GREEN REDUCTION OF GRAPHENE OXIDE BY USING PHYTOEXTRACTS FROM BANANA PEELS

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ABSTRACT

Graphene is a 2-dimensional (2D) material that attracts many researches interest due to its significant properties and applications. Graphene can be synthesize from oxidation of graphite flakes and reduced by using reductant to become graphene nanosheets. Graphene oxide can be reduced chemically by using reducing agents such as hydrazine or dimethlyhydrazine. However, these chemicals are highly poisonous and toxic, which will bring harmful effect to human beings and environment. Therefore great care is needed when handling these materials and it requires extra routes to remove the impurities introduced by the chemical reduction of graphene oxide such as C-N. To ease the synthesis of good quality and environment friendly graphene, green reduction of graphene oxide becomes an alternative way. In this study, phytoextracts from banana peels was used as the reducing agent due to its high phenolic contents and antioxidant activity. Graphite oxide was fabricated using graphite flakes before undergoing ultrasonication for exfoliation to form the graphene oxide. The graphene oxide was reduced by using phytoextracts from banana peels at room temperature and refluxed temperature. Optimization of phytoextracts reduction was carried out by varying the phytoextracts concentration, reduction time and reduction temperature. The graphene oxide and graphene were characterized by using Ultraviolet-visible spectrophotometer (UV-Vis), Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and cyclic voltammetry analysis (CV) for the fabrication of glucose sensor. UV-Vis result for graphene oxide shows an absorption peak at range of 230 nm and red-shifted to 270 nm for phytoextract reduced graphene oxide (PRGO). Graphite oxide (GO) in FTIR study shows intense band at 1623 cm^{-1} (C=O stretching), 1053 cm^{-1} (for C-O stretching), and a broad band around 3332 cm^{-1} for hydroxyl group. PRGO shows the a decrease in the intensity at 3332 cm^{-1}, but does not remove the peak at 1052 cm^{-1} and 1623 cm^{-1}. PRGO also exhibits a comparable solubility as conventional reduced graphene oxide and in the application of glucose sensor; PRGO was able to detect a glucose concentration of 0.1 mM by using glassy carbon electrode (GCE) at a scan rate of 50 mVs^{-1}.

ABSTRAK

Graphene adalah bahan 2- dimensi (2D) yang menarik banyak perhatian para penyelidik kerana sifat-sifat yang unik. Graphene boleh disintesis daripada pengoksidaan kepingan grafit dan penurunan graphene oksida secara kimia adalah cara yang paling menyerlah untuk menghasilkan graphene yang berkualiti. Grafit oksida boleh diturunkan secara kimia dengan menggunakan agen penurunan seperti hidrazin. Walau bagaimanapun, bahan kimia yang digunakan adalah sangat toksik dan akan membawa kesan berbahaya kepada manusia dan alam sekitar. Oleh yang demikian para penyelidik harus berhati-hati apabila mengendalikan bahan-bahan kimia tesebut dan ia juga memerlukan laluan tambahan untuk mengurangkan toksik diperkenalkan oleh penurunan kimia oksida graphene seperti C-N. Untuk memudahkan sintesis graphene yang mesra alam dan berkualiti, penurunan hijau graphene oksida menjadi cara alternatif. Dalam kajian ini, phytoekstrak daripada kulit pisang digunakan sebagai agen penurunan kerana kandungan fenolik dan aktiviti antioksidan yang tinggi. Grafit oksida akan disintesis menggunakan kepingan grafit sebelum menjalani ultrasonikasi untuk pembentukan graphene oksida. Grafit oksida akan menjalani ultrasonikasi untuk pengelupasan untuk membentuk graphene oksida. Graphene oksida dikurangkan dengan menggunakan phytoextracts dari kulit pisang pada suhu bilik dan suhu refluks. Pengoptimuman pengurangan phytoextracts dilakukan dengan mengubah penumpuan phytoextracts, masa dan suhu pengurangan. Graphene oksida dan graphene telah dicirikan dengan menggunakan spektrofotometer Ultraviolet-Visible (UV - Vis) , Fourier Transform Infrared spectroscopy (FTIR), Mikroskopi Elektron Imbasan (SEM) dan analisis voltammetry kitaran (CV) untuk menghasilkan dan menggunakan sensor glukosa . Hasil UV-Vis untuk graphene oksida menunjukkan satu puncak pada jarak 230 nm dan beralih kepada 270 nm untuk graphene oksida (PRGO) . Grafit oksida (GO) dalam kajian FTIR menunjukkan band sengit pada 1623 cm^{-1} (C = O) , 1053 cm^{-1} (CO), dan jalur luas sekitar 3332 cm^{-1} untuk kumpulan hidroksil. PRGO menunjukkan band pada 3332 cm^{-1}, tetapi tidak menghilangkan puncak pada 1623 cm^{-1} dan 1053 cm^{-1}. PRGO juga mempamerkan larutan setanding dengan konvensional graphene dan dalam aplikasi sensor glukosa , PRGO dapat mengesan kepekatan glukosa 0.1 mM dengan menggunakan elektrod karbon berkaca (GCE) pada kadar imbasan 50 mVs^{-1}.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

ALET	Atomic layer etching
CVD	Chemical vapour deposition
ErGO/GCE	Reduced graphene oxide modified/glassy carbon electrode
FAS	Formamidinesulfinic acid
GCE/RGO-GOx	Glassy carbon electrode/reduced graphene oxide-glucose oxidase
GO	Graphene oxide
GOD/Pt/chitosan	Glucose oxidasa/platinum/functional graphene sheets/chitosan
HRGO	Hydrazine reduced graphene oxide
RGO	Reduced graphene oxide
NADPH	Nicotinamide adenine dinucleotide phosphate
PANNI	Poly (N-acetylaniline)
PRGO	Phytoextract reduced graphene oxide
QHE	Quantum Hall effect
RT	Room temperature
RZB	Rizatriptan benzoate
TP	Tea polyphenol

1 INTRODUCTION

1.1 Background

Graphene is one of the hottest materials in the scientific community due to its unique properties such as structure, electrical conductivity, mechanical and catalytic properties (Thakur & Karak, 2012). Graphene can be synthesized from raw material which is graphite flakes. Natural graphite flakes exists in polycrystalline forms of carbon comprising layered planes containing hexagonal arrays of carbon atoms to form an atomically flat stacked material in three dimensional (Sadasivuni *et at.*, 2014). Thin sheets with large surface area of graphite oxide can be produced when the multi-layered graphite is exfoliated. The resulting graphite oxide which is further exfoliated will form graphene sheets that has extraordinary electrical conductivity. It can be defined as a flat monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice, which is a basic building block for graphitic materials of all other dimensionalities (Geng *et al.*, 2009). These superior properties have guaranteed the applications of graphene in fields such as nanoelectronics, electrochemical sensors, (Teradal *et al.*, 2014) and elastomers composites (Sadasivuni *et al.*, 2013).

The synthesis of good quality monolayer graphene has became one of the prominent research topic recently. There are several synthesis routes for the production of graphene which are exfoliation of graphite (Wang *et al.*, 2009), chemical vapor deposition (Wu *et al*., 2010; Liu *et al.*, 2014) and chemical solution method (Jin *et al.*,2012). Among the synthesis routes for graphene, chemical oxidation of graphite to graphene oxide (GO) and subsequent reduction to graphene by using strong reducing agent is the most common and preferred method due to its simple, cost effective, high efficiency, high yield of graphene, and its ability to hybridize graphene with other materials such as polymers, organic molecules and metal oxides (Dinh *et al.*, 2013). Graphene oxide reduction usually is completed by adding hydrazine or dimethylhydrazine, which is highly toxic and may introduce impurities to the reduced graphene oxide (RGO). Hence, this chemically reduction of graphene oxide require great care bacause the reaction will give harmful effect to the environment (Wang *et al.*, 2013).

Due to the harmful effects to the environment brought by hydrazine, green reduction of graphene oxide becomes an alternative to synthesize graphene nanosheets. From previous study, wild carrot root (Kuila *et al.*, 2011), tea solution (Akhavan *et al.*, 2012) and reducing sugars (Zhu *et al.*, 2010) had been used to reduce graphene oxide and in this study, the phytoetracts from banana peels act as the green reducing agent to reduce the graphene oxide to graphene. Banana peel is rich in phytochemical compounds, mainly antioxidants. Banana peels also contain other compounds such as anthocyanins delphinidin, cyanidin, carotenoids like β-carotenes and α-carotene. (Montelongo *et al.*, 2009). The high level of phytochemicals in banana peels have sufficient potential to reduce the graphene oxide and the RGO produced is characterized by different analytical and spectroscopic techniques.

1.2 Motivation

Graphene, the carbon allotrope, is as versatile as any material discovered on Earth. Its amazing properties as the lightest and strongest material, compared with its ability to conduct heat and electricity better than anything else, mean that it can be integrated into a huge number of applications. Recently, a group of researchers from Nanjing University had studied the properties of graphene and their work had shown that moving a single drop of sea water on the monolayer graphene can generate electricity under pressure gradient. This research can be the key for the future electricity generation in large scale for domestic usage. The application of graphene not just limited to electricity generation, monolayer graphene also able to act as glucose biosensor to detect blood glucose level. The bionanocomposite film consisting of glucose oxidase/platinum/functional graphene sheets/chitosan (GOD/Pt/chitosan) for glucose sensing was able to detect 0.6 μM glucose (Wu *et al.*, 2009). These great applications of graphene have made it as an important material in the science and engineering society.

In the production of monolayer graphene, hydrazine is one of the common reducing agents to chemically reduce graphene oxide (Dinh *et al.*, 2014), where this chemically reduction method is not environmental friendly and will bring effects to the environments and living organisms. More care is needed while carrying out the chemically reduction process of graphene oxide.

Hence, the main motivation for this study is to abort the usage of hydrazine in the conventional method and produce environmental friendly graphene monolayer by using green reductant that is the phytoextracts from banana peels. Banana peel is a household and industrial food waste discarded in large quantities in nature. It contains high level of antioxidant activity and it is an ideal reducing agent to reduce graphene oxide (Rebello *et al.*, 2014). By the end of this study, graphene will be synthesized by using phytoextracts from banana peels and the optimum concentration of phytoextracts to reduce graphene oxide under room temperature and refluxed conditions. In addition, the RGO reduced by phytoextracts also has been used to fabricate glucose sensor and the electrocatalytic properties of the biosensor is studied by using cyclic voltammetry.

1.3 Problem statement

Synthesis of graphene through chemically reduced process usually involved toxic materials such as hydrazine (Dinh *et al.*, 2013; Wang *et al.*, 2013) that will bring detrimental effects to the environments and living organisms. Therefore, reducing the toxicity in reduced graphene oxide is a limiting factor in large scale production. Even though previous researches had shown that urea and other sulphur compounds (Su *et al.*, 2014) were used as the reducing agents; when the compounds were employed, the reduction process was limited the bulk production of graphene. Therefore, an alternative solution for this is to reduce graphene oxide by green reduction, that is by employing environmental friendly reducing agents such as wild carrot root (Kuila *et al.*, 2011) and tea solution (Akhavan *et al.*, 2012). Recently, there were few researches focus on green synthesis of graphene, however, most of the green reductant used was from expensive element and food source such as starch based material and rose water.

Hence, for this study, the green reductant that was used to overcome the toxicity of graphene from chemical reduction process was the phytoextracts from banana peels. This study applies a green approach for the reduction of graphene oxide by using readily available non-edible or waste part of plant products. The reducing agent for the reduction process must contains high level of antioxidants which has high tendency to get oxidized and these requirements can be full filled by phytoextracts in banana peel. Phytoextracts are phenolic compounds that can be found in leaves and fruit peels. (Thakur & Karak, 2012). The phenolic contents can be found abundantly in banana peels which is far more higher than other fruits such as blackberry (Jacques *et al.*,2010), blueberry (Moraes *et al.*, 2007) and grapes (Yang *et al.*, 2009).

1.4 Objectives

The following are the objectives of this research:

1. To determine the concentration of phenolic compounds in the phytoextracts from green and yellow banana peels by using Folin-Ciocalteu reagent.
2. To optimize the reduction of graphene oxide by phytoextract under different concentrations, reduction time and reduction temperature.
3. To fabricate glucose sensor by using reduced graphene oxide and glucose oxidase (RGO-GOx).

1.5 Scope of this research

To achieve the objectives for this research, six scopes have been identified:

i. Quantification of phytoextracts in banana peels.

   The concentration of phenolic compounds can be quantify or determine by using Folin-Ciocalteu reagent. Folin-Ciocalteu calorimetry is based on the chemical reduction of the reagent and it will have a blue absorption with a maximum at 765 nm. The intensity of the light absorption at that wave length is proportional to the concentration of phenols. By using standard gallic acid calibration curve, the measurement was made based on the concentration of phenolic content in gallic acid total equivalence using unit's mg/g (GAE) (Narender *et al.*,2012).

ii. Fabrication graphene oxide.

   Fabrication of graphene oxide was done through the combination of Hummer and Hummer Improved method, by using graphite powder as raw material. This method was modified by adding the pre-oxidation stage before oxidation by using potassium permanganate, $KMnO_4$.

iii. Reduction of graphene oxide by phytoextracts in green and yellow banana peels.

The effect of phytoextract on the reduction of graphene oxide to graphene was observed. This was done by following previous study on the reduction by aqueous extract of orange peel (*Citrus sinensis*) and leaf extracts of *Colocasia esculenta* and *Mesua ferra Linn* (Thakur & Karak, 2012)

iv. Optimization of reduction of graphene oxide by phytoextract.

Different concentrations of aqueous phytoextracts obtain from banana peels, reduction time and reduction temperature were used to study the effects of reduction on graphene oxide in order to determine the optimum the reduction process by phytoextract.

v. Examination of structural characteristics of reduced graphene.

This study was conducted to identify the structural characteristics of graphene reduced by phytoextracts. Several equipments were used for the characterization such as ultraviolet visible spectroscopy (UV-Vis), Fourier transform infrared (FTIR) and Scanning Electron Microscopy (SEM).

vi. Fabrication of glucose biosensor.

Glucose oxidase (GOx) was immobilized on reduced graphene oxide (RGO) in a single step without any cross linking agents or modifiers. The electrocatalytic application of glucose biosensor was examined by using cyclic voltammetry (CV).

2 LITERATURE REVIEW

2.1 *Graphene*

2.1.1 *Properties of graphene*

Graphene is a single atomic layer of graphite; an abundant mineral which is an allotrope of carbon that is made up of very tightly bonded carbon atoms organized into a hexagonal lattice (Geim & Nocoselov, 2007). Graphene is unique in terms of its sp^2 hybridization (Kumar *et al.*, 2013) and has very thin atomic thickness which is range from 3 to 100 nm (Prolongo *et al.*, 2014). After suspended graphene sheets were studied by transmission electron microscopy, scientists believed that graphene can be isolated is due to the fact that the carbon to carbon bonds in graphene are so small and strong that they prevent thermal fluctuations from destabilizing it. Figure 2.1 shows the structures of graphene in different forms.

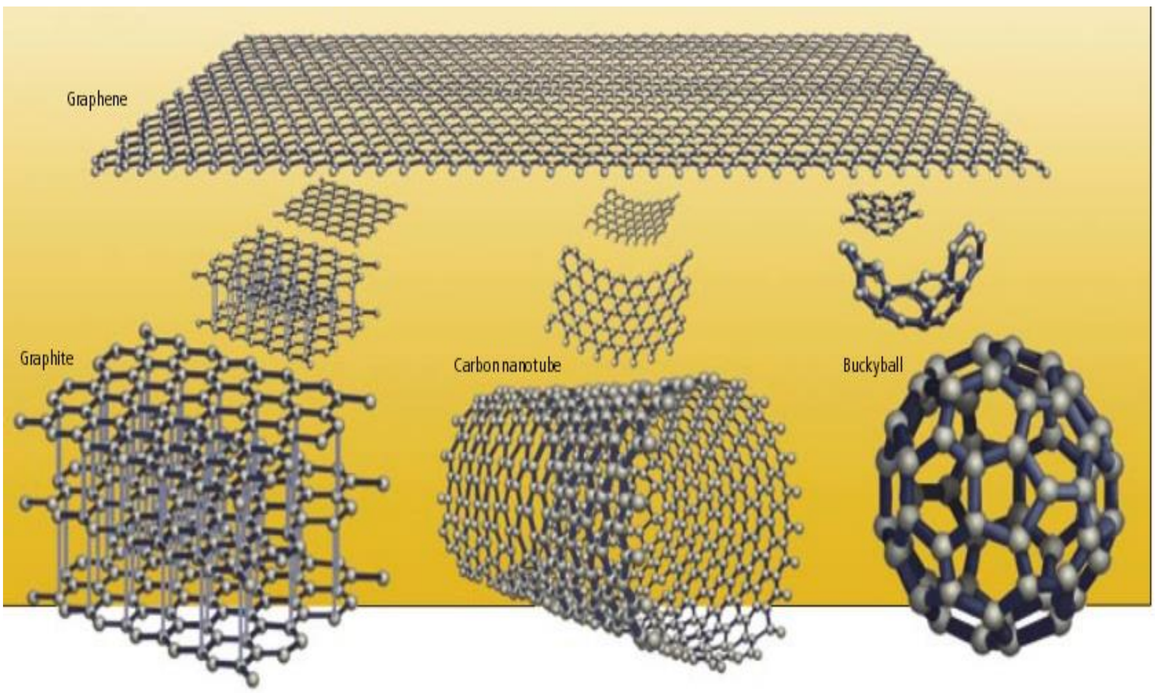

Figure 2.1: Structures of graphene (Geim & Nocoselov, 2007)

Based in Figure 2.1, graphene can be wrapped up into 0D, which is the fullerene. They include honeycombed cylinders called carbon nanotubes and soccer ball-shaped molecules known as bucky balls.

Although just one atom thick, graphene possesses outstanding electronics, mechanical, optical, thermal and chemical properties. One of the hottest areas of graphene research is the focus of intrinsic electronic properties, where how electrons are flowed through the graphene monolayer sheet under the influence of various external forces. Graphene is a good conductor, electrons are able to flow through graphene more easily than on copper. The speed of electrons flowing through graphene monolayer sheet is one hundredth of the speed of light. It has high intrinsic mobility of 15000 $cm^2/V.s$ at room temperature (Geim & Nocoselov, 2007). When limiting the properties of electrons into two dimensions, graphene exhibits interesting properties such as “Quantum Hall Effect” (QHE) and “Klein paradox.” QHE is a quantum mechanical version of Hall effect. Hall effect is the production of a voltage difference across an electrical conductor, which will then transverse into electric current and magnetic field. At most quantum phenomena, QHE always associated with low temperature (< 4 K) and strong magnetic fields. QHE in graphene with above 30 T magnetic fields can be observed at room temperature (Jiang *et al.*, 2007). Beside QHE, spin Hall effect also can be determined in AA-stacked bilayer graphene (Dyrdal & Barnas, 2014). The Klein paradox has never been observed in laboratory experiments due to the requirement of high electric field, 10^{16} Vcm^{-1}. However, this phenomenon is able to be observed by using graphene, which was sufficiently to check experimentally for Klein tunneling (Sanudo & Lopez-Ruiz, 2014) where it can generate electric field of 10^5 Vcm^{-1} (Novoselov *et al.*, 2004).

On the other hand, graphene can serve as a perfect thermal conductor. Its thermal conductivity was measured recently at room temperature and it was much higher than the value observed in all other carbon structures as graphite or diamond. The thermal conductivity for graphene with length and width of 3.6 μm and 5.52 μm respectively was more than 2000 W/mK (Yoon *et al.*, 2014). The thermal conductivity of graphene was isotropic, which mean it was same in all directions. Thermal conductivity study always relates with phonon, a phenomemon where the atoms or molecules in condensed matter with elastic arrangement in collective excitation in a period. In the study by Sadeghi and co workers (2012), the thermal conductivity in graphene was dominated by the contribution from phonons. For suspended single layer graphene, the thermal conductivity measured at room temperature was ranged from 1500 to 5800 W/mK, where it was five times higher than graphite which was around 1000 W/mK.

The mechanical properties was another interesting properties of graphene where scientists were paying much attention on it, by applying a technique called Atomic Force Microscopy (AFM), to measure the mechanical strength of graphene monolayer. In graphene oxide, with thickness of 50-60 nm, was found to have a Young's modulus of 695-697 GPa (Kang *et al.*, 2013). It was found that graphene is harder than diamond and even steel where the tensile stength can exceeds 1 TPa. Even though graphene was so robust, it can be very elastic and stretchable too. It is expected that graphene with strong mechanical properties is able to make a significant contribution in super strong composite materials.

In terms of optical properties for graphene, it is the thinnest material ever made, but still visible to the naked eyes. This is due to its optical properties, where it is able to absorb 2.3% (Apell *et al.*, 2010) of light that passes through it. To enhance the visibility of graphene, scientists have deposited the graphene layer to the silicon wafers which have a thin layer of silicon dioxide. They found that graphene was much more visible in reflection than in transmission with a layer of oxide surface. (Abergel *et al.*, 2007). Figure 2.2 shows the color frequency depend on the visibility of graphene on an silicon slab with oxide layer and silicon carbide slab and Table 2.1 shows the summary for the properties of graphene.

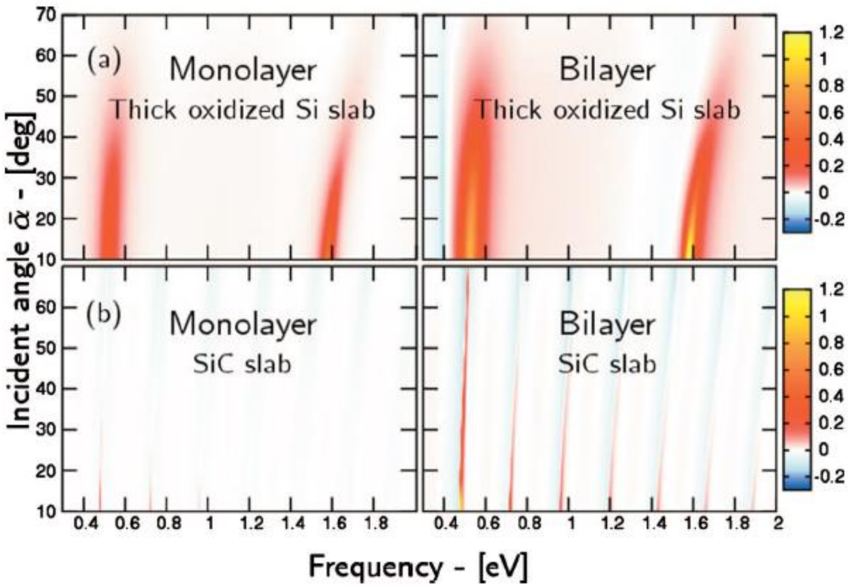

Figure 2.2: Frequency dependence of visibility of graphene on (a) an infinite silicon slab with a thin oxide layer of width 300 nm, and (b) a silicon carbide slab of width 1 m

Table 2.1: Summary for the properties of graphene

Graphene Properties	Notes	References
Structure	Single atomic layer of graphite which is arranged into hexagonal lattice.	Geim & Nocoselov, 2007
	Graphene is sp^2 hybridization.	Kumar *et al.*, 2013
	Consist of a very thin monolayer of graphene, the thickness is range from 3 to 100 nm.	Prolongo *et al.*, 2014
Electronic	High intrinsic mobility of15000 $cm^2/V.s$ at room temperature.	Geim & Nocoselov, 2007
	Exhibit QHE and Klein paradox.	Jiang *et al.*, 2007, Sanudo & Lopez-Ruiz, 2014
Thermal conductivity	Graphene with length and width of 3.6 μm and 5.52 μm respectively is more than 2000 W/mK.	Yoon *et al.*, 2014
	suspended single layer graphene thermal conductivity measured at room temperature is range from 1500-5800 W/mK.	Sadeghi *et al.*, 2012
Mechanical	In graphene oxide, with thickness is 50-60 nm, was found to have a Young's modulus of 695-697 GPa.	Kang *et al.*, 2013.
Optical	Graphene is able to absorb 2.3% of light that passes through it.	Apell *et al.* , 2010
	Graphene is much more visible in reflection than transmission with a layer of oxide surface.	Abergel *et al.*, 2007

2.1.2 Applications of graphene

One of the most useful properties of graphene is that it is a zero-overlap semimetal with very high electrical conductivity. Carbon atoms have a total of six electrons; two in the inner shell and four in the outer shell. The four outer shell electrons in an individual carbon atom are available for chemical bonding, but in graphene, each atom is connected to three other carbon atoms on the two dimensional plane, leaving one electron freely available in the third dimension for electronic conduction. These highly-mobile electrons are called pi (π) electrons and are located above and below the graphene sheet (Kuila *et al.*, 2012). These pi orbitals overlap and help to enhance the carbon to carbon bonds in graphene. Fundamentally, the electronic properties of graphene are dictated by the bonding and anti-bonding of these pi orbitals (Gogotsi, 2012).

Researchers have shown that the electronic mobility of graphene is very high, with previously reported results above 15,000 $cm^2 \cdot V^{-1} s^{-1}$ and theoretically potential limits of 200,000 $cm^2 \cdot V^{-1} s^{-1}$ (Geim & Nocoselov, 2007) . These superior properties enable graphene to be applied in touch panels, flexible thin film, solar cell and etc. (Kuila *et al.*, 2012; Thakur & Karak, 2012).

Graphene has the possibility to fabricate into a full graphene device due to its high optical properties, as it can absorb 2.3% of the light passing through it (Apell *et al.*, 2010). A full graphene device fabrication was studied by Lim and co workers, (2012), by utilizing atomic layer etching (ALET) technology, where oxygen radical adsorption occcurs and followed by removal of the oxygen chemisored on carbon, and this can increase the transmittance of graphene by 2.3% after one ALET cycle (Lim *et al.*, 2012).

Graphene is known for its strong and stiff properties over other materials, and these properties enable itself to be mixed with other material such as epoxy to produce composites which have good specific physical properties. The graphene-plastic composites make the plastics conductive as well. Besides, study had shown that Poly (N-acetylaniline) (PAANI) can be successfully electrodeposited on the surface of graphene. The composites exhibit good electrochemical properties, with enhanced maximum capasitance of 1126 F/g which is greatly higher than the single material PANNI (365 F/g) and graphene (301 F/g) (Li *et al.*, 2014). Therefore, PANNI/graphene composites can serve as a good supercapasitor with high capasitance ability. Besides PANNI, other materials such as activated carbon (Zheng *et al.*, 2014) and iron (II) oxide (Zhao *et al.*, 2014) had been used to hydrothermally deposited on graphene layer to produce electrode materials for supercapasitors.

Graphene with its good electrical and thermal conductivity properties made it an good sensor for various compounds or molecules. A sensor with graphene sheet as the base can be fabricated using different materials. For example, a reduced graphene oxide modified glassy carbon electrode (ErGO/GCE) can be fabricated as a sensor to detect an antimigraine drug, rizatriptan benzoate (RZB). This sensor has a detection limit of 0.0571 μM of RZB (Teradal *et al.*, 2014). The ErGO/GCE sensor has shown high sensitivity, selectivity and remarkable reproducibility for electrochemical response of RZB. Another example is the hygrogen sensor by using graphene/zinc oxide nanocomposite. The graphene/ZnO was fabricated by in situ reduction of zinc acetate and graphene oxide and the sensing result shows that 1.2 wt% graphene/ZnO composite give the best result for the detection of 200 ppm hydrogen at 150 ^{o}C. (Anand *et al.*, 2014). Table 2.2 below shows other examples of sensors by using graphene sheet.

Table 2.2: Examples of graphene sensors

Sensors	Detection	Detection Limit	References
Graphene-$ZnFe_2O_4$	Acetone gas	0.125% G- $ZnFe_2O_4$ (180^{o}C, 10 h)-10 ppm acetone vapor	Liu *et al.*, 2013
Graphene/CuO (non-enzymatic)	Glucose	0.09 μM L^{-1} of glucose.	Alizadeh & Mirzagholipur, 2014
Graphene/flexible acetate sheet	*Escherichia coli*	Sensitivity of 60% is achieved for E.*coli* concentration of 4.5 x 10^7 cfu/ml.	Basu *et al.*, 2014
Gold nanoparticles-graphene-chitosan	Hygrogen peroxide	Concentration range of 5.0 μM to 35 nM with detection limit of 1.6 μM.	Jia *et al.*, 2014

In terms of how far alone the true properties of graphene, this is just the tip of the iceberg. Before graphene is heavily integrated into the areas more time need to be spent in order to understand just what makes it such an amazing material.

2.1.3 Stability of Graphene

Reduced graphene oxide can be obtained by removing the functional groups in graphene oxide through chemical reduction. However, the reduced graphene oxide tends to clump together, due to the weak van der Waals forces caused by the functional groups have been removed (Stankovich *et al.* , 2006). The weak force will create a repulsion between the layers of graphene oxide; when it is reduced, the RGO formed tends to agglomerate, and therefore cannot dispersed properly in water or solvent. Hence, it is quite challenging in maintaining and producing RGO with excellent stability. From previous research from Li *et al.*, (2008), to achieve optimum dispersion of RGO in water, the weight ratio of hydrazine to GO was determined at 7:10. An increase in the concentration of hydrazine will decrease the stability of the dispersion for RGO. Therefore, excess hydrazine must be immediately removed after reduction.

For RGO that was reduced by hydrothermal reduction, the RGO suspensions can be obtained in water at conditions of GO concentration less than 0.3 mg/mL, with heating time between 2 to 6 hours, and heating temperature higher than 160 ^{o}C. The results have further confirmed that the suspensions thus obtained under these conditions mentioned above contained RGO sheets (Ding *et al.*, 2012).

The dispersion behaviour of GO and RGO also has been studied by using DI water and different organic solvents such as acetone, methanol, ethylene gylcol, N,N-dimethylformamide (DMF),N-methyl-2-pyrrolidone (NMP), toluene, chloroform and others. The GO and RGO suspensions were sonicated for 1 hour and centrifuged at 500 rpm to remove any aggregates and left for two weeks. The result has shown that NMP, ethylene glycol and DI water presented a significant long-term stability for GO and RGO after two weeks compared to other organic solvents (Konios *et al.* , 2014).

2.2 Synthesis of graphene

2.2.1 Exfoliation

Exfoliation of graphene can be classified into two different techniques, which are the cleavage or “scotch tape method” and the directly “grow” the graphene layer on a substrate surface.

Exfoliation of graphene is also called as cleavage. This method uses scotch tape to split the graphene and therefore this method also called ‘scotch tape’ method. The adhesive tape is used to split the graphite crystal and multilayer graphene will be attached on the tape. This technique requires multiple exfoliation steps, until only one layer of graphene is left. The graphene flakes are deposited on a silicon wafer after exfoliation using “dry deposition” method (Geim & Nocoselov, 2007). Even though this method shows low level of complexity, however, this method is limited to bulk production due to the reason of lack of controllability and labour intensive (Sun *et al.*, 2011).

To produce graphene in large scale, the simplest method is by dispersing graphite into organic solvent with nearly same surface energy as graphite so that the energy barrier can be reduced and detached from graphite crystals to form the graphene. The solution is then ultrasonicated for several hundred hours. This method allows the production of graphene in large quantities, but the size of the graphene formed is relatively small.

2.2.2 Epitaxial growth

Epitaxial growth refers to the production of graphene by heating and cooling down on electrical insulating surfaces such as silicon carbide. Single or bilayer of graphene will form on the Si face of crystal, while few layers of graphene grow on C face. The result of the graphene formation is depended on temperature, pressure and heating rate. If temperature and pressure are too high, it will lead to formation of graphene nanotubes.

2.2.3 *Chemical Vapour Deposition (CVD)*

Chemical vapour deposition (CVD) is a method where graphite is exposed to gaseous compounds such as hydrogen gas. The compounds decomposed on the surface to grow a thin film and the by-products will evaporate. The most common way is by exposing graphite to nickels film with methane gas at temperature of 1000^{o}C (Allen *et al.*, 2010). Under this condition, methane gas will decompose and carbon will diffuse into the nickel film. After cooling, a layer of graphene will grow on the surface.

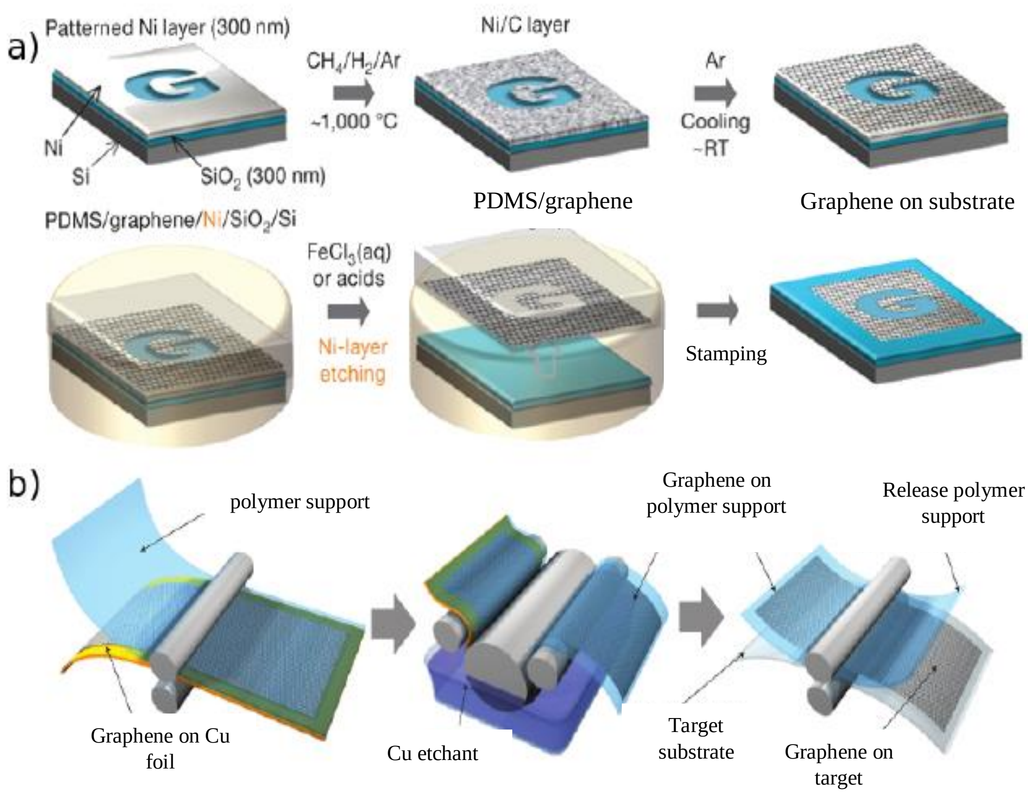

Figure 2.3: (a) Scheme of preparation of graphene by CVD and transfer via polymer support. The carbon solves into the Ni during the CVD and forms graphene on the surface after cooling. With a polymer support the graphene can be stamped onto another substrate, after etching of the Ni layer. (b) Roll-to-roll process of graphene films grown on copper foils and transferred on a target substrate. (Allen *et al.*, 2010).

2.2.4 *Chemical solution method*

Another approach to synthesize graphene is by chemical solution method. This method uses graphite powder as the raw material, and undergoes oxidation by strong oxidizing agents such as sulphuric acid in a water free condition to form graphite oxide. This method is called the “Hummer’s method” (Hummers & Offeman, 1958) and it is modified into “Hummer’s method and improved method” (Marcano, et al., 2010). In the improved method, a pre-oxidation stage is added by using oxidizing agent such as potassium permanganate.

For the synthesis of graphene, there are generally three methods to reduce graphene oxide which are electrochemical, thermal and chemical. By using these methods, graphene can be synthesized in large quantities.

Thermal reduction is a green method to reduce graphene oxide where no hazardous reductants are used but this process requires a rapid heating, which is usually more than 2000 ^{o}C/min in an oven under argon gas or up to 800 ^{o}C under the existing of hydrogen gas. However, rapid reduction of graphene oxide under mild or low temperature conditions is yet a challenge to achieve. Hence, to improved this method so that reduction can occur faster and under mild temperature, the process is assisted by using microwaves in a mixed solution of N,N-dimethylacetamide and water (DMA_C/H_2O). The mixed solution works as both a solvent for the produced graphene and a medium to control the temperature of the reactive system up to 165 ^{o}C (Chen *et al.*, 2011). The yield of graphene by using this method is very high and it is easily achieved without high temperature condition.