# SYNTHESIS OF REDUCED GRAPHENE OXIDE BY USING PALM OIL MILL EFFLUENT (POME)

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## Abstract

The increase of world palm oil demand has driven a significant increase in palm oil production. Indirectly, palm oil mill effluent (POME) production also has increased drastically. In the material science field, graphene is a marvellous material due to its high specific surface area (theoretically 2630 $m^2/g$ for single-layer graphene), extraordinary electronic properties and electron transport capabilities, unprecedented pliability, strong mechanical strength and excellent thermal and electrical conductivities. The abundance β-carotene (strong reducing agent) found in POME can be utilized to synthesize graphene. β-carotene can be used for reduction of graphene oxide instead of hydrazine as this approach is more environmentally friendly. The objectives are to reduce graphene oxide by using β-carotene extracted from POME, optimise the β-carotene concentration to reduce graphene oxide and analyse reduced graphene oxide using Ultraviolet-visible Absorption Spectrophotometry (UV-Vis), Fourier Transform Infrared (FTIR) and cyclic voltammetry (CV). Fabrication of graphene oxide, extraction of β-carotene, and reduced of graphene oxide by β-carotene will be covered in this research. Firstly, the pre-oxidation step was carried out to help to achieve a higher degree of oxidation. Subsequently, the graphite was oxidized by potassium permanganate and undergoes ultrasonication to produce graphene oxide. After that, β-carotene was extracted from POME by using soxhlet extraction. Graphene oxide was reduced by extracted β-carotene from POME and un-treat POME. 4mM of extracted β-carotene was illustrated a successfully reduced result monitored by UV-Vis and FTIR. Quantification of reduced graphene oxide treats by extracted β-carotene from POME has been monitored by using UV-Vis and the peak detected will be shifted from 230 nm to 270 nm. For FTIR analysis, the oxygen associated intensities bands were reduced, such as 3400 $cm^{-1}$ (for hydroxyl stretching) was completely disappeared in the CrGO spectrum. Besides that, cyclic voltammograms of several types of rGO by applying in the sensor field also have been monitored.

# ABSTRAK

Peningkatan dunia permintaan minyak sawit telah mendorong peningkatan yang ketara dalam pengeluaran minyak sawit. Secara tidak langsung, efluen kilang minyak sawit (POME) pengeluaran juga meningkatkan secara drastik. Dalam bidang sains bahan, graphene merupakan bahan marvellous kerana kawasan permukaan yang tinggi ( secara teori 2.630 m2 / g untuk satu lapisan graphene ), ciri elektronik yang luar biasa dan keupayaan pengangkutan electron yang luar biasa, sifat kelembutan yang menakjubkan, mekanikal kekuatan yang kuat dan haba dan elektrik konduksi yang sangat baik. β -karotena didapati berkemampuan untuk graphene oksida reduksi. Kekayaan β -karotena (ejen reduksi yang kuat ) boleh terdapat dalam POME dan ia boleh digunakan untuk sintesis graphene . Hidrazin boleh digantikan oleh β -karotena untuk reduksi graphene oksida proses kerana kaedah ini lebih mesra alam. Objektif eksperimen ini adalah untuk menjalankan reduksi proses bagi graphene oksida dengan menggunakan β -karotena , yang diekstrak daripada POME , mengoptimumkan kepekatan β -karotena untuk reduksi proses graphene oksida dan menganalisis tahap reduksi bagi graphene oksida dengan menggunakan UV- Vis, FTIR dan CV. Fabrikasi graphene oksida, pengekstrakan β -karotena, dan graphene oksida reduksi dengan menggunakan β -karotena akan dibincangkan dalam kajian ini. Kaedah ubah suai Hummers telah dipilih kerana tahap tinggi pengoksidaan grafit berbanding dengan Brodie dan Staudenmaier kaedah. Pertama, langkah pra- pengoksidaan telah dijalankan untuk mencapai tahap pengoksidaan yang lebih tinggi. Selepas itu, grafit telah teroksida oleh kalium permanganat dan diikuti dengan unltrasonication untuk menghasilkan graphene oksida. Selepas itu, β -karotena telah diekstrak dari POME dengan menggunakan pengekstrakan soxhlet. Ekstrak β -karotena daripada POME dan POME mentah telah dipilih sebagai ejen reduksi bagi graphene oksida reduksi proses. 4mM ekstrak β-karotena telah berjaya mengurangkan graphene oksida yang telah dianalisis oleh UV-Vis dan FTIR. Kuantiti β-karotena yang digunakan untuk mengurangkan graphene oksida telah dianalisis dengan menggunakan UV-Vis dan puncak dikesan akan beralih daripada 230 nm hingga 270 nm. Untuk analisis FTIR, oksigen dikaitkan jalur keamatan dikurangkan, seperti 3400 cm$^{-1}$ (untuk regangan hidroksil) telah hilang sepenuhnya dalam spektrum CrGO. Di samping itu, voltammograms kitaran bagi beberapa jenis rGO dengan memohon dalam bidang sensor juga telah analisis dalam pengajian ini.

## Table of Contents

# LIST OF FIGURES

# LIST OF TABLES

# 1. Introduction

## 1.1 Background of Study

The increase of world Palm Oil demand has driven a significant increase in palm oil production. Indirectly, palm oil mill effluent (POME) also increases drastically. However, POME becomes an issue of great concern due to palm oil mills develop drastically. After investigation, approximate $0.65m^3$ of POME will produce for every ton of fresh fruit bunch (FFB) processed (King & Yu, 2013). POME is a thick brownish liquid with very high biochemical oxygen demand (BOD) and chemical oxygen demand (COD). According to the statistics, palm oil mills in Malaysia were increased greatly from 334 mills in 1999 to 426 mills in 2011. Approximate a tonne of crude palm oil (CPO) will generated 2.5-3.75 tonnes of POME. POME comprises of 12.5 wt% crude protein, 10.2 wt% crude lipid, 29.5 wt% carbohydrate, 26.3 wt% nitrogen-free extract, and 0.019 wt% carotene. Research data shows that a litre of raw POME has 50,000 - 65,000 mg COD (Rupani *et al*., 2010). Several papers have proposed that carotene residuals within the POME can use for synthesis graphene (graphene oxide reduction).

Graphene has been studied for 60 years (A.K Geim and K.S Novoselov, 2007). In 2004, Konstantin Novoselov, Andre Geim and their collaborators have proposed that the existence of isolated graphite sheets by mechanical exfoliation (Wang & Hu, 2011). In July 2005, they published the single layer of carbon is what we call graphene. Graphene is a monolayer carbon atoms which tightly packed into hexagonal lattice (Novoselov *et al*., 2010). It is tightly packed into a two dimensional (2D) honeycomb lattice (Novoselov *et al*., 2010) with a carbon-carbon distance of 0.142 nm. It can wrap up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite (A.K Geim and K.S Novoselov, 2007). Graphene is composed of $sp^2$ carbon networking material (Haque *et al*., 2012; Park *et al*., 2011; Marcano *et al*., 2010) carotene is an anti-oxidant. β-carotenes are able to terminate radical chain reactions. It will bind to free radicals and experience decay to generate non-radical products. So, the environment friendly approach is more preferable. Hydrazine reduced graphene oxide (HRCO) and β-carotene reduced graphene oxide (CRGO) was studied and compared both reducing performance by spectroscopic and microscopic techniques.

## 1.2 Problem Statement and Motivation

In large scale production, toxicity of reduced graphene oxide is a major issue. The conventional reductants such as hydrazine monohydrate and sodium borohydrate are highly toxic and detrimental to environments and organisms. Recently, there were few studies focus on green reduction of graphene oxide. Usage of toxic reductants can be avoided by applying green reductants for reduction of graphene oxide, which can give the same production amount of desired products and environmentally friendly. Several green reductants were proposed such as polyphenol alcohol, wild carrot, reducing sugar, Vitamin C, tea solution and aqueous phytoextracts.

So, in this research green reductant was employed to avoid the detrimental effect brought by conventional reduction of graphene oxide to environments. In this study, β-carotene was chosen as green reducing agent. It can be obtained from vegetables, fruits and also agriculture waste (POME). β-carotene of POME was selected due to increases of world palm oil demand has driven a significant increase in production of POME.

### 1.3 Objectives

The objectives of this research are

i. To reduce graphene oxide by using β-carotene, which extracted from POME,
ii. To optimise the β-carotene concentration to reduce graphene oxide
iii. To analyse reduced graphene oxide using UV-Vis, FTIR and CV.

### 1.4 Scope

This experiment was done using the modified Hummer’s method, extraction of β-carotene and redox reaction.

i. Fabrication of graphene oxide

   Modified Method was used for fabricating graphene oxide as well as the raw material used is graphite.

ii. Extraction of β-carotene

   Impurities have been isolated with β-carotene. The purpose of this process increases the purity of β-carotene for graphene oxide (GO) reduction.

iii. Reduction of graphene oxide by β-carotene

   This research is conducted to observe the degree of reduction of graphene oxide to reduced graphene oxide by using β-carotene from POME. In this study, optimal concentration, and time to yield the reduced graphene oxide from graphene oxide reduction within the specific range are estimated.

# 2. Literature Review

## 2.1 Overview

This paper presents the experimental studies of synthesized of reduced graphene oxide (rGO) by using green reductant (β-carotene) with different concentrations. The minimal concentration of β-carotene required to reduced 2 g/L of GO into rGO has been determined, which is 4 mM. Raw POME and extracted POME have been selected as kinds of green reductants in this study. The soxhlet extraction has been used to extract the β-carotene from the raw POME. Reduction of GO was carried out by using raw and extracted POME at the same amount of β-carotene concentration.

## 2.2 Graphene

### 2.2.1 History of graphene

Graphite is composed of multilayers of strongly interacting graphene. It is basically a two-dimensional carbon sheet with the thickness around 1nm and lateral dimensions varying between a few nanometers and several microns. It can wrap up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite (A.K Geim and K.S Novoselov, 2007). It has several advantages over amorphous carbon. For example, graphene has excellent mechanical, electrical, thermal and optical properties (Wen *et al.*, 2010), very high specific surface area, and ability to influence these properties through chemical functionalization (Park & Ruoff, 2009). Nowadays, there are various methods were developed by Brodie, Staudenmaier, and Hummers (You *et al.*, 2013).

In 1859, B. C. Brodie a British chemist was the first graphene oxide explorer, and graphene oxide became very popular in the scientific community due to its potential to be an important precursor to graphene (a single atomic layer of graphite). Brodie Method was developed by a British chemist, B.C. Brodie in the nineteenth century (Wang & Hu, 2011). B.C. Brodie was interested in the molecular formula of ‘‘graphite’’ and its discrete molecular weight. He was the first proposed that the oxidation of graphite by employing potassium chloride ($KClO_3$) into slurry of graphite in fuming nitric acid ($HNO_3$) (Wang & Hu, 2011; Dreyer *et al.*, 2010). Nearly 40 years after Brodie discovery of the ability to oxidize graphite, L .Staudenmaier did some modification on Brodie’s work (Dreyer *et al.*, 2010) by increasing the acidity of the reactants via replaced nitric acid with a mixture of sulphuric acid and nitric acid. Staudenmaier’s method is not applicable because it is hazardous and time-consuming (Gao, 2012). In 2005, Professor Andre Geim’s group first studied the experimentally temperature quantum hall effect on a real piece of graphene, which was obtained by mechanical exfoliation of Highly Oriented Pyrolytic Graphite (HOPG) (Mart ńez, 2013; Allen *et al.*, 2010). In 2010, Andre Geim and Konstantin Novoselov won the 2010 Nobel Prize in Physics due to the discovery of graphene.

After 60 years of Staudenmaier’s strategy, chemists Hummers and Offeman in Mellon Institution of Industrial Research developed a different method for synthesis graphene oxide. Hummers’ method is a less hazardous oxidation process by using potassium permanganate ($KMnO_4$) instead of potassium chlorate ($KClO_3$) as oxidizing agent (Wang & Hu, 2011). Potassium chlorate ($KClO_3$) is flammable chemical oxidizing agents, so it is hazardous for the environment, whereas potassium permanganate ($KMnO_4$) has none of flammable characteristics. The whole oxidation process of Hummers’ method can finish within 2 hours (Gao, 2012) and final products have a higher degree of oxidation than Staudenmaier’s product. However, Hummers’ method usually incompletely oxidized graphite core with graphene oxide shells (Gao, 2012), so Kovtyukhova done some modification of Hummers’ method in 1999 (Gao, 2012). Modified Hummers’ method was adopted to synthesize graphite oxide in this study. The purpose of the modification was to assist graphite to achieve a higher degree of oxidation via pre-oxidation.

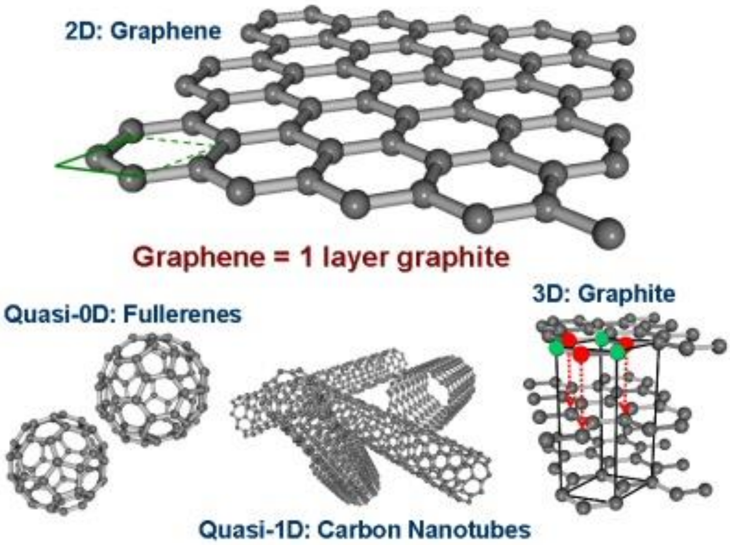

Figure 2-1 : Graphenes come in a variety of structures from atom-thick sheets to Buckyballs and Nanotubes (Thomas, 2011).

### 2.2.2 Properties of graphene

Graphene is a hexagonal carbon lattice which tightly packed into a two dimensional (2D) atomic crystal (Novoselov *et al.*, 2010). It has a high specific surface area, which is 2630 $m^2/g$ for single-layer of graphene (Chen *et al*., 2012). Over hundred years, graphite has been commonly used as marking instrument such as pencils today, where it is commonly called lead. Basically, carbon atoms consist of 4 valence electrons. Carbon is inorganic compounds which can exhibit its oxidation state in +4 or +2 (found in carbon monoxide and other transition metal carbonyl complexes). Graphene is composed of $\pi$-conjugated $sp^2$ carbon networking material (Haque *et al*., 2012; Park *et al*., 2011; Marcano *et al*., 2010).

In graphene, 3 valence electrons are contributed to form 3 covalent bonds with 3 other carbon atoms on the two-dimensional (2D) plane. Each carbon atom in the lattice contributes a pi ($\pi$) orbital to form a delocalized network of electrons (Zhu *et al*. 2010). The 1 available valence electron remained is contributed to form a delocalized network of electrons. These highly mobile electrons are located above or below of graphene sheet which allow electron delocalization to the adjacent plain. Graphene is insoluble in water.

The electronic configuration of graphene contributes conduction bands composed of pi ($\pi$) orbitals. These outstanding characteristics of graphene enhances its thermal and electrical properties (A.K Geim and K.S Novoselov, 2007). Graphene displays a conductivity up to 15000 $cm^2V^{-1}s^{-1}$ in room temperature, while excess of 200 000 $cm^2V^{-1}s^{-1}$ (Zhu *et al*., 2010) can be achieved by minimizing the presence of impurities (Zhu *et al.*, 2010). Besides that, graphene provides excellent thermal conductivity, which is about 2000–4000 $W\ m^{-1}\ K^{-1}$ at room temperature (Pop *et al*., 2012). Mechanical strength of graphene can be investigated by atomic force microscopy (AFM) (Zhu *et al.*, 2010). It shows a Young’s modulus of 1.0 TPa and a fracture strength of 130 GPa by AFM (Zhu *et al*., 2010).

Table 2-1 : Properties of Graphene

| Properties | Explanation | References |
|---|---|---|
| Structure | A hexagonal carbon lattice which tightly packed into a two dimensional (2D) atomic crystal. | Novoselov *et al*., 2010 |
| Physical properties | It has high specific surface area, which is theoretically predicted (>2500 $m^2g^{-1}$) and experimentally measured surface areas (400–700 $m^2g^{-1}$) | Bruinsma *et al*., 2004 |
| Electronic conductivity | Electronic conductivities up to 15000 $cm^2V^{-1}s^{-1}$ in room temperature, while excess of 200 000 $cm^2V^{-1}s^{-1}$ can be achieved by minimizing the presence of impurities. | Zhu *et al*., 2010 |
| Thermal conductivity | thermal conductivity of graphene at room temperature is about 2000–4000 W $m^{-1}$ $K^{-1}$ | Pop *et al*., 2012 |
| Mechanical properties | Graphene shows a Young’s modulus of 1.0 TPa and a fracture strength of 130 GPa by AFM. | Zhu *et al*., 2010 |

### 2.2.3 Application of graphene

Graphene has viewed as ‘wonder material’ in nanotechnology and biotechnology field (Barnard & Snook, 2010).The graphene applications demand has driven a significant increase due to graphene with properties appropriate for the specific application. Graphene has excellent mechanical, electrical, thermal and optical properties, high specific developed several applications such as energy-storage materials, polymer composite, mechanical resonators (Park & Ruoff, 2009), and biosensor (Chen *et al.*, 2012).

Photonic devices are most actively studied kind of graphene photodetectors (Novoselov *et al*., 2012). Electrons in graphene are significant wavelength-independent (Novoselov *et al*., 2012) due to it behave as massless two-dimensional particles. In addition, mono-layer and bi-layer of graphene is completely transparent under condition of optical energy is smaller than double the Fermi level (Novoselov *et al*., 2012). Last but not least, graphene possessed of high operating bandwidth, which makes it suitable for high-speed data communications (Novoselov *et al*., 2012). These properties induced graphene suit many controllable photonic devices.

The purpose of paint coating is to improve the surface properties of a substrate, wettability, corrosion resistance and adhesion (Tong *et al*., 2013). Graphene-based paints are developed for conductive ink, antistatic, electromagnetic-interference shielding, and gas barrier applications (Novoselov *et al.*, 2012) due to its highly inert, and its corrosion barrier properties against water and oxygen diffusion. Excellent mechanical, chemical, electronic and barrier properties of graphene, make it becomes attractive for applications in composite materials.

Graphene’s potential has been proposed in sensor application due to its conductance changing as a function of extent of surface adsorption and large specific surface area (Zhu *et al.*, 2010). Besides from that, graphene is expected to have important advantages in biosensor devices (Punckt *et al*., 2010) due to its excellent electrochemical behaviours (Shao *et al*., 2010). For the chemical response, target molecules will adsorb to the surface of graphene, the region of adsorption undergone charge transfer from molecules to graphene, and graphene as a donor or acceptor of charge. (Zhu *et al*., 2010). Fabrication of glucose biosensors are through covalent attachment between the carboxylic groups on the graphene oxide sheets and the amine groups of the glucose oxidase (Chen *et al*., 2012).

Graphene materials have been used as ultracapacitors. An ultracapacitors unit cell is comprised of two porous carbon electrodes that are isolated by a porous separator to avoid the electrical contact between two carbon electrodes. Chemically modified graphene (CMG) has been reported as a potential material for used as an electrode in ultracapacitors (Das & Prusty, 2013 ; Stoller *et al*., 2008) due to its high specific surface area and excellent electrical conductivity (Stoller *et al*., 2008).

There various methods can utilize to synthesis graphene and different grade of graphene can obtain from different methods. Quality of graphene is strongly affected by synthesized methods. Graphene of various dimensions, shapes and quality can be prepared from dozen of methods such as mechanical exfoliation, chemical exfoliation chemical, vapour deposition (CVD), and Synthesis on silicon carbide (SiC) (Novoselov *et al*., 2012). Applications of graphene depend on its grade or quality. The table below shows the properties obtained by different methods.

Table 2-2 : Properties obtained by different methods (Novoselov *et al.*, 2012)

| **Method** | **Crystallite size (µm)** | **Sample size (mm)** | **Charge carrier mobility (at ambient temperature) ($cm^2V^{-1}s^{-1}$)** | **Applications** | **Reference** |
|---|---|---|---|---|---|
| **Mechanical exfoliation** | >1,000 | >1 | $>2\times10^5$ and $>10^6$ (at low temperature) | Research | Novoselov *et al.*, 2012 |
| **Chemical exfoliation** | ≤0.1 | Infinite as a layer of overlapping flakes | 100 (for a layer of overlapping flakes | Coatings, paint/ink, composites, transparent conductive layers, energy storage, bio-applications | Novoselov *et al.*, 2012 |
| **Chemical exfoliation via graphene oxide** | ~100 | Infinite as a layer of overlapping flakes | 1 (for a layer of overlapping flakes) | Coatings, paint/ink, composites, transparent conductive layers, energy storage, bio-applications | Novoselov *et al.*, 2012 |
| **CVD** | 1,000 | ~1,000 | 10,000 | Photonics, nano-electronics, transparent conductive layers, sensors, bio-applications | Novoselov *et al.*, 2012 |
| **SIC** | 50 | 100 | 10,000 | High-frequency transistors and other electronic devices | Novoselov *et al.*, 2012 |

## 2.3 Synthesis of graphene

### 2.3.1 Exfoliation

There are several approaches for graphene synthesis such as mechanical exfoliation, chemical vapour deposition (CVD), and chemical exfoliation.

Mechanical Exfoliation or Scotch Tape method obtained graphene by detached from graphite crystals by adhesive tape (Jabari Seresht *et al*., 2013). The graphene flakes obtained by mechanical exfoliation are differ in size and thickness. However, productivity of graphene is quite low (Ghosh & Oh, 2012)due to lack of controllability of this method.

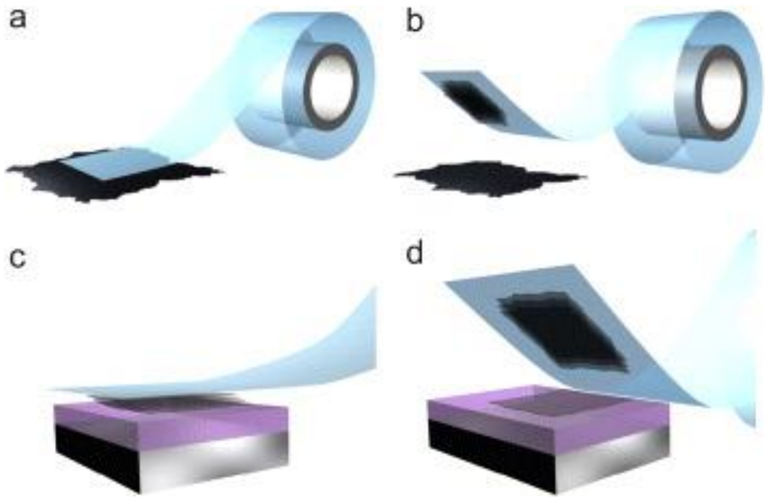

Figure 2-2 : Graphene layers are separated by scotch tape (Novoselov & Castro Neto, 2012)

Second method will be discussed is chemical vapour deposition (CVD). CVD is grown of graphene films on transition metal films (Novoselov *et al*., 2012). For example, graphene is grown on copper in the furnace around 1000 ℃, while methane and hydrogen gases are then flowed through it (Pollard, 2011). This method is highly depends on the metals' ability to absorb carbon. High impurities content of graphene will produced by this method due to the various materials required for CVD (Pollard, 2011).

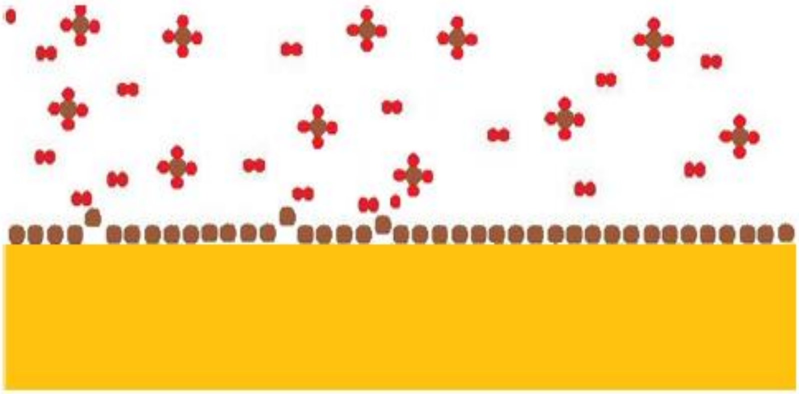

Figure 2-3 : Diagram of chemical vapour deposition on copper (Pollard, 2011)

Chemical exfoliation of graphite or graphite oxide (Novoselov *et al*., 2012) is known as most common and efficient method among these three methods. Before exfoliation process, the graphite had undergone oxidation and became graphite oxide (Ghosh & Oh, 2012) then followed by the reduction process. The purpose of oxidation of graphite is for weakening the π-π interaction and strong Van der Waals forces between graphite planes. Afterward, the graphite oxide is exfoliated into graphene oxide by ultrasonication process. This method was chosen due to it allow suspensions with well-defined distributions of graphene platelets to produce (Novoselov *et al*., 2012).

### 2.3.2 Chemical reduction of graphene oxide

There are several ways to accomplish the chemical reactivity reduction process of graphene oxide (GO). Common reduction methods are electrochemical reduction, thermal reduction and chemical reduction. Exfoliation is a process that isolated two-dimensional sheet of carbon lattice from three-dimensional graphite. A successful exfoliation process, the c-axis spacing by oxidation to 0.7 nm and completely eliminate the 0.34 nm graphite interlayer spacing (Mcallister *et al.*, 2007). Graphite flakes break down into smaller graphene oxide flakes with size of 10 µm in diameter (Mcallister *et al.*, 2007). Final size of graphene oxide flakes does not depend on initial size of graphite flakes.

Electrochemical reduction is the reduction process of graphene oxide relies on the electrochemical removal of the oxygen functionalities. This method is able to create a very high quality of the reduced graphene oxide (almost identical with the structure of pristine graphene). The graphene oxide can be electrochemically reduced by cyclic voltammetry technique in alkaline solution (Zhang *et al.*, 2012). Usually this process, the graphene oxide will coated onto various substrates such as Indium Tin Oxide or glass. A common aqueous solution used in the electrochemical reduction of graphene oxide is 6 mol $L^{-1}$ of KOH (Zhang *et al.*, 2012). The reduction process will begin the cyclic voltammetry scans at -0.9 to 0 V (vs Hg/HgO) (Zhang *et al.*, 2012). This method was found to be very effective as reduced graphene oxide can be produced without the involvement of any hazardous chemical reductants. Therefore, the production of hazardous by-products can be avoided. However, the reduction mechanism of electrochemical reduction was still uncleared and there were no sufficient previous studies to demonstrate the reduction process.

Thermal reduction is the rapid heating processes of graphite oxide in a furnace, which has the possibility to create thermodynamically stable of carbon dioxide species. Thermal reduction of GO has involved the removal of oxygen groups by formation of CO and $CO_2$ gasses which will evolve into the space between graphite oxide sheets during rapid heating of the graphite oxide (Ganguly *et al.*, 2011).

Exfoliation of the stacked structure of graphite oxide through thermal reduction occurs at high temperature (900 1000 °C – 1000 °C) (Ganguly *et al.*, 2011). It is found to be high efficiency under ultra-high vacuum (UHV) condition (Ganguly *et al.*, 2011). The higher the temperature of thermal reduction of GO, the higher the C/O ratio of reduced graphene oxide will be produced. This process simulates the dual effect where it is involved both exfoliation of graphite oxide an also reduction functionalized graphene sheets by decomposing the oxygen containing groups at high temperature (Ganguly *et al.*, 2011).

Chemical based of reduction technique is obtained the reduced graphene oxide by exfoliating the graphite oxide into graphene oxide in some polar solvent, such as water. Chemical reduction, but strong chemical reductant is a promising way in the reduction process to obtain reduced graphene oxide from GO. Chemical reduction involves a simple reflux equipment by moderate heating or it also can be done in room temperature. Common chemical used during reduction is hydrazine (Stankovich *et al.*, 2007).

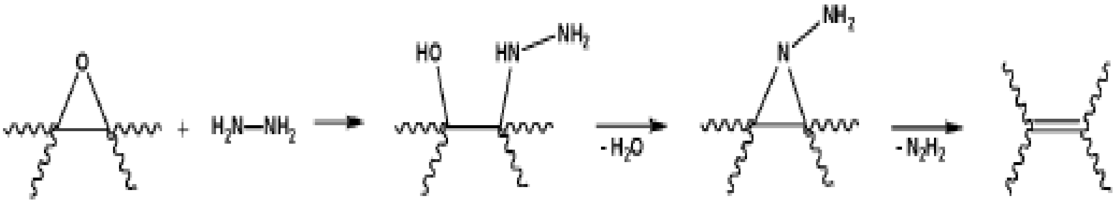

Figure 2-4 : reaction pathway for epoxide reduction by hydrazine (Dreyer *et al*., 2010)

Hydrazine is a highly toxic chemical and potentially explosive chemical. The use of these poisonous and explosive reducing agents requires great cautious.

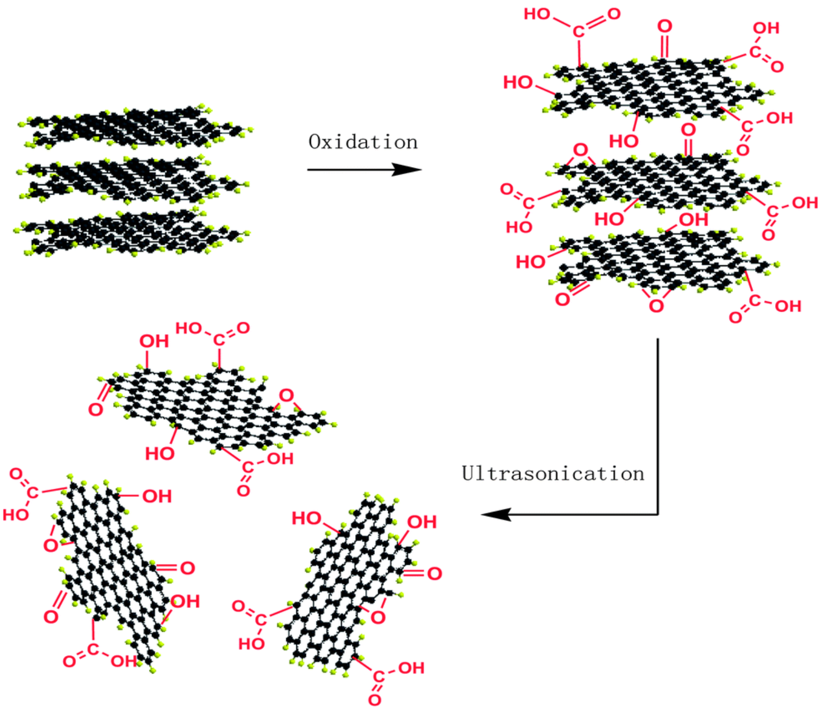

Figure 2-5 : Synthesis of graphene oxide by chemical exfoliation (Fu *et al*., 2014)

### 2.3.3 Green Reduction of graphene oxide

Green reduction becomes a phenomenon to overcome the toxic nature of chemical reductants such as hydrazine. Green reduction is eliminated by chemical reduction of graphene by using small organic molecules, bio-molecules and polymers. Few natural reducing agents have been attempting to replace toxic reducing agents (hydrazine, di-methylhydrazine, hydroquinone, sodium borohydride) (Thakur & Karak, 2012) for the graphene oxide reduction. The presence of trace amount toxic reducing agents would cause detrimental effect to bio-related applications of graphene. There are two factors of green reduction should be concerned. The first factor to be concerned is green reduction of graphene oxide should be as effective as hydrazine reduction. Second factor is the structure of reduced graphene oxide obtained after green reduction should similarly with hydrazine reduction, which is remained as monolayer sheets in aqueous solution.

Several papers have been proposed reduction of graphene oxide by environmental friendly reductants which are by using Vitamin C (Thakur & Karak, 2012), wild carrot root (Kuila *et al*., 2011), and aqueous phytoextracts (Thakur & Karak, 2012). β-carotene found in POME (Thakur & Karak, 2012) is a kind of phytochemicals that capable to reduce graphene oxide and without cause any detrimental effect to our environment. So, POME is selected to reduce graphene oxide instead of harmful reducing agent (hydrazine) in this study. Various kinds of investigations have been carried out to discover a green approach and the best ways to obtain high yields of graphene production.