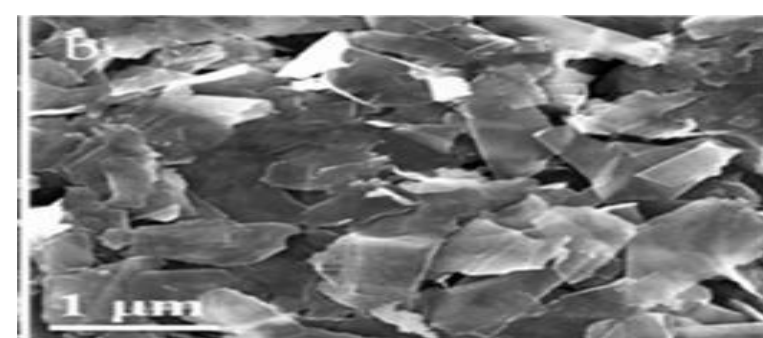
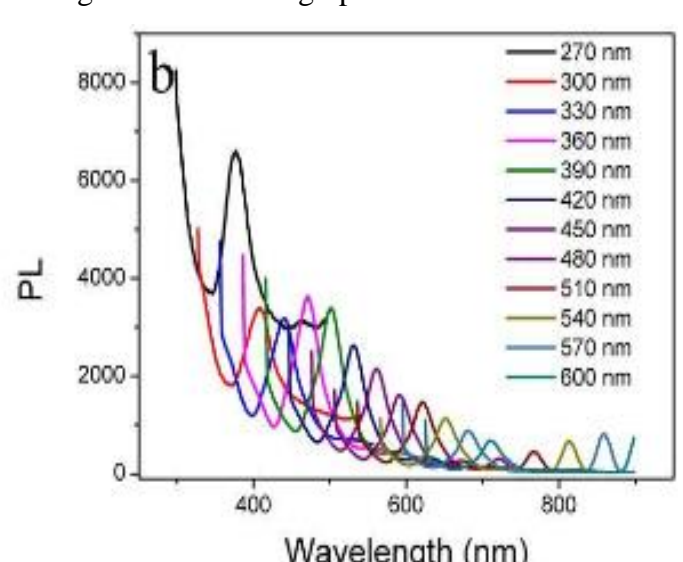
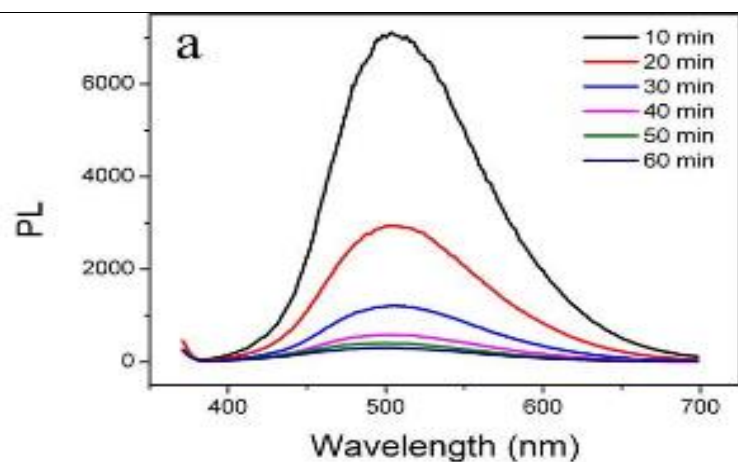
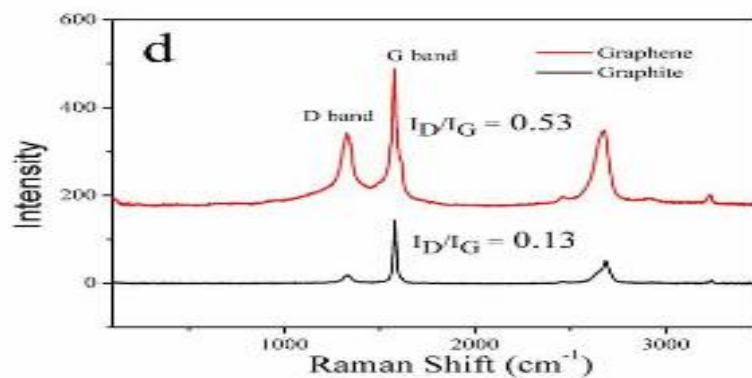
| Solvent  | Structural Characterization  | Reference                 |
|--|--|---------------------------|
| Water  |  | (Xu <i>et al.</i> , 2015) |
| AFM images of exfoliated graphene  |  |                           |
|   |  |                           |
| FE-SEM images of exfoliated graphene   |  |                           |
|  |  |                           |
| PL spectra - different excitation wavelength (270 nm to 600 nm)                      |  |                           |

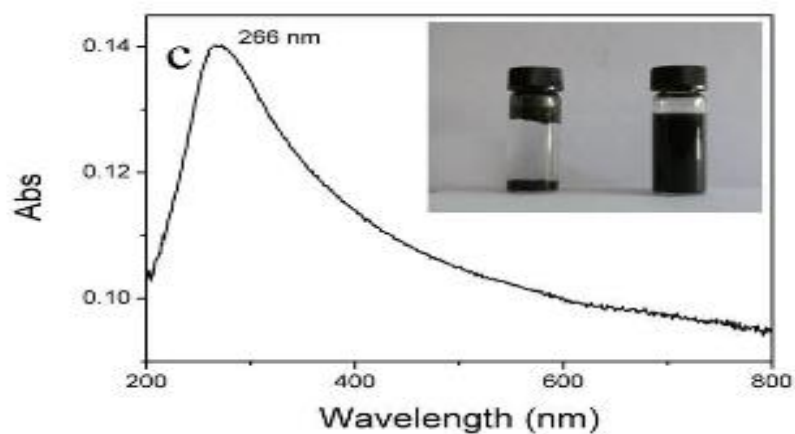
Table 2.8  
Continued



PL intensity of decreasing exfoliated graphene solution with increasing of sonication time



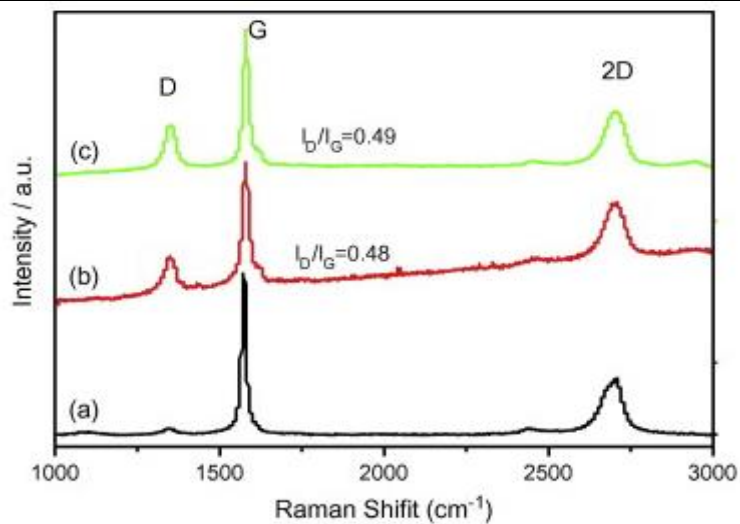
Raman spectra of pristine graphite and exfoliated graphene



UV-Vis spectrum - exfoliated graphene (pristine graphite, left) and exfoliated graphene (right) in water

Table 2.8  
*Continued*

NMP with  
addition of  
naphthalene



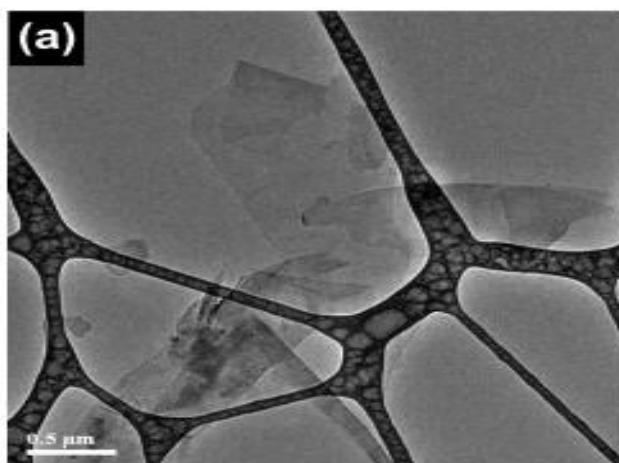
(Xu *et al.*,  
2014)

Raman spectra at 532 nm for graphite powders and  
graphene:

(a) graphite powders

(b) the as-prepared graphene without addition of  
naphthalene in the sonication process

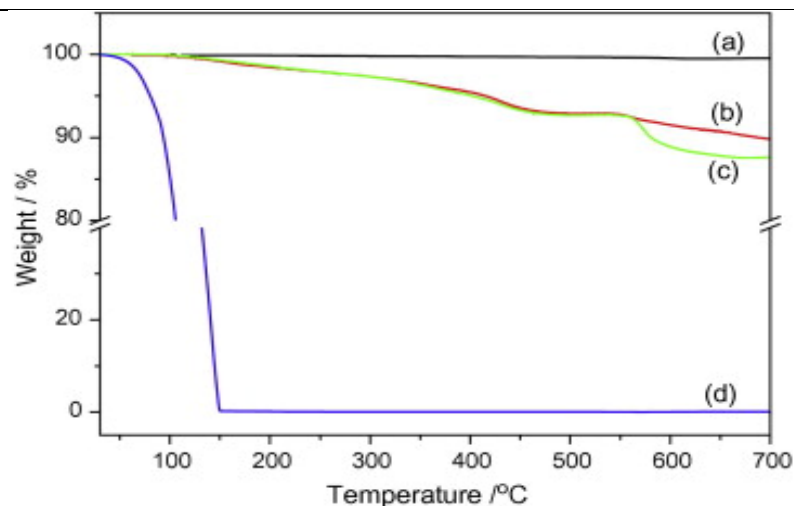
(c) the as-prepared graphene with addition of naphthalene in  
the sonication process



TEM image of a representative graphene sheet

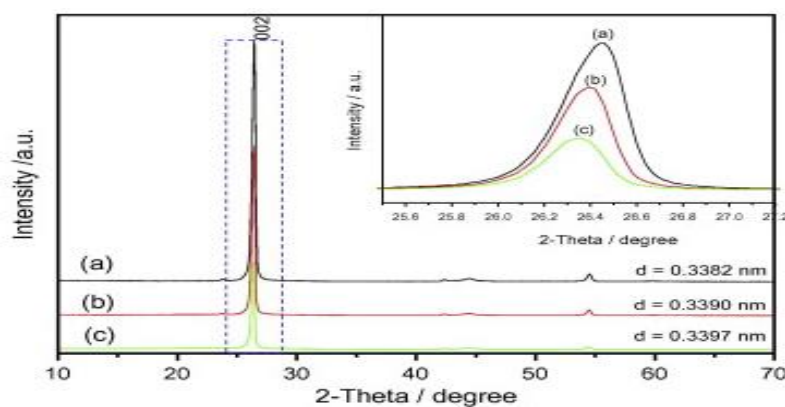


Table 2.8  
Continued



Thermo gravimetric analysis:

- (a) graphite powders
- (b) the as-prepared graphene without addition of naphthalene in the sonication process
- (c) the as-prepared graphene with addition of naphthalene in the sonication process
- (d) naphthalene.

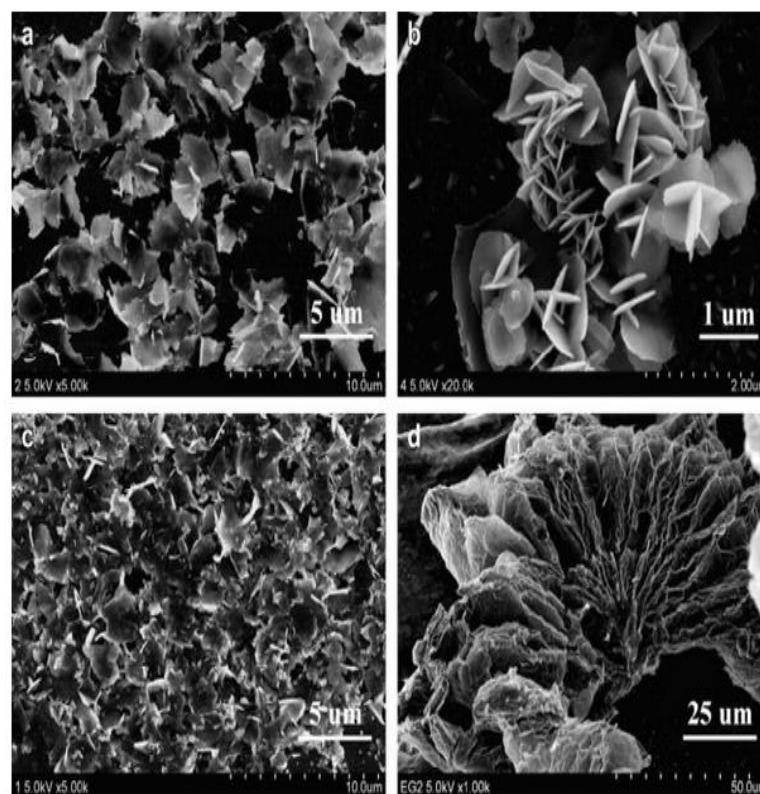


XRD diffraction patterns:

- (a) raw graphite powders
- (b) the sediment of graphite exfoliated without addition of naphthalene
- (c) the sediment of graphite exfoliated with addition of naphthalene.

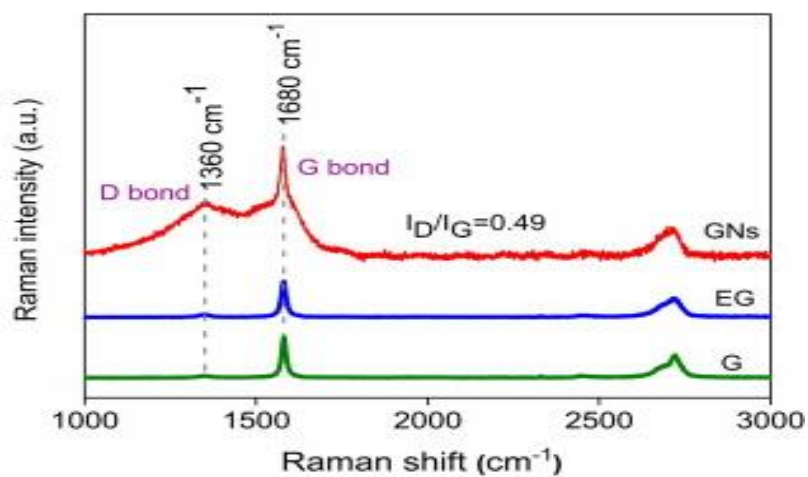
Table 2.8  
Continued

(DMF) with  
addition of  
water (9:1)



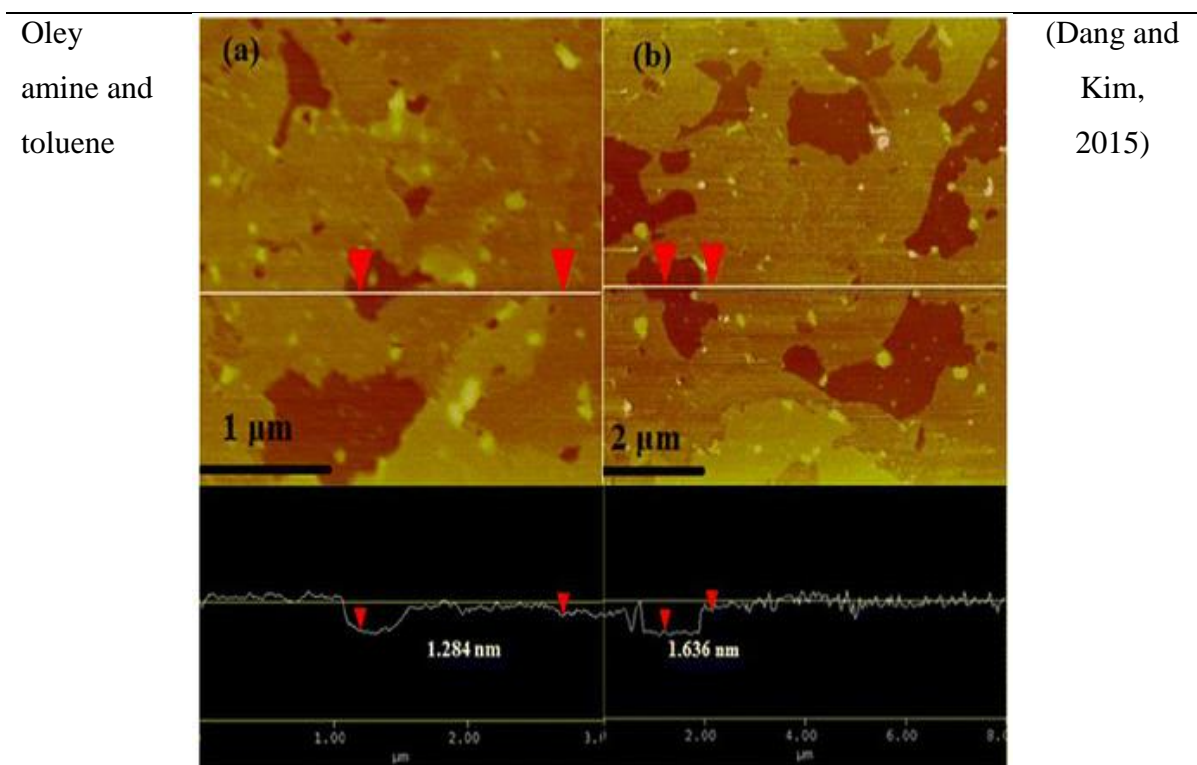
(Zhu *et al.*,  
2013)

FESEM images - GNs from graphene DMF–H<sub>2</sub>O (9:1, v:v)  
after 6.5 h sonication at various powers: (a) 80 W (b) 120 W  
(c) 80 W, after preservation for 2 months (d) EG as a  
comparison.

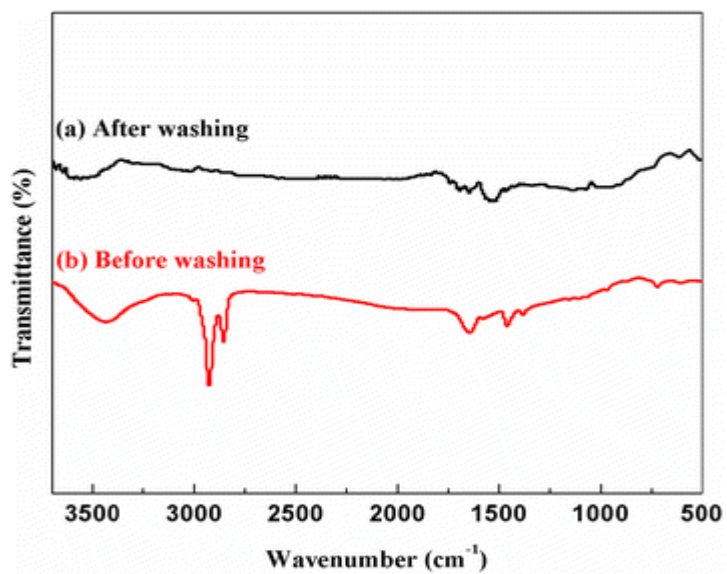


Raman spectra - graphite powder (G), expanded graphite  
power (EG) and graphene nanosheets (GNs).

Table 2.8  
*Continued*



AFM images - graphene sheets with a height profile taken along the straight line (a, b).

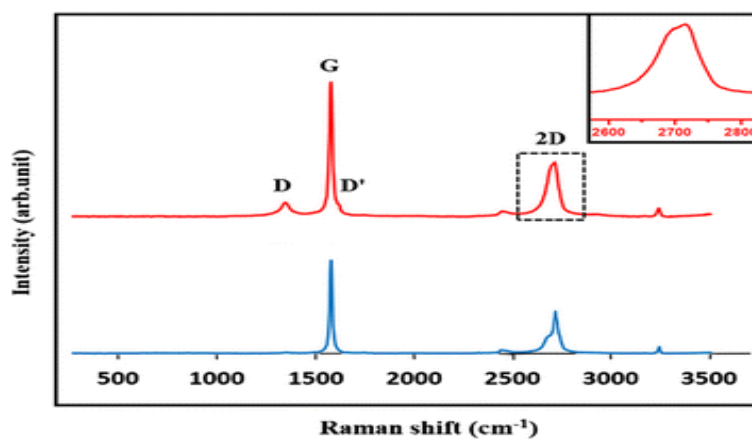


FTIR spectra - graphene sheets (b) before and (a) after washing with toluene/ethanol.

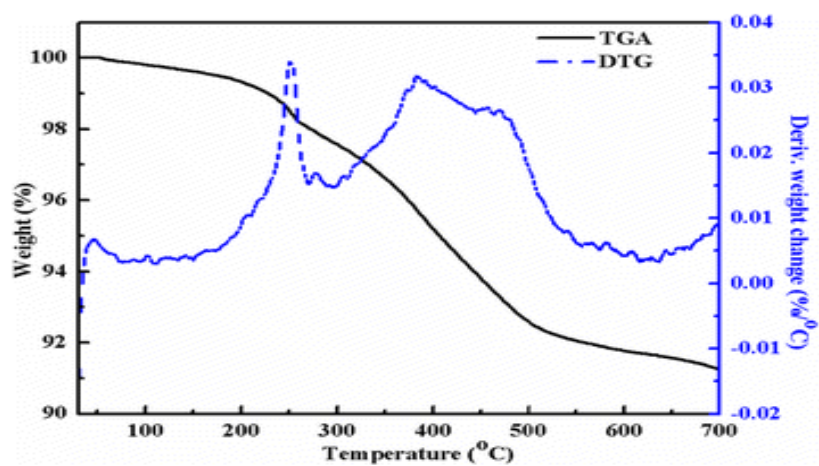
Table 2.8

Continued

Oley amine  
and toluene

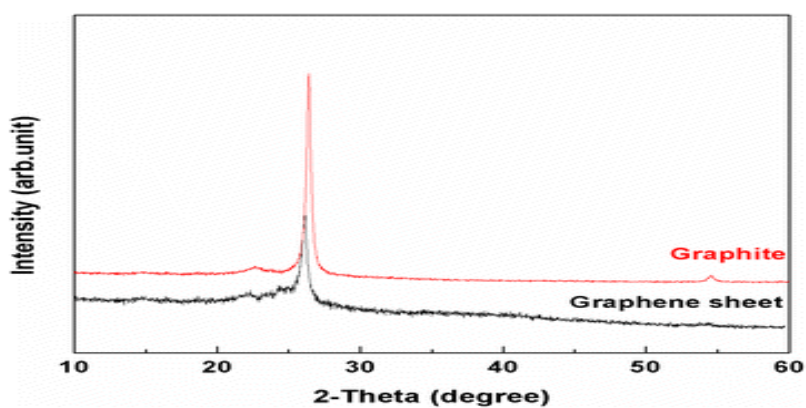


Raman spectra - graphite (down) and graphene product (top).



(Dang and  
Kim,  
2015)

Thermo gravimetric curves of the prepared graphene sheets



XRD patterns - graphite and the prepared graphene sheets

## CHAPTER 3

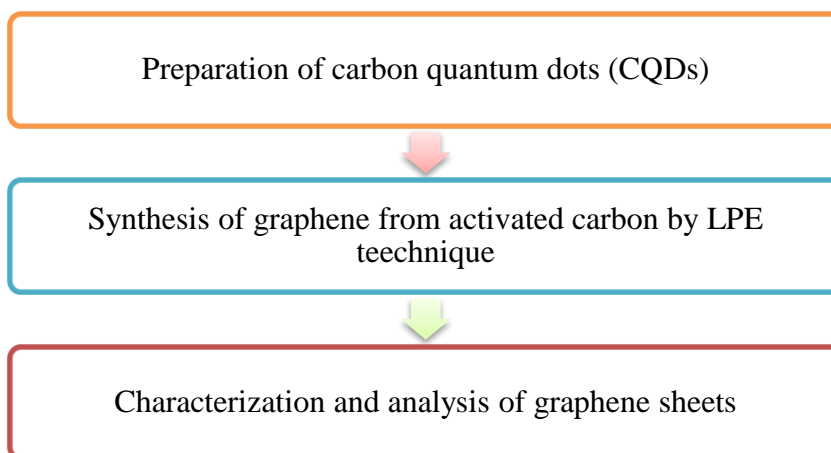
### RESEARCH METHODOLOGY

#### 3.1 Introduction

This chapter explains the method employed to synthesis graphene from activated carbon by liquid phase exfoliation (LPE) technique, the instruments and methods used for characterization of graphene. An overview of work flow from the synthesized graphene sheets and characterization of graphene is briefly presented.

#### 3.2 Flow Chart

This research is designed and followed the flow chart in Figure 3.1:



*Figure 3.1.* Flow chart of synthesised and characterization of graphene

### **3.3 Synthesis of Graphene**

#### **3.3.1 Preparation of carbon quantum dots (CQDs)**

The CQDs was prepared following the method used based on report by (Xu *et al*, 2015) with minor modification. Citric acid (15 g, 78 mmol) and urea (15 g, 250 mmol) were added into 40 mL of deionized water and stirred until it completely dissolved into a clear solution. The solution is then irradiated in commercial microwave (800 W) for 5 minutes until it is converted into a black solid. The solid is dissolved in water and the obtained solution is filtered twice to obtain fine solution. The solution is filtered using normal filter paper to remove large and agglomerated particles and the filtered solution is collected and filtered again using cellulose filtration membrane of 0.22  $\mu\text{m}$  pores. The solution is dialysed for 7 days to remove unreacted molecules. During dialysis process, water is changed every 24 hours to reduce buffer and to ensure smooth flow between water and CQDs solution. The solution is then evaporated into solid powder for further characterization and usage.

#### **3.3.2 Synthesis of graphene**

Activated carbon (1 mg) and CQDs (30 mg) is dissolved into deionized water (DI) (50.0 mL) and the solution is tip-sonicated for 1 hour using sonication probe. The obtained dispersion is left for 24 hours to allow any un-exfoliated graphite to precipitate and stable. It is then centrifuged for 30 minutes at 500 rpm and the supernatant of the dispersion is collected by pipette and is centrifuged again for 10 minutes at 11000 rpm to obtain the sediment. The supernatant is collected and dried for further characterization and usage.

### 3.4 Structural Characterization

The morphological and characterization studies of resulted graphene is carried out by using UV-Vis spectrometer, Fourier Transform Infrared (FT-IR) spectrometer and Field Emission Scanning Electron Microscopy (FESEM).

#### 3.4.1 Fourier Transform Infrared (FT-IR) spectrometer

The graphene sample is mixed with potassium bromide (KBr) in the ratio of 1:10 and grounded using mortar and pestle. The mixture of powder is pressed into pellet form at a pressure of 5 tons and undergoes FTIR spectra analysis using Spectrum One (PerkinElmer, USA) in the range 400–4000  $\text{cm}^{-1}$ . It was performed to identify the functional groups or chemical bonds presence in CQDs and graphene.

#### 3.4.2 UV-Vis spectrometer

UV-Vis is used to determine the concentration of dispersed graphene sheets by using Beer-Lambert equation.

$$A = \alpha cl \quad (3.1)$$

where A: absorbance unit obtained in UV-Vis

$\alpha$ : constant value of 2460  $\text{Lg}^{-1}\text{m}^{-1}$

c: concentration of dispersed graphene

l: length of cuvette

#### 3.4.3 Field Emission Scanning Electron Microscopy (FE-SEM)

The morphologies of the obtained graphene samples are examined by FESEM using JEOL (JSM-7800F) with the accelerating voltage of 5 kV. The samples were prepared by coating the powders with platinum and then transferred onto the sample holder and analysed in the vacuum chamber.

## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Synthesis and characterization of CQDs and exfoliated graphene

In this chapter, results obtained from FESEM, FTIR, and UV-Vis were discussed including all of the plotted graphs.

##### 4.1.1 Carbon Quantum Dots (CQDs) preparation

Figure 4.1 shows FT-IR spectra of CQDs where it indicates the surface functional groups of CQDs. Absorption band at a wavelength of  $3445.84\text{ cm}^{-1}$  is assigned to  $\nu(\text{O-H})$  which is a hydroxyl functional group allowing improvement in the hydrophilicity and stability of carbon quantum dots in aqueous system (Qu *et al*, 2012). Meanwhile, absorption bands at  $1714.6\text{ cm}^{-1}$ ,  $1641.8\text{ cm}^{-1}$  and  $1403.1\text{ cm}^{-1}$  are assigned to  $\nu(\text{C=O})$ ,  $\delta(\text{C=C})$  and  $\delta(\text{CH}_2)$  respectively where it indicates functional group of carboxylic acid, alkene and alkane (Qu *et al*, 2012). The stretching of C=C at wavenumber  $\sim 1641\text{ cm}^{-1}$  confirms the formation of CQDs from citric acid as carbon precursor. Absorption band at  $1714.6\text{ cm}^{-1}$  is the stretch of C=O from  $-\text{CH}_2-\text{C}=\text{OOH}-$  due to broad O-H stretching absorption. Other than that, the obtained CQDs has similar fingerprint region as reported by (Xu *et al*, 2015) where it indicates the same pattern of absorption in this region ranging from  $500\text{ cm}^{-1} - 1500\text{ cm}^{-1}$  (Kalsi, 2006). From the FT-IR spectra, it can be concluded that the presence oxygen functional group at the surface of CQDs increase the hydrophilicity that enables it to bind in water molecules.



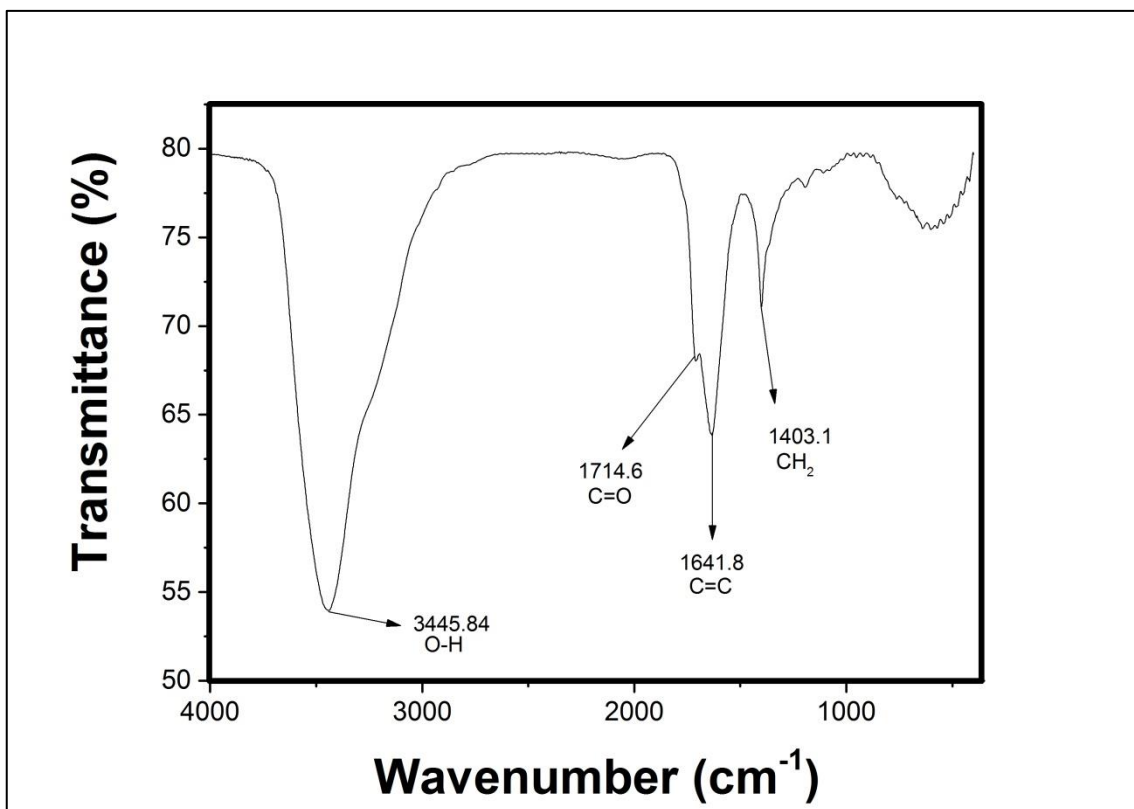


Figure 4.1. FT-IR spectrum of carbon quantum dots (CQDs)

In order to produce optimum yield of graphene production, the amount of CQDs added into the solution as exfoliating agent of graphene is taken into consideration. This is due to the number of CQDs added may result in the yield of graphene. Surface tension is one of the main factors in determining the yield production of graphene. Therefore, to find the optimal amount of CQDs added to reduce surface tension of water to match with that of the graphene, dilution of 5 mg CQDs in 5 mL of water to produce concentration of 1 mg/ml is done where it will be further dilute to check the surface tension at each concentration. Based on Figure 4.2, it can be seen that as amount of CQDs added to the solution increases, the surface tension of the solution also increases. However, the trend observed from the graph is opposite to what is expected which is as amount of CQDs added to the solution increases, the surface tension of the solution decreases. This may indicate that only small amount of CQDs is required to lower the surface tension of water to get surface tension value nearing  $\sim 40 \text{ mN/m}^2$ . It is important for solvents to have surface tension value that matches well with graphene because it will allow strong interaction with graphene surface and balancing the energy required to exfoliation and thus improving the effect of exfoliation (Liu, 2015). Therefore, it can be calculate that 0.2 mg/ml is the optimum amount of CQDs needed to lower the surface tension of water. The CQDs is use as exfoliation agent in this research due to the presence of hydrophilic group on the surface of CQDs that can be validated from previous FT-IR analysis. Hence, enables it to dissolves completely in water. Hence, lowering the surface tension of water to match that with graphene by taking weak interaction with surface of activated carbon.

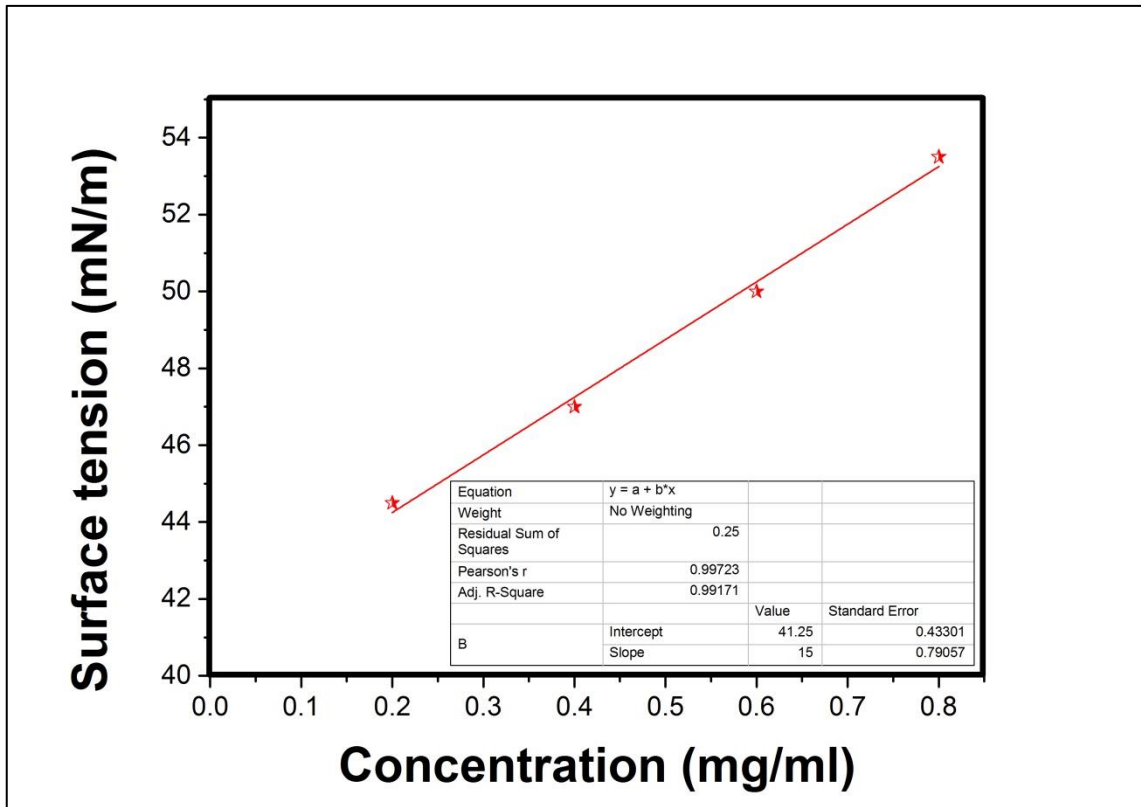


Figure 4.2. Optimal amount of CQDs to reduce surface tension; Surface tension vs concentration graph

Figure 4.3 shows UV-Vis absorption spectra of CQDs in water. The UV-Vis spectra of CQDs exhibited strong absorbance below 400 nm and a smooth tail extending into the visible range which is similar to the previously reported CQDs by (Bhaisare *et al*, 2015).

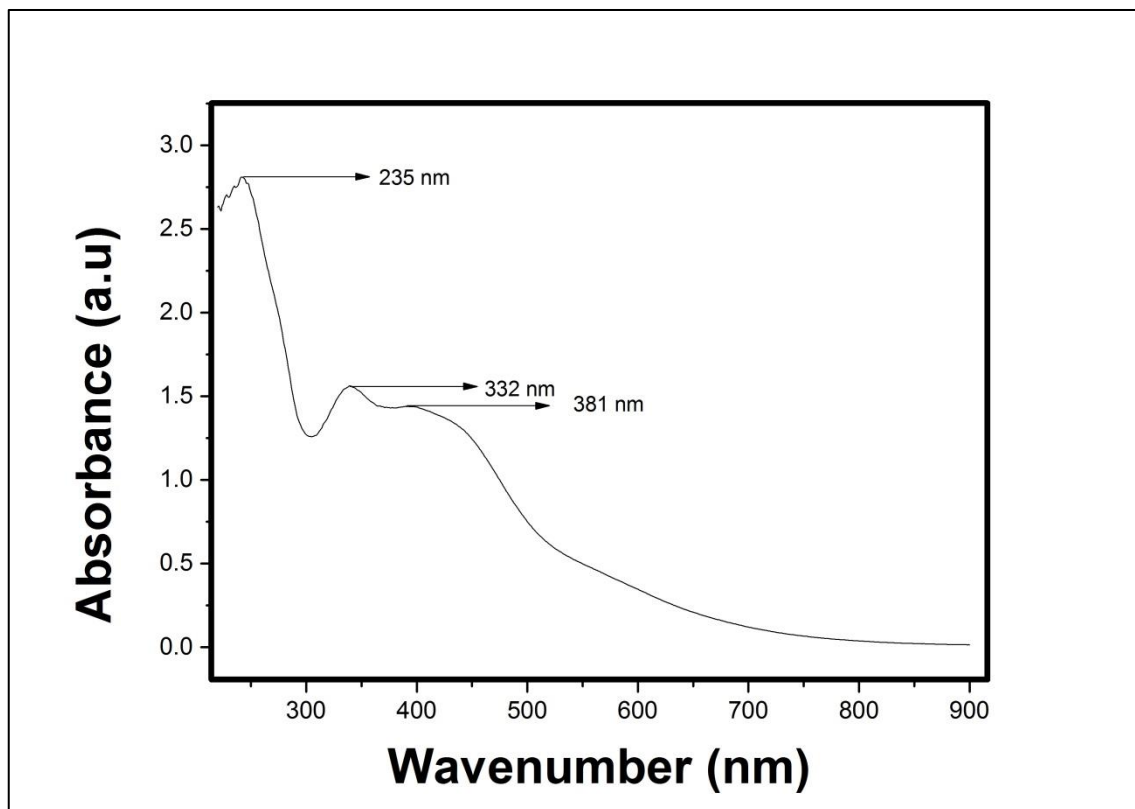


Figure 4.3. UV-Vis spectrum of carbon quantum dots (CQDs)

The CQDs has an absorption peak at 235 nm, 332 nm and 381 nm that may attribute to the overlap of  $n \rightarrow \pi^*$  (non-bonding to anti-bonding) transition of C=O and  $\pi \rightarrow \pi^*$  (bonding to anti-bonding) transition of C=C functional group (refer Figure 4.4) where it can be validated from FT-IR spectra analysis which represent a typical absorption of an aromatic  $\pi$  system of CQDs.

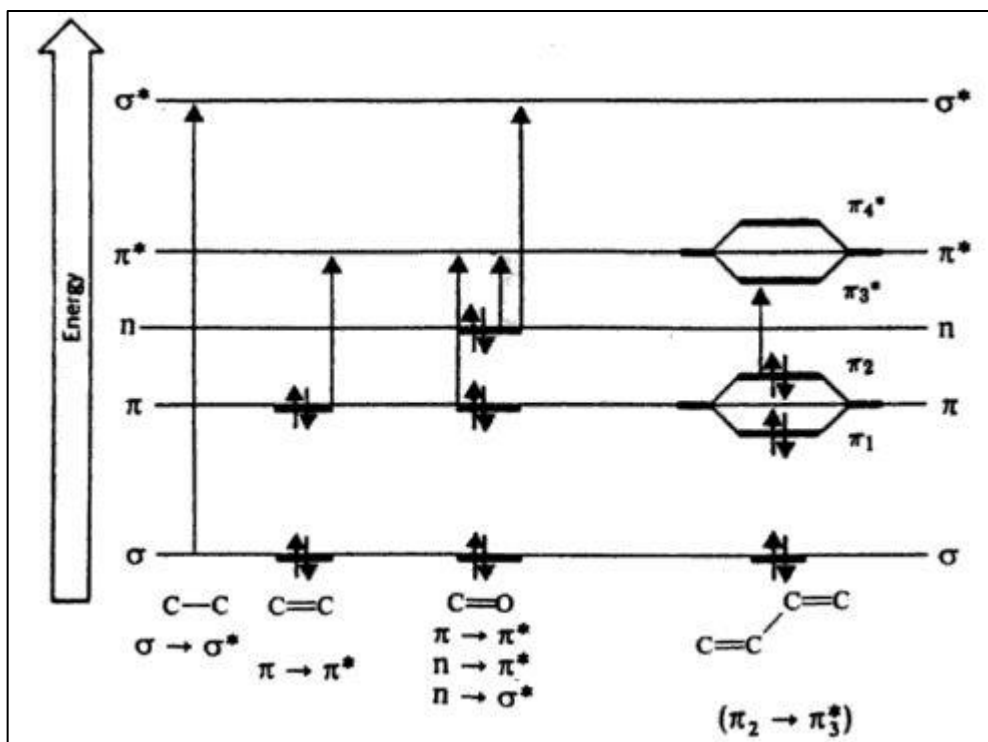


Figure 4.4. Energy changes of electronic transitions

Source: Reproduced from (Kalsi 2006)

Based on the lewis dot structure of citric acid and urea (Figure 4.5), the 'n' electrons are the ones located on the oxygen of carboxyl group of citric acid where we assume urea is completely dissolved in water. Thus, leaving oxygen as the reactive element to excite. This is according to the electronegativity of the element due to its partially negative charged nature.

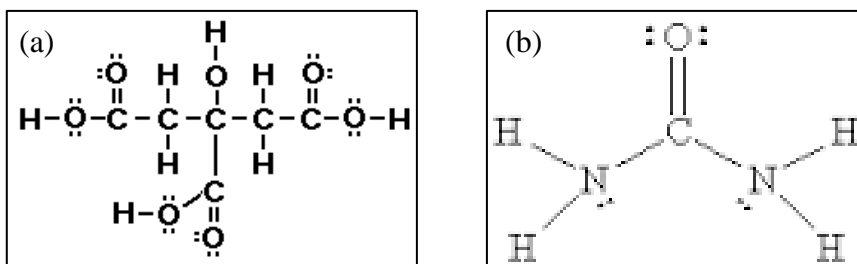
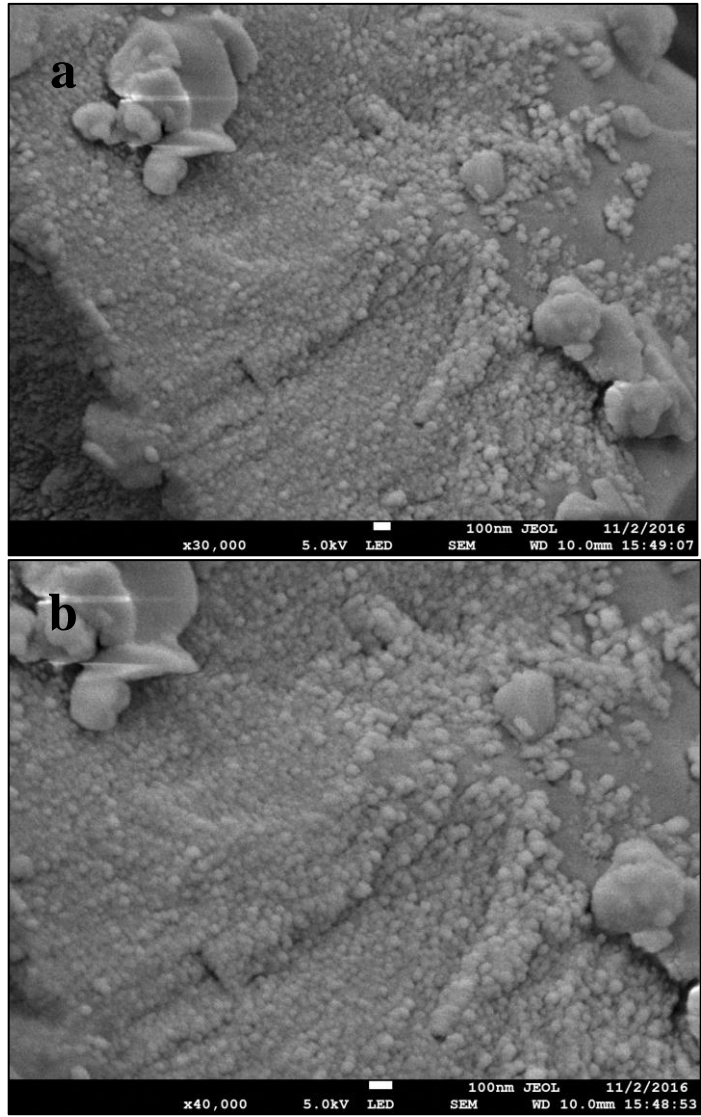


Figure 4.5. Chemical structure of (a) citric acid and (b) urea

Hence, the  $n \rightarrow \pi^*$  transition correspond to the excitation of an electron from one the unshared pair to the  $\pi^*$  orbital (Kalsi, 2006). This transition required the least amount of energy and usually located at absorption band with longer wavelength (lower energy).

Figure 4.6 shows a FESEM images of CQDs synthesized from citric acid and urea by microwave irradiation. The size of CQDs nanoparticles obtained is not uniform and ranging from several tens of nanometres to 100 nm. The nanoparticles of CQDs is not a regular spheres and the surface is rough and uneven. The formation of spheres are not visibly clear. The average size of CQDs nanoparticles calculated using ImageJ software is 66.48 nm.



*Figure 4.6.* FESEM images of CQD with magnification (a) 30 kx (b) 40 kx

### 4.1.2 Exfoliated Graphene

Figure 4.7 shows FT-IR spectra of exfoliated graphene, commercial graphene and activated carbon. The materials having intense absorption band at range between  $3500 - 3300 \text{ cm}^{-1}$  and  $1700 - 1500 \text{ cm}^{-1}$  where it indicate hydroxyl functional group in surfaces and alkene (double bond) respectively. Both exfoliated graphene and activated carbon have absorption band at  $\sim 1700 \text{ cm}^{-1}$  where it indicate functional group of carboxylic acid. However, low absorption of carboxylic functional group is detected in commercial graphene. This might be due to reduction process where most of the oxygen containing and hydrophilic groups such as hydroxyl, epoxide and carboxyl will be completely remove (Hu and Su, 2013).

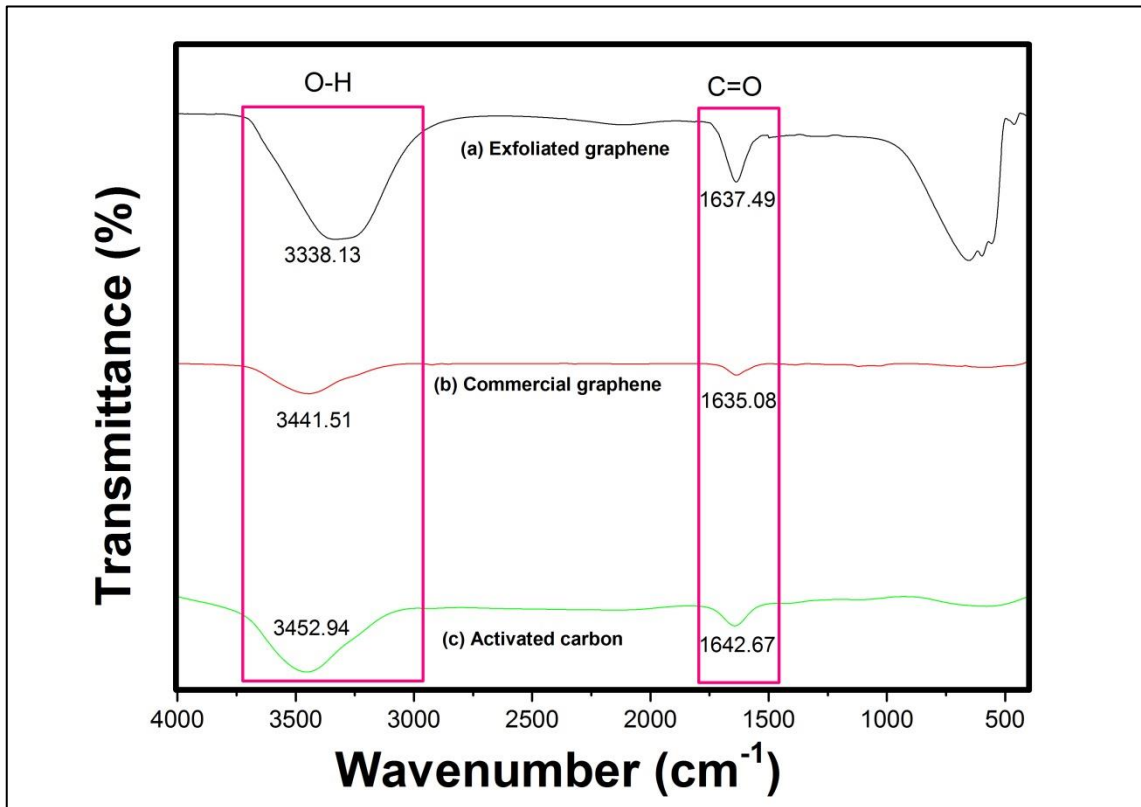


Figure 4.7. FT-IR spectrum of (a) exfoliated graphene (b) commercial graphene (c) activated carbon



The quantity of exfoliated graphene can be determined using two methods viz., (i) using calibration curve and (ii) Beer-Lambert equation. On the first method, the absorbance ( $A$ ) at wavelength of 660 nm of individual pure graphene is determined at various concentrations. Figure 4.8 shows a standard curve graph of graphene in water solvent. Standard curve is often prepared and used to determine the concentration of an unknown sample. It is a quantitative technique where it allows a sample with known properties to be measured and graphed. This curve is used to determine an unknown sample having same properties by interpolation of graph. An ideal standard curve of graphene should have a regression value of  $R^2 = 0.999$  nearing a value of 1 where it indicates a better linear relationship between  $A$  and concentration ( $C$ ). The concentration of unknown sample is determined by mathematical equation obtained from linear fit of standard curve where experimental value obtained is used to determine  $x$  value from  $y$  value which in this research  $y$  value is the absorbance value at 660 nm.

A linear relationship that obeys Beer-Lambert Law equation (Eq. 4.1) where it gives absorbance per unit length at given 660 nm wavelength shows that absorbance is directly proportional to concentration.

$$\frac{A}{l} = \alpha_{660nm} C \quad (4.1)$$

Another way to calculate concentration is by utilizing Beer-Lambert Law equation where the absorption coefficient has to be determined and usually  $\alpha_{660nm} = 2460 \text{ L g m}^{-1}$  is used. The absorbance value is taken at 660 nm due to its suitability for characterization purpose since it is a common wavelength for light source use and least likely to be obscured by instrument fluctuation. The obtained  $R^2$  value in this research is  $R^2 = 0.99205$ . From the graph obtained, the concentration of exfoliated graphene will be calculated using equation  $y = 2.4204x + 0.0325$  where  $y$  is the absorbance value at 660 nm and  $x$  is the concentration of exfoliated graphene. The concentration of exfoliated graphene calculated from  $y = 2.4204x + 0.0325$  is 0.01177 mg/ml which is much smaller than previously reported by (Xu *et al*, 2015) where the obtained concentration is 0.4 mg/ml.

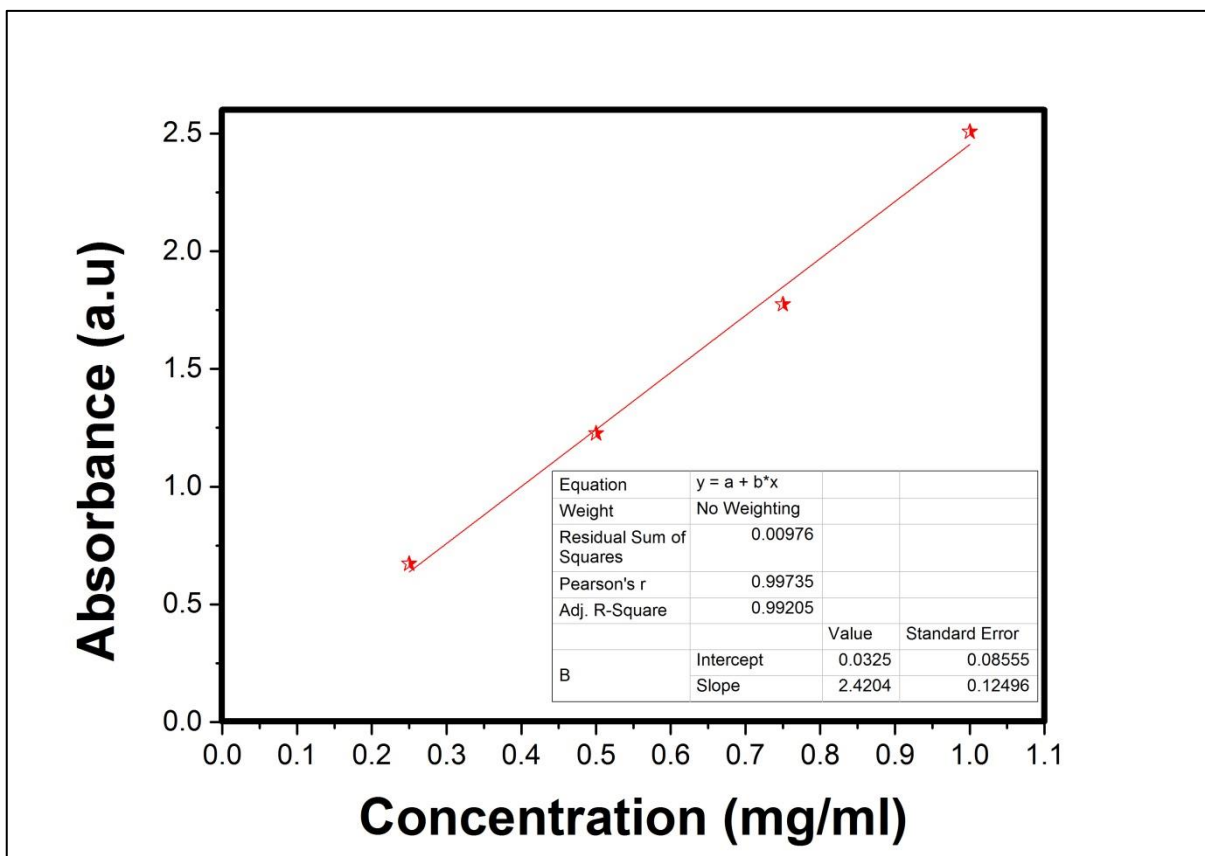


Figure 4.8. Standard curve graph of commercial graphene

Figure 4.9 shows the illustration of light travelling through the cuvette during UV-Vis analysis. There are difference in concentration obtained when the suspension is left to stable or not after sonication process. Hence, this will affect the actual concentration of graphene dispersed in the solution. Therefore, it is better to have the analysis done right after sonication. Thus, a more reliable data can be collected.

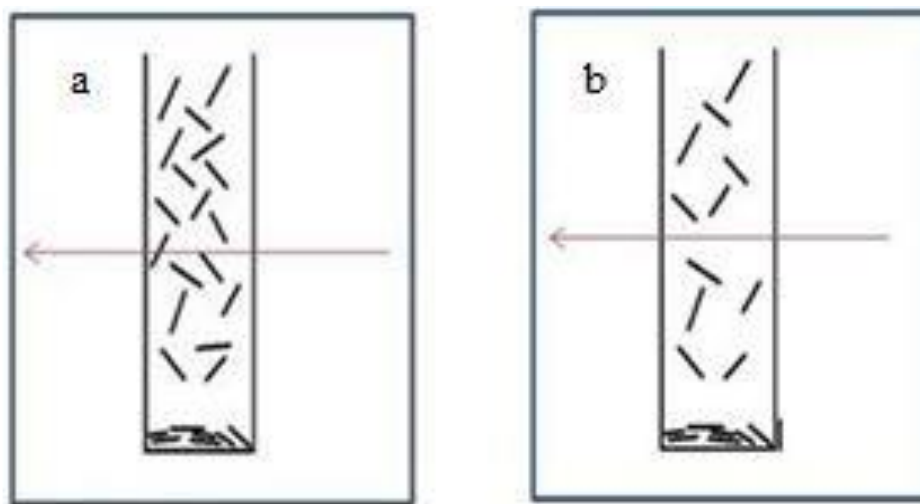


Figure 4.9. Illustration of light travelling through the cuvette (a) suspension graphene after sonication (b) suspension of graphene after left to stable

Figure 4.10 shows the UV-Vis absorption spectra of exfoliated graphene where it have absorption peaks at 315 nm, 327 nm, 333 nm and 337 nm. The tail is extending smoothly into the visible region. However, the absorption peak shown below does not equivalent to the previously reported by (Xu *et al*, 2015) where the absorption peak obtained is at 266 nm. Graphene oxide should have peak at ~230 nm which indicate transition of  $\pi \rightarrow \pi^*$  where it is due to conjugation arises from C=C (Lai *et al*, 2012). From the result obtained, the peak shown is at range of ~315 nm where it usually indicates shoulder attributed by  $n \rightarrow \pi^*$  transitions of C=O bonds (Liu *et al*, 2012).

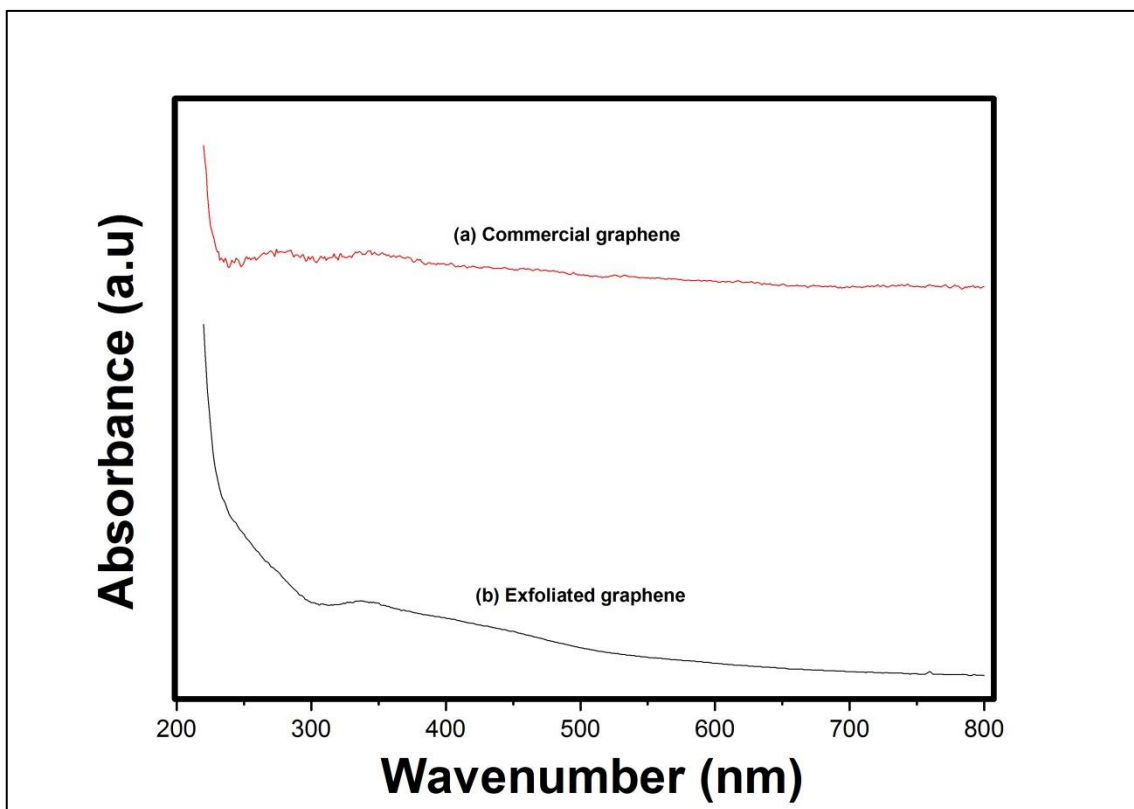


Figure 4.10. UV-Vis spectrum of (a) Commercial graphene (b) exfoliated graphene

Figure 4.11 shows FESEM images of exfoliated graphene. Since the starting material used to exfoliate graphene is activated carbon, the porous structure of activated carbon can be seen. From the images, it can be observed that the sonication process is unable to totally break up the bulk structure of activated carbon. The structure is still in bulk shape. However, as highlighted below, there might have graphene exfoliated in flakes structure where the presence of 3 layer graphene can be seen. The thickness of exfoliated graphene calculated using ImageJ software is  $\sim 29$  nm which is thicker than previously reported by (Xu *et al*, 2015) which is  $\sim 0.64$  nm. This may happen due to difficulty (insufficient energy) to break up bulk activated carbon structure into smaller and thinner graphene flakes as shown in Figure 4.11.

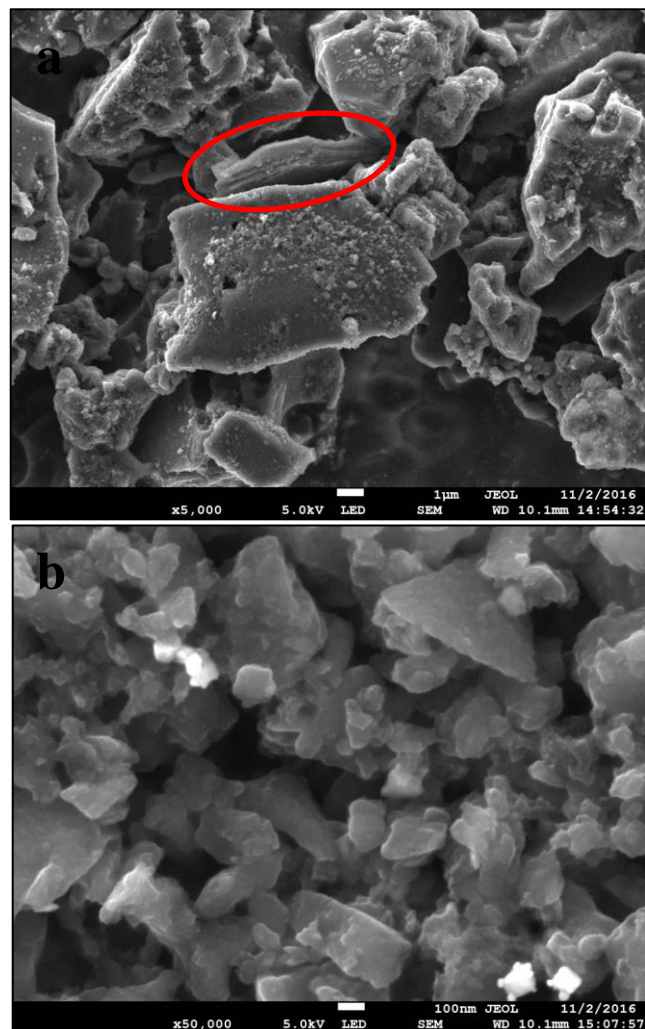


Figure 4.11. FESEM images of exfoliated graphene with magnification of (a) 5000 and (b) 50000

Figure 4.12 shows the FESEM images of graphene exfoliated from sugarcane baggase which is a type of agriculture waste. The surface morphology obtained from FESEM shows a clear sheet-like structure. This is the structure of graphene that should be obtained. The comparison is done since, the starting material used to exfoliate graphene is similar which is AC eventhough the sources are different.

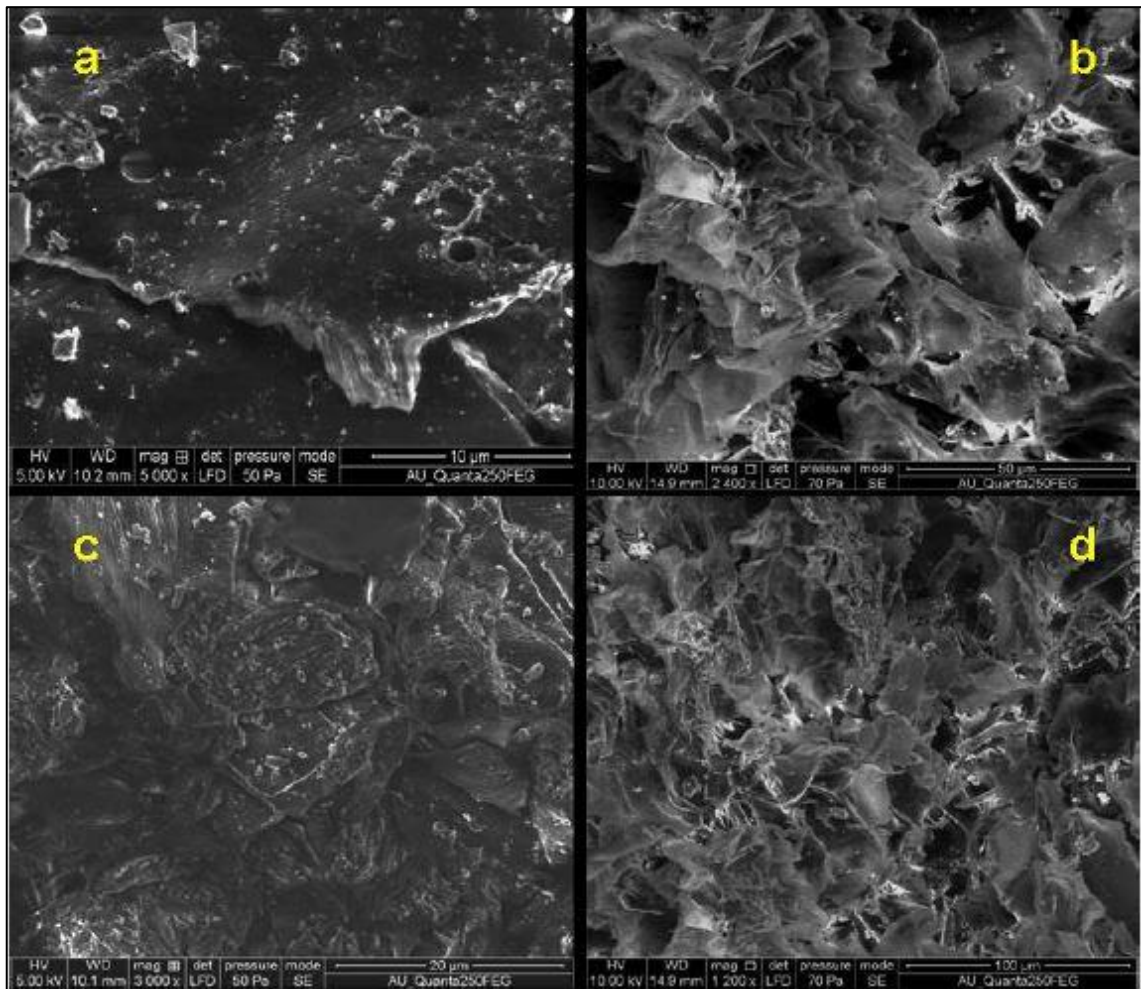


Figure 4.12. FESEM images of exfoliated graphene from sugarcane baggase

Source: (Somanathan *et al*, 2015)

## CHAPTER 5

### CONCLUSION AND RECOMMEDATIONS

#### 5.1 Conclusion

In conclusion, this project has demonstrated exfoliation of graphene by liquid phase exfoliation method by using PKS AC as starting material, water as solvent and CQDs as exfoliation agent. The FESEM images shows the presence of partially exfoliated few layer graphene (< 5 layers). The concentration of exfoliated graphene calculated from standard curve equation is 0.01177 mg/mL which is less than 0.4 mg/mL as reported by (Xu *et al*, 2015). The size of CQDs synthesized is 66.48 nm which is higher than 1.76 nm as reported by (Xu *et al*, 2015). This work failed to get higher concentration of exfoliated graphene due to short sonication time and water is not a suitable solvent to exfoliate graphene due to its high surface tension. Addition of CQDs does not reduce to the surface tension of water to optimum range of  $\sim 40$  mN/m<sup>2</sup> to match with graphene surface. This may happen due to lack of stability of graphene dispersion in water-CQDs mixture.

#### 5.2 Recommendations

Graphene is a wonder material where it's full potential is still being discovered. There are many methods that can be done to improve yield production of graphene. From this project, the produced graphene can be further improved by considering the following factors:

- i. Increasing the sonication time for exfoliation from 1 hour to 3 or 5 hours. This is due to the starting material used is activated carbon instead of graphite where the structure is not orderly arranged like stacked graphite.
- ii. Centrifugation time (30 minutes) and speed (5000 rpm) can be increased since centrifugation plays an important role to exfoliate graphene by separating single and few layer graphene from bulk unexfoliated graphene where the bulk unexfoliated graphene will sediment to bottom.
- iii. Other types of activated carbon also can be used. In this project, palm kernel shell activated carbon is used. Activated carbon derived from bamboo, rice husks, sugarcane bagasse and tea leaves can also be used as substitute for palm kernel shell activated carbon.
- iv. Quality of CQDs exfoliation agent plays an important role to exfoliate graphene from activated carbon. The CQDs can also be synthesized from citric acid and amines or citric acid and boron instead of using urea. Meanwhile, CQDs solution can also be centrifuged to remove large and suspended particles instead of going through the dialysis process which consume time.
- v. Another alternatives to improve this project is by using other bio-dispersant other than CQDs to reduce surface tension of water. Surfactant can also be used to reduce surface tension to optimum range to match that with graphene as surfactant can prevent re-aggregation of graphene by overcoming the attractive Van der Waals forces between graphene flakes. As reported by Mahmood Aliofkhazraei in '*Advances in graphene science*', polymeric surfactants such as Pluronic is used to improve the stability of suspension due to the strongly bound nature of the hydrophobic components (M. *et al*, 2013).



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