

**SYNTHESIS OF LARGE AREA GRAPHENE AND
GRAPHENE FLAKE VIA CHEMICAL VAPOR
DEPOSITION USING COPPER CATALYST AND
METHANE**

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METHANE**

by

MOHD KHAIRUL NIZAM BIN MOHD ZUHAN

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LIST OF ABBREVIATIONS

μm	micron
APCVD	Atmospheric pressure chemical vapour deposition
APS	Ammonium persulfate
Ar	Argon
C	Carbon
CH ₄	Methane
Cu	Copper
Cu/MgO	Copper supported on MgO
CuO	Copper oxide
CVD	Chemical vapour deposition
EDS	Energy dispersive X-ray spectroscopy
eV	Electron volt
Fe	Iron
GNP	Graphene nanoplatelet
GO	Graphene oxide
H ₂	Hydrogen gas
HOPG	Highly oriented pyrolytic graphite
HRTEM	High resolution transmission electron microscope
In	Indium
ITO	Indium Tin Oxide
LAG	Large area graphene
M	Molar
meV	Mili-electron volt
min	Minute

mL	Mililiter
N ₂	Nitrogen gas
Ni	Nickel
nm	Nanometre
O ₂	Oxygen gas
PECVD	Plasma enhanced or plasma assisted CVD
PMMA	Poly(methyl methacrylate)
rGO	Reduced graphene oxide
SAED	Selected area electron diffraction
sccm	Standard cubic centimetre
SEM	Scanning electron microscope
SiC	Silicon carbide
Si/SiO ₂	Silicon oxide on silicon wafer
TGA	Thermogravimetric analysis
UV	Ultra-violet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

%	Percent
°	Degree
°C	Degree Celsius
λ	wavelength
Ω/\square	Ohm per square
Å	Angstrom

**SINTESIS GRAFIN BERLEMBARAN LUAS DAN GRAFIN SERPIH
MELALUI KAEDAH PEMENDAPAN WAP KIMIA MENGGUNAKAN
PEMANGKIN KUPRUM DAN METANA**

ABSTRAK

Grafen adalah karbon dua dimensi yang tersusun dalam struktur *honeycomb* heksagon dan merupakan lapisan asas bagi grafit. Grafen memiliki pelbagai ciri-ciri fizikal yang menarik seperti amat konduktif dan lutsinar. Kajian grafen dijangka menyumbang ke arah kemajuan elektronik, sel solar, komposit, dan sektor perubatan. Dalam kajian ini, pependapan wap kimia atmosfera (APCVD) digunakan sebagai kaedah sistesis. Metana telah digunakan sebagai bahan mentah karbon, nitrogen sebagai gas pembawa dan hidrogen sebagai agen pengurangan dan telah digunakan untuk mensintesis dua jenis grafen iaitu grafen berlembaran luas (saiz sisi $> 1 \text{ cm}^2$) dan grafen serpih (saiz sisi $< 1 \text{ }\mu\text{m}^2$) dengan menggunakan pemangkin Cu. Kajian ini juga memberi tumpuan kepada menyelesaikan kecenderungan polihabluran grafen berlembaran luas yang besar daripada terpecah kepada serpihan kecil semasa proses pemindahan basah yang dilalukan melalui proses punaran basah dengan mengurangkan ketegangan permukaan antara muka grafen / air dengan menggunakan n-heptana sebagai sokongan serta mengelakkan pencemaran polimer pada permukaan grafen. Kaedah yang dicadangkan lebih mudah dan lebih mesra alam kerana amalan itu mengurangkan penggunaan banyak pelarut organik untuk menanggalkan lapisan polimer kerana proses ini menghasilkan banyak bahan buangan kimia. N-heptana sebagai bahan sokongan untuk proses punaran basah lebih mudah dikendalikan, menghasilkan kurang sisa dan tidak menyebabkan pencemaran yang ketara pada grafen, boleh digunakan semula untuk pemindahan grafen seterusnya dan menghasilkan kurang sisa toksik berbanding

penggunaan sokongan polimer. Di samping itu, kaedah punaran basah memerlukan penggunaan bahan punar dan menghasilkan sisa buangan mengandungi logam yang biasanya dilupuskan dalam penggunaan tunggal. Amalan ini mengehendkan penggunaan substrat logam dan berbahaya kepada alam sekitar. Oleh itu, pemulihan logam daripada sisa buangan ini yang boleh digunakan sebagai pendahulu kepada pemangkin baru bagi sintesis grafen yang serpih adalah disarankan. Kajian ini menggunakan kadar aliran gas 30 sccm dan 50 sccm CH_4 dengan masa tindak balas ditetapkan selama 30 minit dan 60 minit dengan suhu pertumbuhan ditetapkan 950°C untuk sintesis grafen berlembaran luas. Sembilan kerajang logam digunakan di tiga lokasi zon di dalam relau berbentuk tiub mendatar. Disamping itu, kesan kadar alir H_2 terhadap kualiti kristal grafen yang ditetapkan pada 0, 25, 50, 75, 100, 125 dan 150 sccm juga dikaji. Selepas itu, pemindahan grafen dari foil Cu ke Si / SiO_2 dilakukan dengan menggunakan 0.1 mol larutan ammonium persulfate sebagai larutan punar dan n-heptana sebagai lapisan sokongan. Seterusnya, kerajang Cu terukir dipulihkan dan digunakan semula dengan suhu rawatan haba 800°C selama 3 jam untuk mendapatkan CuO untuk sintesis grafen serpih. Dua formulasi 10% MgO dengan 90% CuO dan 1% MgO dengan 99% CuO yang diserak dalam etanol dan disimpan semalaman dalam oven pada 60°C sebelum menjalani proses pengkalsinan pada 950°C untuk menghasilkan CuO / MgO yang digunakan bagi sintesis grafen serpih. Sintesis grafen serpih dilakukan pada 950°C selama 60 minit dengan 10 sccm CH_4 . Analisis gravimetrik haba (TGA), pembelauan sinar-x (XRD), pendarflour sinar-x (XRF), pengimejan optik, Raman spektroskopi (titik tunggal dan pemetaan), mikroskop elektron penghantaran resolusi tinggi (HRTEM), pelepasan bidang mikroskop elektron imbasan (FESEM), dan spektroskopi foto-elektron sinar-x (XPS) telah digunakan untuk menilai sifat-sifat grafen yang disintesis dan, CuO / MgO.

Hasilnya menunjukkan grafen berlembaran luas dan grafen serpih telah berjaya disintesis menggunakan kerajang Cu dan Cu terpulih, kedudukan Cu memperlihatkan mutu grafen yang berbeza dan kadar aliran hidrogen dengan 50 hingga 100 sccm menunjukkan kesan positif pada pembentukan grafen dan kesan negatif apabila tiada (0 sccm), kekurangan (25 sccm) atau berlebihan (>125 sccm) kadar aliran hidrogen dibekalkan. Lokasi pemangkin di zon 1 dan zon 2 menunjukkan pembentukan struktur grafit crystallinity yang baik manakala di zon 3 pembentukan karbon amorfus lebih dominan. N-heptana didapati sebagai bahan yang sesuai untuk pemindahan grafen berlembaran luas dengan mengurangkan pencemaran pada permukaan grafen. Cu daripada sisa larutan punaran boleh digunakan semula untuk pembentukan CuO dan sintesis grafen serpih menggunakan kaedah yang sama bagi sintesis grafen berlembaran luas. Kesimpulannya, lokasi pemangkin dalam relau mendatar dan kadar aliran hidrogen memainkan peranan penting dalam pembentukan grafen. Kaedah pemindahan menggunakan n-heptana sebagai lapisan sokongan membantu dalam proses pemindahan grafen dengan mengurangkan pencemaran dan kerosakan pada struktur grafen. Disamping itu grafen serpih telah berjaya disintesis menggunakan pemangkin CuO/MgO yang disintesis dari Cu yang digunakan semula.

SYNTHESIS OF LARGE AREA GRAPHENE AND GRAPHENE FLAKE VIA CHEMICAL VAPOUR DEPOSITION USING COPPER CATALYST AND METHANE

ABSTRACT

Graphene is a two-dimensional material arranged in hexagonal honeycomb structures and is a single layer of graphite. Several fascinating properties of graphene such as a very conductive and highly transparent material is expected to contribute significantly towards the advancement of electronics, solar cell, composites, and medical sector. In this study, atmospheric chemical vapour deposition (APCVD) was used as synthesis method. Methane was used as carbon feedstock, nitrogen as a carrier gas and hydrogen as reducing agent for two types of graphene synthesis which is large area graphene (lateral size $>1 \text{ cm}^2$) and graphene flakes (lateral size $<1 \text{ }\mu\text{m}^2$) with Cu was used as a catalyst. The study is also focusing on solving the tendency of polycrystalline large area graphene from breaking into small fragments during the transfer process via wet etching by reducing the surface tension of graphene/water interface using n-heptane as support and avoiding polymer contamination on the graphene. The proposed method is easier and more environmentally friendly as the practice reduce the use copious amount of organic solvent to remove the polymer layer as the process often creates plentiful of chemical waste. N-heptane as support material for wet etching process is easier to conduct, generated less waste and does not cause significant contamination on the graphene and can be reused for another graphene transfer and create less toxic waste as compared by using polymer support. In addition, a wet etching method requires the use of an etchant and the process produce wastes contain metal that generally disposed of in single-use. The practice limits the use of the metal substrate and harmful to the environmentally. Hence, recovery of the metal

from the waste as a precursor to a new form of catalyst for graphene flake synthesis is suggested. The study utilised 30 sccm and 50 sccm of CH₄ gases flow-rate with reaction time were set for 30 min and 60 min with growth temperature was set at 950 °C for large area graphene synthesis. Nine metal foils were used in three zones locations inside the horizontal tubular furnace. Furthermore, the effect of H₂ flow rate on graphene crystallinity which was set at 0, 25, 50, 75, 100, 125 and 150 sccm was also studied. Subsequently, graphene transfer from Cu foil onto Si/SiO₂ was performed using 0.1 mol ammonium persulfate solution as an etching solution and n-heptane as supporting layer. Next, the etched Cu foil was recovered and reused by heat treatment temperature of 800 °C for 3 hours to obtain CuO for graphene flakes synthesis. Two formulations of 10% MgO with 90% CuO and 1% MgO with 99% CuO were dispersed in ethanol and was kept overnight in an oven at 60 °C before undergoing calcination process at 950 °C to produce CuO/MgO that was used for graphene flake synthesis. The graphene flakes synthesis was conducted at 950 °C for 60 min with 10 sccm of CH₄. Thermogravimetric analysis (TGA), X-Ray Diffraction (XRD), X-ray Fluorescence (XRF), optical imaging, Raman spectroscopy (single point and mapping), high-resolution transmission electron microscopy (HRTEM), Field emission scanning electron microscopy (FESEM), and X-Ray Photoelectron Spectroscopy (XPS) were used to evaluate the properties of the synthesized graphene and CuO/MgO. The result shows large area graphene and graphene flakes were successfully synthesized using Cu foil and recovered Cu, the positions of the Cu shows the different quality of graphene and the hydrogen flow rates shows the quality of the graphene is affected by the hydrogen flow rates with positive effect on graphene formation at 50 to 100 sccm and negative effect when no (0 sccm), inadequate (25 sccm) or excessive (>125 sccm) hydrogen flow rates were supplied. The locations of

the catalyst at zone 1 and zone 2 of the horizontal furnace show good graphitic structure formation while at zone 3 amorphous carbon formation is more dominant. N-heptane is found as a useful material for large area graphene transfer that reduces contamination on graphene surface. Cu from etching solution waste can be reused for CuO formation and graphene flakes synthesis using a similar method for synthesis of large area graphene. In conclusion, the catalyst locations in the horizontal CVD and hydrogen flow rates play an important factor in graphene formation. The transfer method using the n-heptane as support layer assisting in graphene transfer process that reduces contamination and damage to graphene structure. Also, the graphene flakes have been successfully synthesized using the CuO / MgO catalyst obtained from recovered Cu.

CHAPTER ONE

INTRODUCTION

1.1 Nanotechnology and carbon element

Nanotechnology is a cross-disciplinary research field which involves studies and manipulation of nanoscale objects with a dimension of less than 100 nm. The term ‘nanotechnology’ was first used in 1959 when an American physicist, Richard Feynman used this term in his famous lecture ‘There's Plenty of Room at the Bottom’ to describe a technology that enables scientist to manipulate and to control individual atoms and molecules (Feynman, 1960). Years later, commercial production of nanomaterials is still a challenge. At present, nanostructured carbon is one of the nanomaterials used by scientific community mainly for research purposes.

Various properties Properties of nanocarbon were mainly attributed by the ability of carbon to form many faces and shapes is contributed by hybridization ability of its atomic orbitals (Krueger, 2010) that give this element flexibility to form variation of the nanostructured material. Fullerenes, carbon nanotubes, nano-diamonds and graphene are examples of nanostructured carbon material. These nanoscale carbons are especially attractive for researchers due to unusual and exciting properties for practically novel and break-through applications. For example, graphene was observed as a highly flexible material with outstanding mechanical, high optical transparency with 2.3% absorption of incident light over a broad wavelength (up to 97% transparency) , high thermal conductivity, excellent electronics properties, highly conductive and high current density; graphene charge carrier behave as massless relativistic particles or known as Dirac fermions that can be observed even at room

temperature (Neto et al., 2007; Singh et al., 2011). These exceptional properties of graphene have grabbed considerable attention as a next generation material. Furthermore, it was demonstrated that free-standing graphene is chemically inert in ambient condition (Celasco et al., 2017), but in particular condition with surface modification, graphene does involve in reaction (Smerieri et al., 2015). These excellent properties of graphene can be utilised in diverse areas, and high expectation was put on graphene to play a significant role in contributing to new and existing technologies growth. The areas of graphene can directly contribute such as in high-speed electronics and photonics, solar cell, conductive ink, touch screen, composites, electrodes, liquid crystal displays, organic photovoltaic cells and organic light-emitting diodes (OLEDs) (Geim & Novoselov, 2007).

Figure 1.1 presented the structure of the naturally occurring carbon allotropes comprised of graphite, diamond and amorphous carbon and synthetic allotropes comprised of graphene, CNT, and fullerene. Amongst all, graphene is the most attractive material among research communities contributed by its incredibly unique and unusual properties. The selected graphene properties and other carbon allotropes are presented in Table 1.1.

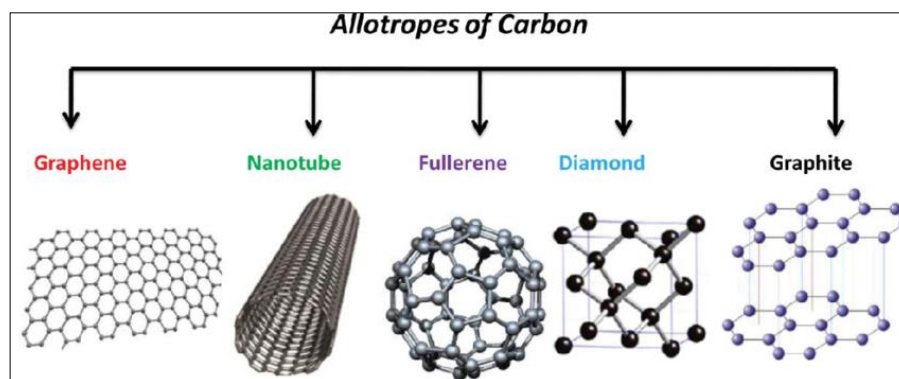


Figure 1.1 Different type of carbon allotropes showing graphene, carbon nanotube, fullerene, diamond and graphite (Tiwari et al., 2016)

Table 1.1: Selected properties of a single layer of pristine graphene, carbon nanotubes and graphite (Azam et al., 2017)

Properties	Graphene	Carbon nanotube	Graphite
Specific surface area, m ² /g	~2630	~2200	~10–20
Thermal conductivity, W/m ·K	4800–5300	3500	1500–2000
Electrical conductivity, S/cm	2000	Structure-dependent	2 to 3 × 10 ⁴
Young's modulus, TPa	~1.0	0.2-1	4.1 × 10 ⁻³ to 8.3 × 10 ⁻³
Fracture strength, GPa	130	11-150	1.2 × 10 ⁻³ to 1.7 × 10 ⁻³

The potential of nanotechnology in Malaysia is immense, and if properly harnessed, the nanotechnology field will significantly impact Malaysia's most important industries such as oil and gas (O&G), automotive, medical as well as electrical and electronics (E&E) sector. It is expected by 2020; nanotechnology will contribute 20 to 30 percent raise in this sector (CIO Asia, 2015). To realize and to exploit the potential of nanotechnology, Malaysia government has established various bodies to regulate and to assist nanotechnology development. This can be seen as in 2010, Ministry of Science, Technology & Innovation (MOSTI) has established National Nanotechnology Directorate (NND) and incorporated a body called Nano Malaysia Berhad, as well as a national plan known as Nanotechnology Action Plan 2020 to further support the growth of nanotechnology in the country. Furthermore, another initiative was provided by the government by providing research grants to research universities and research institutions. As clear example MIMOS Berhad and Advanced Materials Research Centre (AMREC), SIRIM Berhad have dedicated research facilities to produce and to study nanomaterial.

In addition, private sector is expected to play a vital role in investment and international collaboration as can be seen by collaboration between FELDA and Cambridge Nanosystem (a spin-off company under Cambridge University). The collaboration was set to utilize biogas generated from FELDA factories to synthesize graphene, a material which is a primary focus in national nanotechnology development (The Star, 2014). However, in Malaysia, the nanotechnology field is still at infancy level. More intense research and development (R&D) is still required to realize and to exploit the full potential of this field.

‘Graphene’ term was first used in 1987 to differentiate a single layer of graphite within a larger compound of graphite (Mouras, 1987). A single layer of graphene is a two dimensional (2D) material which is atomically thin with the theoretical value of about 0.345 nm (Thakur & Thakur, 2015; Zhou & Cao, 2016). The history of graphene can be traced back to almost a century ago (Iacopi, Boeckl, & Jagdish, 2016), but it is not until 2004, a single layer of graphene was obtained from graphite exfoliation. The exfoliation procedure was carried out by Andre Geim and Konstantin Novoselov from University of Manchester via a simple scotch tape method. This accomplishment has enabled researchers to intensely explore and exploit the properties of this material for the very first time (Novoselov et al., 2004). Since then, research on graphene has been progressing rapidly around the globe. As just over ten years after discovery, almost 200,000 research papers related to graphene have been published (Iacopi et al., 2016).

1.2 Graphene synthesis

Many techniques have been developed to prepare high-quality graphene which includes large area graphene and graphene flakes, which in turn is crucial to exploit its unique properties. The term ‘large area graphene’ will be used in this thesis to refer graphene with a lateral size of at least 1 cm^2 . The term of LAG is commonly used by many researchers to define graphene layer with considerably larger than 1 cm^2 (Bhaviripudi, Jia, Dresselhaus, & Kong, 2010; Jayasena & Melkote, 2015) while graphene with a size smaller than a cm^2 is regarded as graphene flakes. The typical approach of obtaining graphene layers is via isolation process from bulk graphite thorough mechanical, thermal or chemical exfoliation. This method produces graphene flakes as well as graphene oxide which can be used directly into various applications or can be reduced into reduce graphene oxide (rGO) for another different application (Bhuyan et al., 2016; Bonaccorso et al., 2012).

Moreover, graphene also can be grown on the substrate via chemical vapour deposition (CVD) or on silicon carbide (SiC) via epitaxial growth and sublimation method (Bhuyan et al., 2016; Kim et al., 2013). CVD has become one of the most promising ways in synthesizing large-scale graphene films as this method gives transferable high-quality graphene films, relatively low cost and ability to produce large area graphene (Chung et al., 2013). CVD is a bottom-up approach and a versatile method to synthesized graphene. The method utilised a various type of carbon-bearing compound (such as hydrocarbon gases, polymer, alcohols and organic solvents) as a precursor and a transition metal as catalyst and growth substrate for graphene synthesis. Figure 1.2 shows the general assembly of CVD setup uses for the graphene synthesis which comprises of gases reactants, mass flow controllers and furnace with a quartz tube and quartz plate.

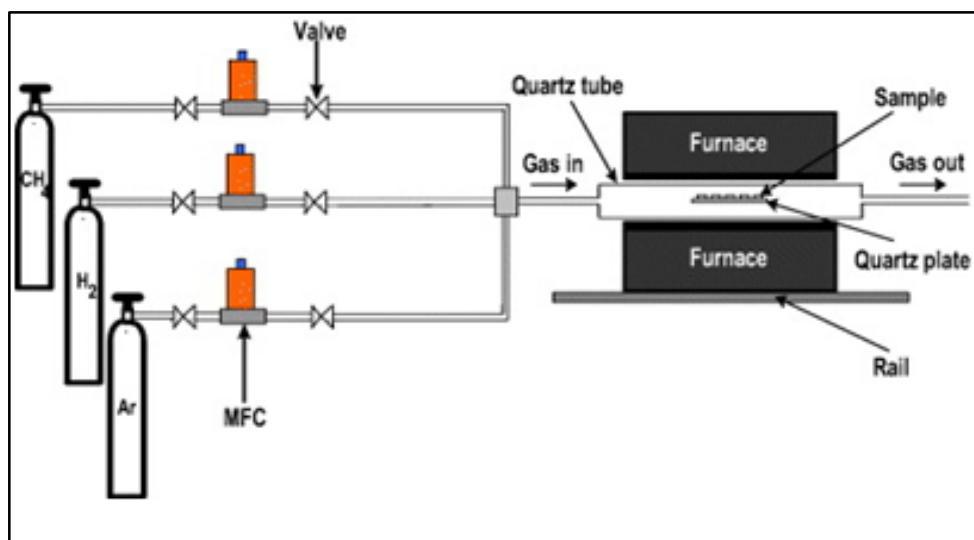


Figure 1.2 Schematic drawing of the assembly of CVD setup uses for the synthesis of graphene films (Nguyen et al., 2012).

In brief, CVD process uses a transition metal (in large area flat foil form or in powder form) as a substrate for graphene growth as well as a catalyst to help in carbon decomposition at a specific temperature. Hydrocarbon gas such as methane is commonly used as carbon feedstock to grow graphene in this process. After graphene growth, the substrate will be etched in order to obtain graphene layer and to be transferred to another substrate. The standard practice is to use wet etching method which involves the use of an etchant to dissolve the metal. A polymer coat on graphene surface (top side) is generally used as mechanical support and to preserve the graphene structure from damage during the etching process. After the process, a new substrate such as Si/SiO₂ is used to host the graphene which subsequently involves cleaning procedure to remove the etching solution contaminant and polymer removal from the graphene surface. Figure 1.3 summarises the typical steps required to obtain large area graphene via CVD processes. The schematic etching process is presented in Figure 1.4.

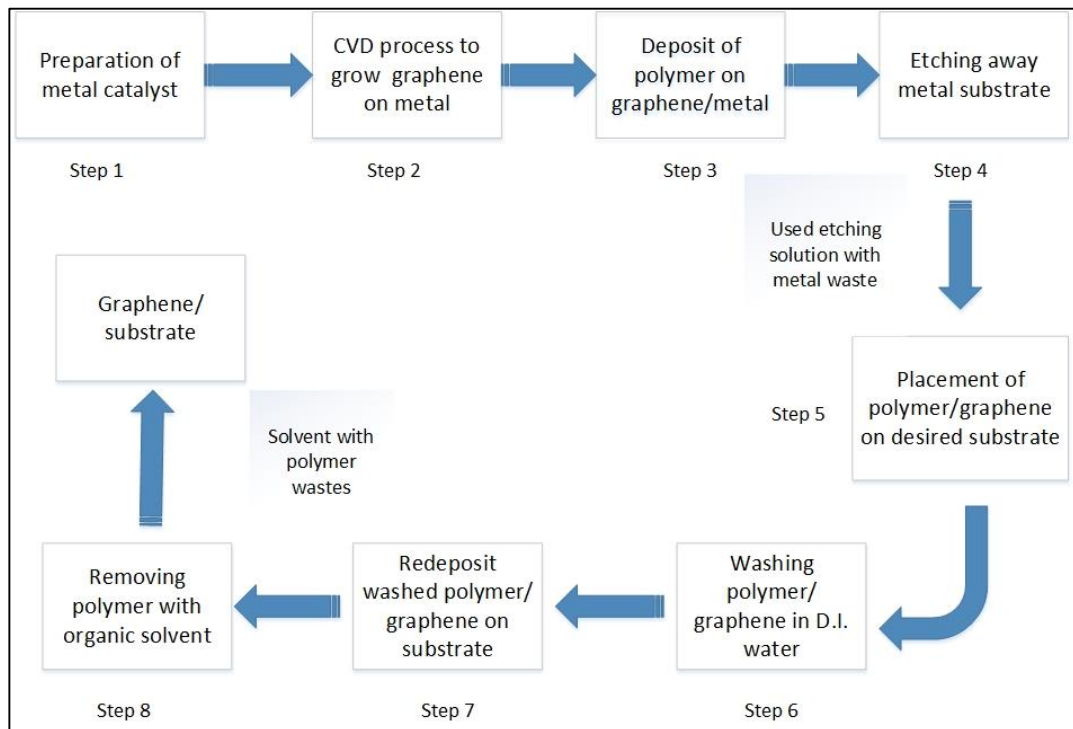


Figure 1.3 Common process and steps of obtaining graphene using CVD method

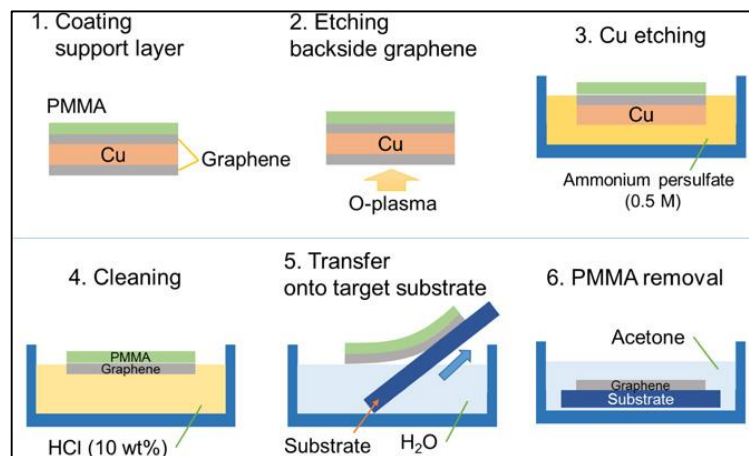


Figure 1.4 Example of a schematic diagram of graphene transfer process (Yasunishi et al., 2016)

For graphene flakes growth on powder metal catalyst; similar CVD process is conducted as large-area graphene. After growth process, a similar etching process has to be conducted to remove the catalyst which using involves diluted acid to remove metal particles. But unlike large-area graphene, no polymer support is used as the

graphene lateral size is very small. In addition, purification steps are required to completely remove the metal catalyst from the graphene flake by a simple washing process with deionized water and filtration process to recover the graphene.

1.3 Research background

Chemical vapour deposition (CVD) is a bottom-up approach and a versatile method to synthesized graphene using the carbon-bearing compound (such as methane gas) as a precursor and a transition metal as catalyst and growth substrate. For large area graphene, flat and large metal catalyst substrate such as copper (Cu) and nickel (Ni) is widely used for the CVD growth of graphene (Biró & Lambin, 2013). Cu is used as the catalyst as opposed to other transition metals due to its low carbon solubility (Hao et al., 2015). CVD on Cu seems to be perhaps the closest to fulfilling the demands of practical applications (Bae et al., 2010) due to low cost and ease-of-use for obtaining graphene layer with reasonable quality (Chung et al., 2013).

Other than large area graphene which is generally used for niche electronic market, graphene in flakes form (lateral size of less than 1 μm) can also be synthesized using metal powder form catalyst. The metal powder can be synthesized using metal salt via a various method such as by impregnation with oxide support (such as MgO) (Dayou et al., 2017; Jugade, Sharma, & Gokhale, 2014). In addition, graphene flakes market segment accounted about two-thirds of the overall graphene market revenue. The demand for graphene flakes is primarily attributed to its lower price and broader ranges of the application as compared to large area graphene (Clark, 2016).

Yet, the methods of obtaining the graphene flakes via CVD and metal powder is not common as this process is more costly as compared to another method. Graphene flakes are commonly produced from natural graphite without the need of using specialised equipment or any catalyst as in CVD synthesis. the cost of natural graphite is at between \$1.50 and \$2.00 per kg, according to “Mineral Commodity Summaries 2013” published by US Department of the Interior and US Geological Survey (Wolf, 2014). However, the process involves tedious steps with a lot of chemicals involved especially for the production of graphene oxide and reduced graphene oxide.

Latest report released by BCC in “Graphene: Technologies, Applications and Markets” expected that the market for graphene would grow very rapidly in the coming decade with the global graphene market is projected to grow to \$67 million in 2015 and to more than \$310.4 million in 2020 and likely to reach \$2 billion by 2025 (McWilliams, 2016). Another report entitled "World Market For Graphene To 2017" by the Future Markets, Inc. 2011 estimates that the production volume of graphene in 2010 was 28 tonnes and is projected to grow to 573 tonnes by 2017. The graphene market in the Asia Pacific is projected to record the fastest growth rate globally thanks to the region’s growing manufacturing sectors, competitive labour costs and increasing graphene-based application patents.

The graphene market is segmented into monolayer & bi-layer graphene, few-layer graphene, graphene oxide and graphene nanoplatelets. In 2015, graphene nanoplatelets (GNP) segment accounted for about two-thirds of the overall market revenue. The demand for GNP is primarily attributed to its lower price and wide application areas as compared to large area graphene. Monolayer, bilayer graphene

and few-layer graphene flakes contributed about one-third of the market share in 2015 and are expected to grow at the highest growth rate during the forecast period (Sarah Clark, 2016).

However, this method has a disadvantage as natural graphite as a resource is limited and of scarce materials. This scarcity of graphite has been recognized by both the United States and the European Union, which each have declared graphite as a supply-critical mineral. In addition, British Geological Survey has ranked graphite right behind the rare earth and substantially ahead of lithium (that commonly used together in lithium-ion battery production) in terms of supply criticality. This problem existed due to various reasons; such as high demand for graphite as a raw material in the production of steel and lithium base battery (Brian, 2014). It is expected the high demand of graphite could not be met in the near future due to the declining of worldwide production of natural graphite (Edwards and Coleman, 2013b; Lifton, 2012; Moradi and Botte, 2016); Consequently, this will pose a problem for graphene production in the long term.

In addition, graphene synthesis via CVD method offer promising future as this method is scalable as compared to mechanical exfoliation of graphite and produce graphene with improved quality over graphene synthesized through chemical exfoliation process that commonly contains a lot of defects and is of low electronic properties for electronic and niche applications (Singh et al., 2011).

1.4 Problem statements

The polycrystalline nature of graphene has a tendency to break into small fragments during the wet transfer process. One of the reasons is due to the high surface tension of aqueous etchant solution that could induce cracks in the large graphene structure (Zhang et al., 2016). Hence, a new method is required to reduce the surface tension of water in order to reduce the possible damage to graphene structure.

In common practice, polymer support such as PMMA is applied to graphene surface to reduce the effect of damage during the transfer process. But the process poses a challenge as the polymeric material is challenging to get rid of that leave polymer residue on the graphene surface. These residues can cause doping effect on graphene, degrades and alter the electronics, thermal and optical properties of the transferred graphene (Li et al., 2016; Suk et al., 2013). In addition, the polymer removal process often creates plentiful of chemical waste (Zaretski & Lipomi, 2015).

To overcome this, new support material for wet etching which is more convenient generated less waste and did not cause significant contamination on the graphene. The proposed n-heptane as support and the solvent can be reused for another graphene transfer after a particular graphene transfer was carried out. Heptane is a non-polar organic solvent which is almost not miscible with a polar solvent (ammonium persulfate solution). Therefore, heptane can be reused and create less toxic waste as compared to regular practice which uses a polymeric material such as polydimethylsiloxane (PDMS) and poly(methylmethacrylate) PMMA. The conventional coating process of polymer on the graphene/substrate involves polymer dissolved in an organic solvent which is followed by spin-coat the dissolved polymer

on the graphene. After etching process completed, the removal of the polymer will use copious amount of organic solvents such as acetone and chloroform to rinse off the polymer.

After growth process, releasing process of graphene from metal substrates require the removal of the metal substrate and is usually carried out by a wet chemical etching method. This process requires the use of a metal etchant and the process produce wastes contains the etched metal. This metal is usually disposed of away only after a single use. However, this practice generates chemical wastes and significantly limits the use of the metal substrate. This practice is not cost-competitive and can be harmful to the environmentally (Yoon et al., 2012). Hence, recovery of the etched metal that can be used as a precursor for a new fresh catalyst for graphene flake synthesis is suggested.

1.5 Research objectives

Objectives of the study are:

- 1) To synthesize large area graphene using polycrystalline Cu by atmospheric pressure chemical vapour deposition
- 2) To study and perform transfer of graphene onto Si/SiO₂ substrate using heptane as non-polar, non-polymeric material support.
- 3) To recover copper from etching solution and to reuse the copper to synthesis CuO supported on MgO catalyst (CuO/MgO).
- 4) To synthesis graphene flakes from recovered and reuse synthesized CuO/MgO catalyst.

1.6 The scope of the study

The large area graphene using polycrystalline Cu foil as catalyst and growth substrate by atmospheric pressure chemical vapour deposition method. The Cu foil size is set to be 1 cm² to 2 cm² and the synthesis to be conducted in an N₂ environment with CH₄ used as a carbon precursor. 0.1 mol ammonium persulfate solution to be employed as a metal etchant for graphene transfer onto Si/SiO₂. The transfer process will utilize heptane, a non-polar organic solvent as soft support. The heptane reusability after then etching and transfer process also will be studied to overcome the issue of solvent and polymer waste as the result of the transfer process. The recovery of etched Cu using thermal treatment to obtain CuO for new catalyst synthesis. Recovered Cu is to be deposited on MgO surface (in the form of CuO) using wet impregnation method to form CuO/MgO. XRD and FESEM to be conducted to analyse and to investigate the structure and morphology of the catalyst the produced catalyst.

Graphene flakes to be synthesized using CuO/MgO and 2 M nitric acid (HNO₃) is used for purification process to remove the catalyst from graphene flakes. Analysis of synthesized large area graphene and graphene flakes to be conducted using Raman spectroscopy, FESEM, HRTEM and selected area electron diffraction (SAED) to observe and to study the carbon species formed.

1.7 Thesis organization

The thesis consists of five chapters. Chapter one discusses the introduction of overall research by introducing carbon element and nanotechnology, carbon allotropes, history of graphene, and large area graphene synthesis via chemical vapour deposition using Cu foil as catalyst and growth substrate.

Chapter two gives an overview of the current progress in graphene synthesis and characterization followed by the current trend of graphene research. This chapter discusses on graphene structure, graphene properties, applications of graphene, graphene preparation, which includes mechanical exfoliation of graphite, epitaxial growth from silicon carbide, chemical vapour deposition (CVD), and CVD parameters with the quality of synthesized graphene. The overview followed with graphene transfer by a wet etching method, and graphene transfer process. The next sections of this chapter cater the topics which include growing graphene on catalyst particles, support in metallic catalyst synthesis. The subsequent part discusses on the defects on graphene and graphene analysis which includes the use of analytical equipment (Raman spectroscopy and microscopy techniques).

Chapter three is dedicated to experimental material and methodology used in this study. The chapter provides detailed information on the overall flow of the research work, methods to conduct experimental work for this research project and in addition to materials, chemicals, equipment used in graphene synthesis and characterization techniques applied in this study.

Chapter four is the centre of this thesis which includes the detail discussion of the results obtained. Chapter four is divided into three parts. Part 1 discusses on the synthesis of large area graphene, the effect of Cu foil position in a tubular furnace, the effect of H₂ partial pressure and other related parameters towards the quality of synthesized graphene on Cu foil. Part 2 discusses the transfer process of graphene from

Cu foil onto Si/SiO₂ substrate. Part 3 discusses the synthesis of graphene flake from recovered Cu and related analysis.

Chapter five is the final chapter which will summarize the results obtained in the current research. This chapter concludes and gives some recommendations for future related studies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In 2004, Prof Andre Geim and Prof Kostya Novoselov from Centre for Mesoscopic and Nanotechnology of the University of Manchester had succeeded to isolate single-layer graphene from a graphite bulk using scotch tape method (Novoselov et al., 2004). The discovery has allowed the graphene to be studied for the very first time and is historically the first truly 2D crystal ever observed and studied. From this point, graphene has become a promising material of which could revolutionize the current technology involving energy, medical, electronics, and so forth.

The science of graphene has bloomed in the last decade following its isolation from bulk graphite. A promising future for this astounding material is foreseen, with various possible applications such as in printable and flexible electronics, solar cells and supercapacitors. Realizing this property, mass production of processable and high-quality graphene is of paramount importance (Wei & Sun, 2015). In production, graphene can be categorized into two primary forms based on its size: large area graphene or small sheets (graphene flakes and graphene platelet) (Ren & Cheng, 2014). Graphene is available in flakes and sheets or “platelets”. Term graphene nanosheets refer to the graphene platelet, flakes or powder. The term “nano” is referring to the magnitude of the thickness of the graphene layer (Wei and Sun, 2015). Furthermore, the chemistry and applications of graphene depend on both the physical form and the number of layers (James and Tour, 2013).

Various methods have been developed for synthesis graphene, and one of the promising methods for high-quality large area graphene and graphene flakes are through chemical vapor deposition (CVD) approach. This chapter is dedicated further to introduce graphene involving the properties of graphene, production methods and potential application. In addition, the contribution of graphene towards economy is briefly introduced, the motivation behind graphene synthesis, development and graphene analysis, graphene transfer methods and reusing catalyst for graphene platelet production.

2.2 Graphene and its properties

Single layers of graphite were observed and defined as ‘graphene’ by the International Union of Pure and Applied Chemistry (IUPAC) terminology in 1994. This definition is to enable independent characterization of a single two-dimensional layers properties from bulk graphite (Boehm, 2010; Boehm, Setton, & Stumpp, 1994). Previously graphene was only considered as part of a theoretical study of 2D material not expected to exist in the free state (Geim & Novoselov, 2007). For more than 60 years before isolated, graphene was theoretically part of graphite and other carbon nano-material related studies (Pinto & Leszczynski, 2014). Theoreticians believed graphene could not exist in suspended form as Mermin-Wagner theorem predicted that low dimensional (2D) crystal a thermodynamically unstable material (Fasolino, Los, & Katsnelson, 2007) due to thermal instability to cause graphene in suspended form to instantly decompose. Atomically thin graphene is believed to experience thermal fluctuations if existed in the free suspended form that led to disintegration and loss its long-range sequence in any finite but non-zero temperature. However, graphene discovery has proven that the 2D material can exist in nature. This can be explained

by the tightly binding of the hexagonal lattice structure with a basic of two atoms per unit cell. The unit cell comprised of sp^2 hybridized carbon atoms bind to each other by one σ -bond in plane and a π - bond perpendicular to plane. This behaviour leads to the super mechanical strength and high charge mobility occurring in graphene (Van, 2015). Graphene is unique and extraordinary material when compared to other carbon allotropes due to it is impressive chemical and physical properties. With this regard, new industrial, commercial and high-technology uses for graphene are continually being discovered.

Graphene, a two-dimensional carbon material has attracted significant attention in many different fields, especially in materials science and condensed matter physics (Novoselov et al., 2004). Graphene is a revolutionary material, and this remarkable discovery has triggered motivation amongst researchers and industrial players to explore the new potential of graphene. Graphene is predicted to be a material of future and the most arguably the most disruptive single invention of all time. This discovery offers new inroads into understanding low-dimensional physics, particularly related to 2D materials. The properties of graphene are explained further in Table 2.1.

Table 2.1 Graphene properties

Graphene Properties	Description	References
Flexible	Graphene is a very flexible material, having rubber-like stiff, and elastic behaviour, graphene can be stretched to 20 % of its original length without breaking up. This was attributed to the graphene's flat planes of carbon atoms which can stretch comparatively easy without the breaking apart.	(Tomori et al., 2011)
Thermal conductivity and heat conduction	Graphene is an excellent thermal conductor approaching $\approx 5000 \text{ Wm}^{-1}\text{K}^{-1}$. Sp^2 covalent bonding between carbon atoms in graphene by which heat moves horizontally through the sheet and significantly contributes to its high thermal conductivity that outperforms carbon nanotubes and 10 times better than copper at room temperature. The excellent thermal conductivity is advantageous for its proposed electronic applications and establishes graphene as an excellent material for thermal management in optoelectronics, photonics, and bioengineering.	(Balandin, 2011; Balandin et al., 2008)
High electron mobility	Graphene charge carriers behave like massless Dirac fermions, has the ability to conduct electricity and has higher electrical conductivity as compared to metal Graphene ability to conduct electricity is better than copper due to high electron mobility in graphene and possess unique charge transport properties. The mobility of charge carriers of monolayer graphene was reported to be $200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.	(Novoselov et al., 2004; Park & Ruoff, 2009; Zhang et al., 2005).
Optical transparency	One atomic thickness of single-layer graphene theoretically allows 97.7% optical transparency of visible light (it only absorbs approximately 2.3% of white light). This makes graphene almost entirely transparent.	(Bae et al., 2010; Li et al., 2009; Sheehy & Schmalian, 2009).

Table 2.1 Graphene properties (Cont.)

Graphene Properties	Description	References
High chemical stability	Graphene is resistant to chemical attacks such as by various types of acids and alkalis. The atomically thin graphene capable of functioning as a protective coating that would give protection against harsh chemicals exposure and corrosion effect.	(Raman & Tiwari, 2014).
Very low density	Specific surface area theoretical value of graphene is $2630 \text{ m}^2\text{g}^{-1}$. The density of graphene is density as being 0.77 mg/m^2 ; thus one m^2 of graphion is only 0.77 mg.	(Kumar & Kumbhat, 2016; Matte, Subrahmanya, & Rao, 2011; Rao et al.,2009)
Mechanical properties of graphene	Defect-free pristine monocrystalline graphene sheet displays a breaking strength measured to be 42 N m^{-1} , high Young's modulus approximately reaching 1100 GPa, the fracture strength of 125 GPa and outstanding mechanical strength which is 100 to 300 times stronger as compared to steel.	(Lee et al., 2008; Shekhawat & Ritchie, 2016).

Three-dimensional crystal (3D) of graphite and diamonds are the only natural occurring polymers of carbon (Lifton, 2012). Meanwhile, 2D graphene is a building block for graphite, and other carbon family allotropes as zero-dimensional (0D) fullerene (discovered in 1985) and one-dimensional (1D) carbon nanotube (CNT) (discovered in 1991). Figure 2.1 (a) shows 2D material of graphene sheet, a fundamental building block for other carbon allotropes of other dimensionalities (0D fullerenes, 1D nanotubes and 3D of graphite). Graphene carbon atoms in the crystal lattice are arranged in a hexagonal honeycomb pattern; carbon atoms in graphene lattice are bonded to other three carbon atoms resulting in 120° angle with a distance of 0.142 nm between the adjacent atoms as shown in Figure 2.1 (b). The figure shows the atomic structure of graphene and its honeycomb arrangement, the dotted blue lines denote the two-atom primitive cell with lattice vectors a_1 and a_2 , and grey spheres represent the carbon atoms.

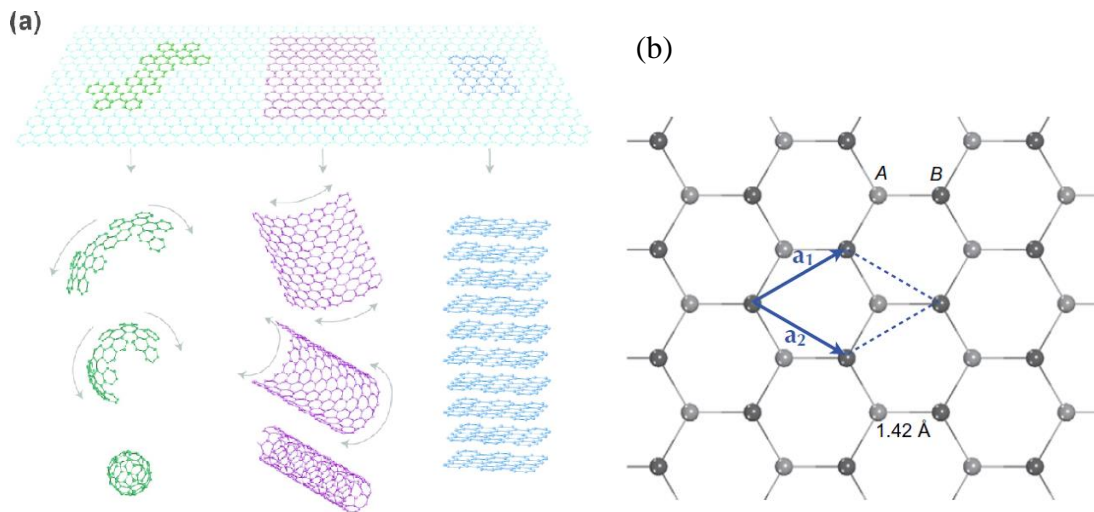


Figure 2.1 (a) Graphene and carbon allotropes of other dimensionalities (0D fullerenes, 1D nanotubes and 3D graphite) (Geim & Novoselov, 2007) (b) Honeycomb structure of graphene (Pinto & Leszczynski, 2014).

2.2.1 Motivation towards graphene synthesis

In Malaysia, National Graphene Action Plan 2020 was launched in 2014 by Ministry of Science Technology and Innovation (MOSTI) and spearheaded by NanoMalaysia Berhad; a company limited by guarantee under MOSTI incorporated in 2011 to act as a business entity entrusted with nanotechnology commercialisation activities and to provide guidelines for collaboration between the Malaysian government with other parties involving private sector, academia and research institutes. After more than three years of National Graphene Action Plan 2020 was commenced, Malaysia now has a cumulative of 30 graphene-based projects with 12 local companies. In which collectively has the potential to contribute to achieving additional gross national income impact of more than RM20 billion and help create 9,000 new jobs for these industries in Malaysia by 2020 (MOSTI, 2017).

2.2.2 Graphene structure

Pristine graphene consists of carbon to carbon covalent bonding network. This covalent bond is very strong with bonding energy is approximately 5.9 eV, slightly higher than the diamond sp^3 bonds (Schabel and Martins, 1992). Furthermore, the formation of σ bonds between carbon atoms contributes to the exceptional structural rigidity of graphene (Peres, 2009). The sp^2 bonding contributes to the stability and robustness of graphene lattices (Figure 2.2(a) and (b)). $2p_z$ orbital of graphene is perpendicular to the XY plane forms a π -bond which are half filled. The π -bond contributes to the conductivity of graphene from one electron per carbon atom. The π -bond gives rise to weak Van-der-Waals-forces between the graphene-graphene layers. Weak Van der Waals interaction (~ 50 meV) linked graphene planes to other planes in graphite crystal with the spacing between planes is equal to 3.35 Å. The existence of

anisotropic and robust bonding of carbon atoms in graphene lattice structure is the reason for the exceptional electronic and extraordinary thermal properties of graphene (Peres, 2009; Pop et al., 2012).

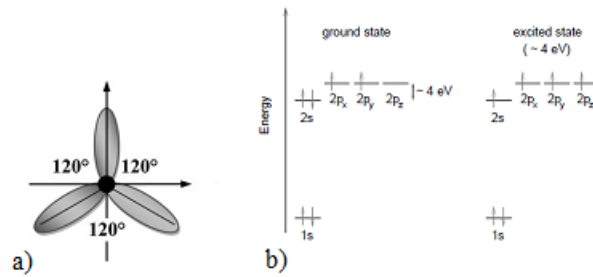


Figure 2.2 a) The hybridization create a planar structure with 120 degrees between hybrid orbital (Du et al., 2017) b) excitation of an electron in 2s orbital to 2p orbital in ground state form new sp² orbital (Fuchs and Oliver, 2008)

2.2.3 Applications of Graphene

Graphene is expected to replace existing materials that are currently used for electronic devices, where materials with high transparency and the conductive layer are required. Graphene can be used as a flexible transparent electrode for touch screen, photovoltaic, solar cells, smart window, light-emitting diodes (LEDs), flexible organic light-emitting diodes (OLED), and in flexible liquid crystal display (LCD). Currently, a typical material for high transparency with high conductivity application is Indium Tin Oxide (ITO) because ITO has high transmittance, high conductivity, and suitable work function for the mentioned applications (Schreiber et al., 2010). Unfortunately, the indium (In) used to produce ITO is a limited resource and due to high demand, the price of ITO increases. Furthermore, ITO like any other amorphous metal oxide film is a brittle and fragile material and not suitable for flexible device applications (Bae et al., 2012). However, for graphene to work as ITO replacement in the commercial market, graphene must satisfy few essential properties which are having a sheet

resistance less than 100 ohms per square (Ω/\square) and visible range transmittance higher than 90%, which is still a challenge in graphene bulk production. Wafer-scale CVD growth graphene can be used into quantum dot photodetectors, with a CMOS (complementary metal-oxide semiconductors) read-out integrated circuit (optoelectronic applications) with applications that include night vision, food inspection, fire control, vision under extreme weather conditions (Goossens et al., 2017). Each application depends on the corresponding resistance range required as shown in Figure 2.3.

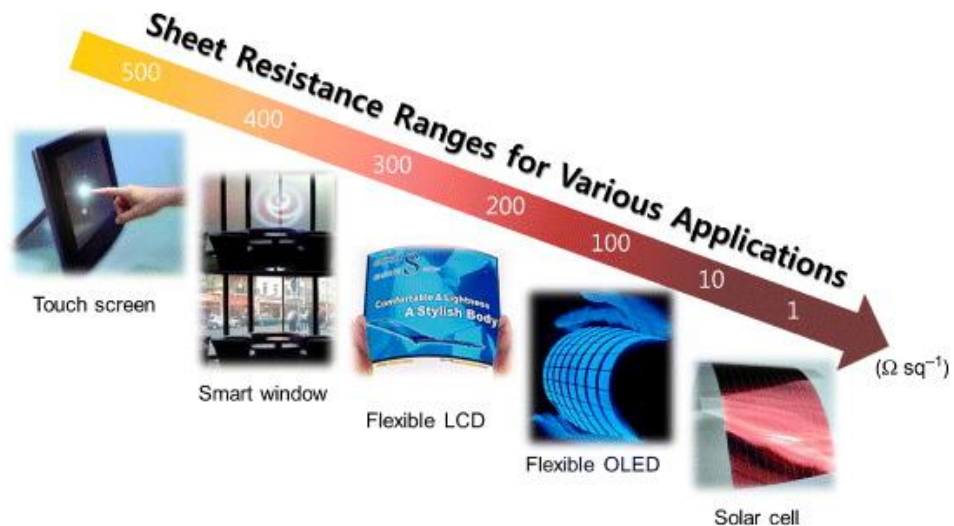


Figure 2.3 Potential applications of graphene (Bae et al., 2012).

Graphene also can be used in the new material formulation to enhance and reinforce any existing properties of materials. Mixing graphene with other materials such as polymers can help to form composites which are more sturdy and stronger as well as thinner and lighter. This makes graphene an ideal material to be used in other than an application in electronics applications. Graphene nanoplatelets (GNP) can be used in the aerospace application as GNP with high mechanical strength, lower density and lightweight can be used in the composite material to create stronger and lighter