SYNTHESIS OF GRAPHENE FROM ALTERNATIVE PRECURSORS AND THE USE OF QUARTZ PLATE FOR CARBON SOURCE MANIPULATION

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by

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LIST OF ABBREVIATIONS

2D	Two-dimensional
3D	Three-dimensional
ABS	Acrylonitrile-butadiene-styrene
APCVD	Atmospheric pressure chemical vapor deposition
Ar	Argon
BNNTs	Boron nitride nanotubes
C	Carbon
CH_4	Methane
C_2H_2	Acetylene
C_2H_4	Ethylene
C_2H_5OH	Ethanol
C_3H_6	Propene
C_3H_7OH	Isopropyl alcohol
$C_3N_6H_6$	Melamine
C_5H_5N	Pyridine
C_6H_{14}	Hexane
$C_{12}H_{22}O_{11}$	Sucrose
$C_{13}H_{10}$	Fluorene
CNTs	Carbon nanotubes
CRM	Carbon dioxide reforming of methane
Cu	Copper
CVD	Chemical vapor deposition
DFT	Density functional theory

EA	Elemental analysis
FWHM	Full width half maximum
GC	Gas chromatography
GNCs	Graphene nanoclusters
H_2	Hydrogen
HBC	Hexabenzocoronene
HCB	Hexachlorobenzene
HHV	High heating values
HIPS	High-impact polystyrene
HOPG	Highly oriented pyrolytic graphite
HRTEM	High resolution transmission electron microscope
LPCVD	Low pressure chemical vapor deposition
N	Nitrogen
Ni	Nickel
PCBM	Phenyl-C_{61}-butyric acid methyl ester
PhD	Doctor of Philosophy
PMMA	Poly(methyl methacrylate)
RFCVD	Radio frequency chemical vapor deposition
RM	Ringgit Malaysia
SAED	Selected area electron diffraction
sccm	Standard cubic centimeter per minute
TST	Transition state theory
UHV-CVD	Ultra-high vacuum chemical vapor deposition
VOC	Volatile organic compounds
XPS	X-ray photoelectron spectroscopy

LIST OF SYMBOLS

€	Euro
%	Percent
π	Pi
$	US dollar
I_{2D}/I_G	Ratio of 2D-peak over G-peak in a Raman spectra
I_D/I_G	Ratio of D-peak over G-peak in a Raman spectra
RM	Ringgit Malaysia
t_D	Dehydrogenation time
wt. %	Weight percent

SINTESIS GRAFENA DARIPADA PENDAHULU ALTERNATIF DAN PENGGUNAAN KEPINGAN KUARZA UNTUK MEMANIPULASI SUMBER KARBON

ABSTRAK

Grafena ialah satu lapisan atom karbon yang tersusun dalam struktur sp^2-hibridisasi dengan sifat yang jauh lebih hebat berbanding dengan bahan lain. Penyelidikan dan pembangunan di dalam bidang sintesis grafena telah berkembang dengan pesat beberapa tahun kebelakangan ini terutamanya dengan menggunakan kaedah pemendapan wap kimia (CVD). Walau bagaimanapun, untuk membolehkan grafena bergerak dari skala makmal ke domain komersial; kos untuk sintesis graphene perlu terus dikurangkan dari masa ke masa. Di dalam tesis ini, masalah ini disentuh daripada beberapa sudut. Salah-satu daripada kajian yang dilakukan dalam tesis ini menunjukkan yang jerami padi dan biogas sintetik; sisa buangan daripada industri padi dan kelapa sawit boleh digunakan sebagai sumber karbon murah untuk penghasilan grafena. Dalam kes jerami padi, pertama sekali ia akan melalui proses pirolisis untuk memperoleh minyak-bio dan arang-bio. Hanya 0.50 mL minyak-bio kemudiannya digunakan sebagai sumber karbon untuk mensintesis 1 cm x 1 cm grafena filem dengan kualiti yang bagus (I_D/I_G = ~0.55) melalui kaedah dua pemanas pemendapan wap kimia pada tekanan atmosfera (APCVD). Dengan melakukan pirolisis, kuantiti sumber karbon yang keluar sebagai efluen dapat dikurangkan memandangkan kebanyakannya telah ditukar kepada produk sampingan sebelum pertumbuhan grafena. Arang-bio juga digunakan sebagai sumber karbon untuk mensintesis grafena tetapi dengan proses APCVD yang dibantu dengan kaedah memerangkap karbon yang baru dan mudah

melalui plat kuarza yang ditempah khas. Di sini, 2.5 mg arang-bio telah dikelilingi dengan plat kuarza dan kepingan kuprum dalam susunan yang khusus untuk bertindak sebagai perisai karbon bagi memerangkap spesies aktif karbon pada suhu tinggi dalam ruangan yang sempit. Dengan melaksanakan perangkap karbon, kuantiti sumber karbon yang diperlukan untuk sintesis grafena pada kadar saiz yang sama adalah lebih rendah; keupayaan pertumbuhan grafena meningkat sekitar 400 %. Akhir sekali, efluen kepada proses pertumbuhan grafena telah ditukarkan menjadi syngas apabila biogas sintetik digunakan sebagai sumber karbon bersama dengan nikel sebagai pemangkin pada 900 ^{o}C dalam proses yang sama; menukar sisa kepada harta.

SYNTHESIS OF GRAPHENE FROM ALTERNATIVE PRECURSORS AND THE USE OF QUARTZ PLATE FOR CARBON SOURCE MANIPULATION

ABSTRACT

Graphene is a single layer of carbon atoms arranged in an sp^2-hybridized structure with properties far superior compared to other materials. Research and development in graphene synthesis have been rapidly growing the past few years especially using chemical vapor deposition (CVD). However, in order to move graphene from laboratory scale to commercial domain; graphene synthesis cost need to be continually reduced. In this thesis, this problem was approached from a few angles. One of the study in this thesis demonstrate that rice straw and synthetic biogas, typical wastes from the rice and palm oil production industries can be used as inexpensive carbon source for the production of graphene. In the case of rice straw, the lignocellulosic biomass was first put through thermal pyrolysis in order to obtain the bio-oil and bio-char. Only 0.50 mL of bio-oil was then used as carbon source to sufficiently synthesized 1 cm x 1 cm of large area graphene with good quality (I_D/I_G = ~0.55) via a two-heating source setup ambient pressure CVD (APCVD) . By doing this, the amount of carbon source going out as effluent is reduced as it has been recovered as side-products prior to graphene growth. The bio-char was also used as carbon source for graphene growth but with a novel and facile carbon trapping assisted APCVD involving customized quartz plate. Here, 2.5 mg of bio-char was encapsulated with quartz plate and Cu foil in a specific arrangement which acted as carbon shields and trapped the carbon active species at high temperature within the confined space of the setup. By implementing carbon trapping, lesser amount of carbon source was needed for graphene growth of the same size; graphene growth efficiency increased

around 400 %. Lastly, the effluent of the graphene growth process was converted into syngas when synthetic biogas was used as the carbon precursor with Ni as the catalyst at 900 ^{o}C in a one-step process; turning waste into wealth.

CHAPTER ONE

INTRODUCTION

This chapter provides an overall introduction to the PhD research project. A brief introduction on two-dimensional materials and graphene as the main theme of this thesis are outlined at the beginning of the chapter followed by a section on chemical vapor deposition (CVD) as the tool to synthesis graphene. At the end of this chapter, the problem statement, objectives, scope of work and thesis organization are laid out.

1.1 Two-dimensional materials

The introduction of new materials has enabled the growth of new technologies that have beneficial impact on society. Currently, the world is in the precipice of a new age of 2-dimensional (2D) materials. Boron nitride (BN) (Örnek et al. 2018; Wang et al. 2018b; Zhuang et al. 2017), bismuth telluride (Bi_2Te_3) (Termsaithong & Rodchanarowan 2017; Wada et al. 2017), bismuth(III) selenide (Bi_2Se_3) (Desai et al. 2018), molybdenum disulfide (MoS_2) (Jiang et al. 2017; Solanki et al. 2017), molybdenum diselenide ($MoSe_2$) (Sathe et al. 2013; Wang et al. 2017), molybdenum ditelluride ($MoTe_2$) (Park et al. 2015), tungsten disulfide (WS_2) (Choi et al. 2017), tungsten diselenide (WSe_2) (Chen et al. 2015; Yun et al. 2016), silicone (De Padova et al. 2017; Vogt et al. 2014), phosphorene (Khandelwal et al. 2017; Woomer et al. 2015), bismuthene (Aktürk et al. 2016), graphyne (Dearden & Crean 2014; Kehoe et al. 2000), graphane (Arguilla et al. 2014) and graphene (Ali et al. 2016; Murdock et al. 2017) are among the 2D materials that have been investigated. Within that group, graphene is the most-researched material since its discovery in 2004 (Geim & Novoselov 2007; Novoselov et al. 2004). It is investigated for use in the next

generation devices due to its outstanding combination of properties not observed in any other type of materials. Its magnificent properties are attributed to the strong bonding between the hexagonal arrangement of carbon atoms that make up graphene.

Graphene can be produced in several forms which include flakes (Chae et al. 2017; Ghaemi et al. 2017; Nizam et al. 2017), ribbons (An et al. 2012; Liu et al. 2016), and large-area sheets (Bhaviripudi et al. 2010; Yan et al. 2012). They differ in lateral dimensions; flakes with limited lateral dimensions (from several nanometers to micrometers), large-area sheets possess macroscopic and extended lateral dimensions, while ribbons have one lateral dimension that is at least one order of magnitude larger than the other (Bianco et al. 2013). These differences allow graphene to be used in various types of application; certain physical forms are more compatible for particular applications. For example, large-area graphene sheets are more suited for wafer-scale thin film-like application such as transparent conductive electrode (Li et al. 2009c) while graphene flakes (GFs) are investigated for conductive ink applications (Arapov et al. 2016; Yang & Wang 2016).

1.2 Graphene

The unique properties of graphene have triggered a sudden drive of graphene researches all over the world. Graphene is expected to be the next generation two-dimensional materials having the potential to enhance current technology and create a new one in the near future. Graphene is a thermodynamically stable species of pure carbon atoms bonded in a single sheet of hexagonal sp^2 structure (Gilje et al. 2007). It represents the base structure of carbon nanotubes (CNTs), graphite and fullerenes. Electron configuration of the carbon atoms is the key factor for the incredible properties of graphene such as its high mechanical strength (Ahmad et al. 2015; Wang

et al. 2014), high surface area (Gadipelli & Guo 2015; Huang et al. 2012), extraordinary thermal conductivity (Wang & Tsai 2016; Wang et al. 2016), ultra-high elasticity (Geim 2009) and high optically transparency (Weber et al. 2014; Zhu et al. 2014). Due to its outstanding properties, graphene has immense potential in many applications. Even if properties of graphene depend on its structure and form (Lee et al. 2017; Pang et al. 2016) and the intended applications depend on graphene characteristics, its potential to improve performances in numerous materials and processes is widely recognized. Among the numerous applications targeted, graphene could be used as transparent conducting electrodes (Casaluci et al. 2016), fillers in reinforced polymer nanocomposites (Kumar et al. 2017b; Mittal et al. 2015; Young et al. 2012), super-capacitors (Ke & Wang 2016; Kumar et al. 2017a, 2017d), lithium ion batteries (Kheirabadi & Shafiekhani 2012; Kucinskis et al. 2013; Zhao et al. 2016a), fuel cells (Devrim & Albostan 2016; Najafabadi et al. 2016), solar cells (Kuhn & Gorji 2016), photo-catalysis (Putri et al. 2015), biosensors (Park et al. 2016), chemical sensors (Zhao et al. 2016b), purification of water (Aghigh et al. 2015) and optoelectronics (Jin et al. 2015; Polat et al. 2016). To face the demand for both fundamental studies and developments for its practical utilization, development of large-scale synthesis methods has never been more vital (Bae et al. 2010; Levchenko et al. 2016).

Since the discovery of graphene through highly oriented pyrolytic graphite (HOPG) mechanical exfoliation (Geim & Novoselov 2007; Seah et al. 2014), a number of alternative methods for graphene synthesis have been developed. Wet chemical exfoliation is one of the most widely used techniques to prepare graphene nowadays but it does have some drawbacks (Botas et al. 2013) including numerous lattice defects, multiple grain boundaries and oxidative traps, which increases its electrical

resistance (Muhammad et al. 2014). Other methods to synthesize graphene include intercalation (Li et al. 2008), epitaxial growth from silicon carbide (SiC) (Robinson et al. 2010), CVD (Sun et al. 2015), plasma and flash pyrolysis of solvothermal materials (Choucair et al. 2009). Among the aforementioned techniques, the growth of graphene by CVD or atmospheric pressure CVD (APCVD) on metal or semi-conductor catalysts has been considered as the most promising technique thanks to its simplicity, scalability, flexibility and capability of achieving large area graphene with high crystalline quality (Wang et al. 2013; Weatherup et al. 2016).

1.3 Chemical vapor deposition

Chemical vapor deposition is the dominant manufacturing route for many nanomaterials such as CNTs (Volder et al. 2013) since it enables not only bulk production but also direct device integration. This bottom up approach involves a carbon precursor being able to dissociate with the aid of a metal substrate and a solubilization-segregation phenomenon leads to graphene formation. The involved mechanisms depend on the transition metals used (Batzill 2012; Seah et al. 2014). Generally, two types of mechanism are reported in graphene synthesis by CVD on transition metals: bulk-mediated and surface-mediated mechanism . For instance, Cu induces a surface-mediated growth mechanism which allows mastering the number graphene layers as compared to many other transition metals (Braeuninger-Weimer et al. 2016; Sun et al. 2016). A bulk-mediated growth mechanism has been proposed for transition metals such as Ru, Ir and Ni (Seah et al. 2016b). The growth mechanism is closely related to carbon solubility from the precursor in the metal substrate at the operating CVD conditions, especially reaction temperature. This is the reason why aside from the metal substrate, the influence of the nature and the state of the carbon

precursor used cannot be neglected since it certainly plays a major role in graphene CVD synthesis and growth mechanisms.

In 2009, it was the first time that CVD growth of monolayer graphene films was realized by using polycrystalline Cu foil as substrate (Li et al. 2009a). CVD was recognized as a proficient method for graphene synthesis and since then, there have been a lot of studies and experimentations aiming at further improving the process. Cu as catalyst has many advantages compared to other transition metals including ease of transfer, economical cost and good control of number of layers. The used carbon precursor can be, a priori, in the form of gas, liquid or solid. However, it always needs to be in the form of gas as it reaches the metal catalyst surface. The most widely used gaseous carbon precursors are hydrocarbons such as methane (CH_4) and acetylene (C_2H_2). The mechanism of graphene synthesis by Cu can be divided into three stages. At first stage, the carbon precursor molecules collide on the metal substrate surface. They can either adsorb on the surface, scatter back to the bulk gas phase, or directly progress to the next stage of the reaction process. At the second stage, the carbon precursor molecules dehydrogenate, partially dehydrogenate or remove non-carbon elements so that it can form active carbon species. Lastly during third stage, these active species coalesce, nucleate, and grow into graphene islands on top of the metal substrate (Li et al. 2011b). These graphene islands enlarge until full coverage. If the used carbon precursor is under the form of liquid or solid, a supplementary stage precedes the collision phenomenon.

1.4 Problem statement

Thousands upon thousands of papers have been written on graphene synthesis in the last few years. However, in order to move graphene towards commercialization

which is the ultimate goal, the most essential factor is the cost of graphene production itself. Producing graphene via top-down methods by breaking down graphite into graphene is a lot cheaper than CVD. Unfortunately, graphite is a supply-critical mineral ranked behind rare earths but ahead of lithium in terms of supply criticality (Lloyd et al. 2012; Luque et al. 2014). Consequently, this will pose a problem for cheap graphene production in the future. With the increase of demand and limited supplies, sooner or later top-down method such as graphite exfoliation will become unfeasibly more expensive. Additionally, graphite exfoliation does not have the capability to produce large area graphene and 3D graphene which is very critical for electronic applications. This is why it is believed that bottom-up method especially CVD is the better long-term answer for graphene synthesis.

CVD is the most widely used method to synthesis graphene sheet or large area graphene because of its scalability and high-quality output. Graphene sheet or film can be defined as a single-atom thick sheet of sp^2 hybridized carbon atom arrangement adhered on a foreign substrate or freely suspended and has a lateral dimension of more than 100 μm (Bianco et al. 2013). Graphene sheet is also widely known in the scientific community as large area graphene. To produce large area graphene which will be the bedrock of this thesis, bottom-up method such as CVD is unavoidable. However, the cost of graphene via CVD is still costly for commercial use. Table 1.1 shows the price of large area graphene from various suppliers. Indeed, it is very expensive from most of the suppliers especially by considering that the price quoted for most is only for 1 cm^2. With the aim of significantly reducing cost production of graphene synthesis by CVD, three key problems areas have been explored in this thesis.

Table 1.1 List of large area graphene prices from various suppliers.

Supplier	Origin	Item	Size	Price/cm^2	Price/cm^2	Ref
Graphenea	Spain	Monolayer graphene on SiO_2/Si	1 cm^2	€ 47.00	RM 221.78	(Graphenea 2018)
Graphene Supermarket	USA	Monolayer graphene on 285 nm SiO_2 wafer	1 cm^2	$ 60.00	RM 237.03	(Graphene Supermarket 2018)
Graphene Supermarket	USA	Multilayer graphene on 285 nm SiO_2 wafer	1 cm^2	$ 50.00	RM 197.53	(Graphene Supermarket 2018)
ACS Material	USA	Monolayer CVD graphene on SiO_2 substrate	1 cm^2	$ 70.00	RM 276.54	(ACS Material 2018)
Sigma-Aldrich	Malaysia	Monolayer graphene on SiO_2/Si substrate	1 cm^2	–	RM 1,945.00	(Merck 2018)
Sigma-Aldrich	Malaysia	Monolayer graphene film on quartz	1 cm^2	–	RM 1,945.00	(Merck 2018)
Sigma-Aldrich	Malaysia	Monolayer graphene film on copper foil	1 cm^2	–	RM 910.00	(Merck 2018)

* Transportation cost is not included for suppliers from outside of Malaysia

** 12 May 2018, RM 1.00 = € 4.73 = $ 3.95

The first one is the **carbon precursor used for graphene synthesis by CVD is expensive** as most of them are already used for certain commercial application. Most CVD methods use methane as the carbon precursor which is used to generate electricity and raw material to manufacture organic chemicals. The use of alternative carbon precursors that is a waste in the ecosystem would directly alleviate the cost of graphene synthesis. Hence, the focus of this work is to use wastes that are available abundantly, cheap and contribute to climate change as alternative carbon precursor for graphene synthesis. Climate change has long been touted by the majority of the

scientific community as a threat to humanity. In April 2016, the Paris Climate Accord was signed between 196 parties throughout the world which aims to maintain the increase in global average temperature to well below 2 ^{o}C above pre-industrial levels. Malaysia also took part in the initiative to cope climate change to a tolerable level (UNFCCC 2018). In this thesis, two sources of climate change contributor in the form of rice straw and biogas were identified. The open burning of rice straw after every harvesting season has become the norm and contributed to annual air pollution (Cuong et al. 1994; Gadde et al. 2009; Nguyen et al. 1994). Biogas is a byproduct from wastewater treatment by breaking down organic matter in the absence of oxygen. It is comprised of primarily methane and carbon dioxide, both of which are greenhouse gases. Therefore, the feasibility of using them as carbon precursor for graphene growth would contribute in lowering greenhouse gases emissions and at the same time give value to wastes.

The second problem is the **low graphene growth efficiency which arises because of minimal contact between the carbon precursor gas flow and the catalyst**. Typical CVD setup for graphene growth has a very poor contact area between the catalyst and the gas flow. A normal CVD setup for graphene growth would normally involve the use of Cu substrate with a thickness of 25 μm which will be cut into 10 mm x 10 mm. This 100 mm^2 dimension for the Cu substrate is a common practice among researchers who studies the area of graphene CVD because transition metal catalyst is very expensive. With smaller size, more samples can be obtained. Relative to the microscale thickness of Cu substrate, the inner diameter of the quartz tube utilized is typically enormous. For example, Lisi et al. (2017) used quartz tube with inner diameter of 55 mm whereas Wang et al. (2014a) used one with inner diameter of 70 mm. When the metal substrate is put side-by-side to the quartz tube,

the difference in size and area would be obvious to see. The gas mixture will coincide with the shape and size of the quartz tube. All in all, less than 1 % of the gas flow will be available for direct contact with the metal substrate. Hence, around 99 % of the gas flow cannot come into contact with the metal substrate for any reaction to occur from the cross-sectional area side. Hence, the use of quartz plates in conjunction with Cu catalyst for carbon trapping in order to increase the graphene growth efficiency was investigated.

The third problem is the **effluent from graphene growth are considered as waste and do not have any value**. In most cases, the effluents only undergo some simple treatment before being discharged into the atmosphere. As discussed previously, the majority of the gas flow will not have any direct contact with the catalyst and this represent a big waste in the process. That is why the author have taken the initiative to explore the possibility of converting the CVD effluents into valuable byproducts for the process.

1.5 Objectives

This thesis objectives if put in one sentence will be "**to produce large area graphene via APCVD from cheap alternative carbon precursors at higher graphene growth efficiency and convert the effluent into value-added product**". Here, these objectives are laid out as the following:

1. To use cheaper alternative carbon precursors for graphene growth.
2. To produce value-added side-products.
3. To increase graphene growth efficiency.
4. To convert effluent into a value added product.

1.6 Scope of study

This research has been devoted to produce large area graphene with lateral sizes around 1 cm^2 from alternative precursors via APCVD using novel techniques to increase graphene growth efficiency and to convert effluent into a byproduct. Both Cu foil and Ni foil was used separately as metal catalysts for the reaction. Cu was utilized for its low carbon solubility as a carbon shield whereas Ni for its capability to catalyze carbon dioxide reforming of methane reaction aside from their dual role of becoming the catalyst and substrate for graphene CVD.

The CVD growth of graphene was done in a fixed bed reactor at atmospheric pressure from carbon precursors of different physical state: rice straw bio-oil (liquid), rice straw bio-char (solid) and synthetic biogas (gas). Novel techniques to improve the CVD process were investigated. Thermal pyrolysis was performed onto rice straw in order to obtain bio-char and bio-oil which was then used as carbon precursor for graphene growth. Quartz plates were used in combination with Cu foil to create a chamber for bio-char to be contained during APCVD reaction (carbon trapping). Ni foil was used to catalyze graphene growth and syngas production as a byproduct.

After undergoing APCVD process, various analytical methods were conducted to investigate and analyze the morphology and quality of the large area graphene produced. The characteristic of the synthesized graphene was examined by Raman spectroscopy, Raman mapping, High Resolution Transmission Electron Microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and optical imaging. On the biomass thermal pyrolysis section, proximate analysis, elemental analysis, bomb calorimeter and thermogravimetric analysis (TGA) were used for characterization.

1.7 Thesis organization

The thesis consists of five chapters. Chapter one (Introduction) discusses the introduction of the overall research by introducing two-dimensional materials, graphene and CVD as the superior method for large area graphene production. The motivations for conducting present study are expressed after identifying current hurdles related to the high cost of large area graphene production. Based on that, a set of objectives are then outlined. This chapter ends with the description about the scope of study and thesis organization by chapters.

Chapter two (Literature review) gives an overview of the current progress in graphene synthesis from various carbon precursors in their physical state (gas, liquid and solid) and their chemical state (aliphatic and aromatic). The mechanisms of the graphene CVD are also discussed and summarized into several categories. Potential alternatives carbon precursors are given with critical parameters for graphene growth via CVD which include reaction effluents and graphene growth efficiency. The subsequent part summarizes the whole chapter which leads out the foundation for the future chapters.

Chapter three (Materials and methods) is dedicated to the materials and methods used throughout this study. Detailed information on the materials, chemicals, equipment and methodologies to conduct the experimental works are described within this chapter.

Chapter four (Results and discussion) is the heart of this thesis where results and discussions are presented. It is divided into three sections. Section 1 discusses the preliminary studies completed for this work. Section 2 covers the thermal pyrolysis of rice straw into bio-oil and bio-char, the feasibility of rice straw bio-oil as carbon precursor for graphene growth and the use of carbon trapping for graphene growth

from rice straw bio-char. Section 3 explores the co-synthesis of graphene and syngas from synthetic biogas.

Chapter five (Conclusion and recommendations) outlines the conclusions of this research along with some recommendations for future related studies.

CHAPTER TWO

LITERATURE REVIEW

This chapter provides an overall introduction to the PhD research by giving an overview on the recent trends in graphene synthesis from various carbon precursors. The details of the synthesis conditions and the mechanisms involve in graphene synthesis using carbon precursors in the form of gaseous, liquids and solids are compared, analyzed and discussed thoroughly. The chemical state of the carbon precursors and the impact toward graphene growth mechanisms are also examined. A number of parameters which can affect graphene synthesis by CVD are also reviewed briefly. This chapter ends with concluding remarks that connect it to the work done in this thesis.

2.1 Growth of graphene via CVD

Numerous CVD setups have been developed to synthesize graphene especially from gaseous carbon precursors. The CVD methods used for liquid and solid precursors as feedstocks are less common. Figure 2.1 illustrates the common CVD setups used by researchers for liquid and solid precursors to grow graphene. All the setups have their own advantages and drawbacks depending on the used starting reactants and materials. Liquid precursors with elevated boiling point do not readily evaporate an external source of heating is required to vaporize them. The common procedure consists in heating up the catalyst until it reaches the desired reaction temperature; then the region with the liquid precursor is heated above its boiling point. A flow of N_2 and H_2 carries the gaseous precursors to the metal substrate location for graphene growth. The common method involves a two-furnace setup which has also

been extensively used for CNTs (Suriani et al. 2015b). Some research groups have also used a bubbling setup (Ouyang et al. 2015) or a heating tape (Li et al. 2011b) to heat and convert the liquid precursor into gas.

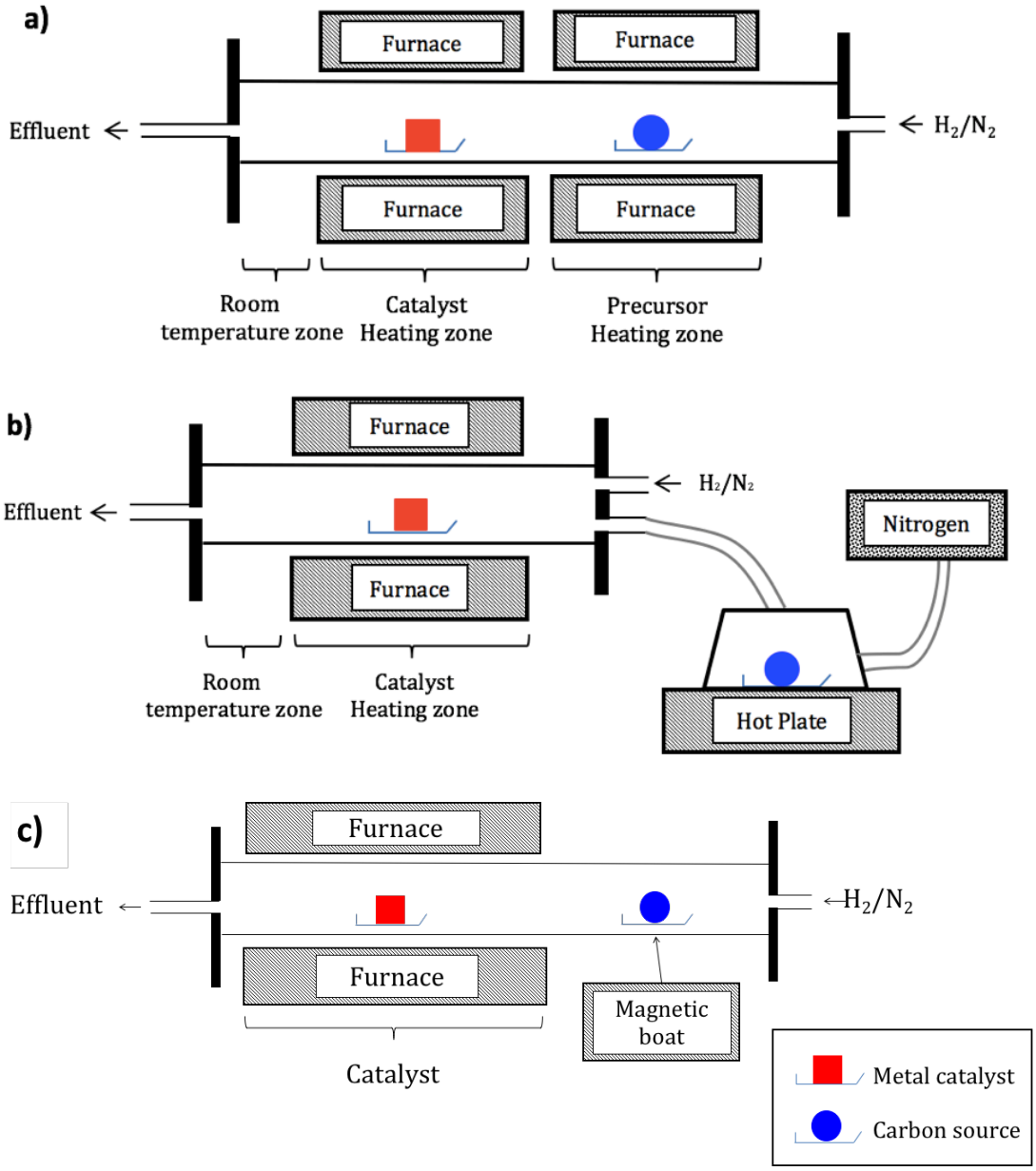

Figure 2.1 Chemical vapor deposition setups: a) Two-furnace; b) Bubbling; c) Magnetic boat (Jacobberger et al. 2015; Kalita et al. 2011; Rosmi et al. 2016; Sharma et al. 2013).

It is vital that the pathway from the external heating point to the heated catalyst zone is above the boiling point of the liquid precursor. Otherwise, the vaporized precursor might return to its original form and deposit onto the hot quartz tube. This represents an additional lead time as the contaminated quartz tube will need to be cleaned before a new experimental run can be performed. A magnetic boat setup can also be used for this particular purpose (Rosmi et al. 2016). The magnetic boat carrying the solid or liquid precursor is initially placed at the front-end of a long quartz tube with the metal catalyst in the furnace-heating region. The furnace is then heated to the desired reaction temperature. Once, the desired temperature is reached, the magnetic boat is moved closer to the furnace heating region using a magnet. The distance between the precursor and catalyst must be within the uniform heating zone of the catalyst. Aside from the CVD bubbling setup, similar setup can be performed for a solid precursor. For example, the two-furnace setup has been used multiple times to produce graphene from camphor (Liu et al. 2015a; Somani et al. 2006). The total energy needed in CVD reaction depends on the type of precursor which is used for the whole process (An et al. 2009; Au et al. 1999).

2.1.1 Gaseous carbon precursors

Methane (CH_4), acetylene (C_2H_2) and ethylene (C_2H_4) represent the typical gaseous carbon precursors used for graphene synthesis by CVD. Methane has been the primary source of carbon for the last decade. However, its strong C-H bonds make methane alone poorly reactive and insusceptible from undergoing chemical reaction. With the addition of a suitable catalyst, methane is a reliable carbon source for graphene growth (Kordatos et al. 2016; Lee & Ye 2016). Normally, thermal CVD method using methane requires reaction temperature around 1000 ^{o}C to produce high

quality graphene on metal substrates (Li et al. 2009a; Reina et al. 2009). However, significant progress in decreasing the reaction temperature could be achieved by means of radio frequency plasma (Kato et al. 2016) or microwave plasma assistance (Fang et al. 2016). In the case of radio frequency CVD (RFCVD), the two-dimensional growth rate of graphene is 1000 times larger than thermal CVD at 750 ^{o}C (Kato et al. 2016).

Consequently, compared to thermal CVD, RFCVD can produce graphene with higher quality in similar temperature range. Guo et al. (2015) reported the use of molten Cu while utilizing methane as carbon precursor to synthesize high quality monolayer graphene. Unfortunately, severe Cu evaporation in the reaction chamber occurred simultaneously with the graphene growth stage. Sun et al. (2015) showed the feasibility to directly form large area high quality graphene (I_{2D}/I_G value from 1.6 to 2.5) on solid glasses using methane. Generally, if the I_{2D}/I_G ratio is more than 1.4, it is postulated that it is a monolayer graphene (Bhaviripudi et al. 2010; Park et al. 2009; Pimenta et al. 2007; Reina et al. 2009). Even if the defect level of the as-produced graphene was quite high ($I_D/I_G > 1$), their work has demonstrated the great potential of a cheaper and scalable production route for graphene on insulating solid glasses (Pollard 2015).

After methane, acetylene is the most widely used gaseous carbon precursor to grow graphene via CVD. There have been many studies performed to improve the process ecosystem and graphene quality. Yang et al. (2016) investigated the effect of pre-oxidized pockets of Cu towards low pressure CVD (LPCVD) graphene growth. The Cu foil was folded into pockets with the remaining three sides crimped with a pincer. Then, the pocket was pre-heated to form Cu_2O layer. At low acetylene flow rate, monolayer graphene with low defect density and large domain size was formed. Growth on metal oxides constitute an important step towards graphene-based

electronics (Gottardi et al. 2015). Direct growth of graphene on non-interacting substrates would eliminate the transfer step and avoid the sacrifice of the used metal catalyst which is one of the major roadblocks for cheaper level of graphene synthesis (Reckinger et al. 2014). In addition, Chen and Hsieh et al. (2015) reported that the quality of few layer graphene films could be increased by reducing the carbon concentration via reduction of acetylene flow rate at 600 ^{o}C in a LPCVD setup. The flow rate of acetylene is very vital as elevated acetylene flow-rate may produce 'carbon smoke' that contaminates the CVD chamber. Monolayer graphene can also be grown on polycrystalline Cu foils isothermally in an ultra-high vacuum CVD (UHV-CVD) setup (Mueller et al. 2014). Qi et al. (2013) synthesized bilayer graphene films by atmospheric pressure CVD (APCVD) with acetylene on a Cu foil with different ratio of H_2 and Ar. It is suggested that H_2 played the role of both soft etchant and activator for the bound carbon within the formed graphene. This work showed that H_2 presence is also important for graphene growth using C_2H_2 as carbon precursor. Table 2.1 illustrates in details, examples of graphene grown by CVD using various gaseous carbon precursors.

The use of gaseous carbon precursors is not just limited for graphene films synthesis but other forms of graphene can also be produced. Trinsoutrot et al. (2014) successfully synthesized three-dimensional (3D) graphene networks on Ni foam between 750-850 ^{o}C at ambient pressure using ethylene as carbon precursor. To create 3D graphene, instead of using a thin sheet of metal catalyst foil to capture graphene, metal catalyst such as foam is used. The metal catalyst foam captures graphene in a similar foam structure which has an additional growth axis than the usual 2D lateral structure. The higher reactivity of ethylene as compared to methane allowed deposition temperature to be significantly reduced (Celebi et al. 2011). Addou et al. (2012) have

successfully grown monolayer graphene at ~550 ^{o}C using UHV-CVD from ethylene. At temperature below ~500 ^{o}C, competing carbide phase formation was reported to impede graphene formation. Meanwhile, Sagar et al. (2014) grew graphene on Ni and Cu foils using ethylene as carbon precursor via CVD. The pressure of the reaction was varied from 0.1 to 0.4 MPa to investigate the role of ethylene partial pressure on the growth of graphene layers with 0.2 MPa coming out on top for this particular setup. Besides that, propene (C_3H_6) has also been reported as a carbon precursor to grow graphene on Rh(111) by Gotterbarm et al. (2013).

It is known that CVD using methane and hydrogen entails a high cost of instrumentation together with a high degree of safety precautions (Liu et al. 2014a). They are hazardous and asphyxiating gases since they can displace oxygen in an enclosed space, similarly to ethylene and acetylene. In terms of storage, gas precursor need to be compressed into liquid which is an energy intensive process. However, there are some advantages in using gas precursor. Firstly, gaseous precursor takes less space than liquid and solid precursor as they can be stored in specialized tank. Secondly, industries that produces gas precursors such as biogas as by-product can potentially be a direct supplier line for graphene grown by CVD in the future. Biogas is primarily comprised of methane and carbon dioxide which have been used before graphene synthesis age (Strudwick et al. 2015).

In summary, gaseous carbon precursors are the main source of carbon feedstock for graphene production by CVD; liquid and solid precursors have already shown to have their own advantages. Next section will discuss the various liquid precursors that have been used as carbon source for graphene synthesis by CVD recently.

Table 2.1 Examples of graphene growth conditions using different gas as carbon precursors and their characteristics.

Carbon precursor	Growth substrates	Growth conditions					Graphene morphology		References
		Method	Temp. (°C)	Pressure (kPa)	Flow ratio	Reaction duration (min)	Type	Raman	
CH_4	Rhodium (111) foil	CVD	1000	101	$Ar:CH_4:H_2$ = 200:12:50	10	Multilayer graphene	I_{2D}/I_G = 0.74	(Kordatos et al. 2016)
CH_4	Cu foil	CVD	1000	0.08	$CH_4:H_2$= 5:50	30	Monolayer graphene	I_{2D}/I_G = 2.3	(Lee & Ye 2016)
CH_4	Quartz, borosilicate, sapphire	CVD	1020	101	$Ar:CH_4:H_2$ = 100: 8: 50	180	Monolayer graphene	I_{2D}/I_G = > 2	(Sun et al. 2015)
CH_4	Cu foil Thickness = 6.3 μm	Radio frequency plasma CVD	750	0.005	CH_4: H_2 = 0.2:100	2.5	Monolayer graphene	I_{2D}/I_G = 2.4 I_D/I_G = 0.12	(Kato et al. 2016)
CH_4	Cu foil Thickness = 25 μm	Microwave plasma CVD	650	7	CH_4: H_2 = 5: 500	0.67	Monolayer graphene	I_{2D}/I_G = 2.86	(Fang et al. 2016)
CH_4	Liquid Cu	Rapid CVD	1090	70	$Ar:CH_4:H_2$ = 960:40:5-30	5-10	Monolayer graphene	I_{2D}/I_G = > 2	(Guo et al. 2015)
C_2H_2	Cu foil	(UHV-CVD)	900	5×10^{-8}	$C_2H_2:H_2$ = 80:600		Monolayer graphene	I_{2D}/I_G =1.9-2.6	(Mueller et al. 2014)

Table 2.1 (Continued)

Carbon precursor	Growth substrates	Growth conditions					Graphene morphology		References
		Method	Temp. (°C)	Pressure (kPa)	Flow ratio	Reaction duration (min)	Type	Raman	
C_2H_2	Cu foil Thickness = 50 μm	CVD	1035	0.12	C_2H_2:H_2 = 2.8:80		Monolayer graphene	I_{2D}/I_G = >2 I_D/I_G = 0-0.2	(Yang et al. 2016)
C_2H_2	Ni foil Thickness = 25 μm	Thermal CVD	600	0.13	C_2H_2:H_2 = 12:12		Few layer graphene	I_{2D}/I_G = 0.4 I_D/I_G = 0.28	(Chen & Hsieh 2015)
C_2H_2	Cu foil Thickness = 25 μm	APCVD	1000	101	C_2H_2:H_2:Ar = 1:100:900	10	Bilayer graphene	I_{2D}/I_G = 0.9-1.3 I_D/I_G = 0-0.1	(Qi et al. 2013)
Ethylene, C_2H_4	Ni foam Thickness = 1.8 mm Size = 40 x 60 mm	CVD	750-850	101	C_2H_4 = 15	5-40	3D graphene 15 wt.% of 3D graphene Thickness = 500-1000 nm		(Trinsoutrot et al. 2014)
C_2H_4	Ni (111) single crystal foil	CVD	550	1.3×10^{-6}			Monolayer graphene		(Addou et al. 2012)
C_3H_6	Rh(111) foil	CVD	973–1273	2×10^{-9}			Graphene		(Gotterbarm et al. 2013)

[a] Full-width-half-maximum (FWHM)

2.1.2 Liquid carbon precursors

In the early years of graphene research, methane gas has become the mainstay as it is easy to setup and very stable at elevated temperature. Once the theoretical groundwork was confirmed, the emergence of liquid and solid precursors has become more apparent. They are expected to change the landscape of the graphene synthesis using the CVD method, especially because liquid carbon precursors are easy to use and relatively inexpensive as compared to gaseous ones (Guermoune et al. 2011).

Srivastava et al. (2010) involved the use of hexane (C_6H_{14}) with which large-area continuous and uniform graphene films were formed. This novel method has also allowed an easier way to dope graphene by using various organic solvents as liquid precursors containing dopant atoms. Since, monolayer graphene has zero band-gap, many researchers have identified the use of dopants to construct a band-gap of its own. The use of organic solvents as liquid precursors containing the desired dopant atoms would allow a better process maneuverability in addition to a safer and cheaper synthesis route. Miyata et al. (2010) managed to synthesize single-layer graphene from ethanol (C_2H_5OH) using flash cooling just after the CVD reaction. The detailed comparison of the flash cooling process against normal natural cooling suggested that the single-layer graphene growth occurred from surface diffusion of carbon atoms on Ni substrate and not from bulk carbon precipitation. Hence, liquid precursors also have similar dependency to that of gaseous precursors on the cooling step in order to produce monolayer or bilayer graphene. Kishi et al. (2012) synthesized single-layer graphene on polycrystalline Ni foils by using isopropyl alcohol (C_3H_7OH) with infrared-lamp heating. However, the Full-Width-Half-Maximum (FWHM) of the graphene produced decreased in the Raman mapping using isopropyl alcohol meaning that ethanol was better than isopropyl alcohol for synthesis of single-layer graphene.

Guermoune et al. (2011) reported growth of monolayer graphene using methanol, ethanol and 1-propanol (C_3H_7OH) as liquid carbon precursor on Cu foil. The used precursor was transported through the reaction chamber using 3-5 freeze-pump-thaw cycles at 10^{-6} Torr. Interestingly, for these different chain length precursors Raman spectra of good quality was observed (Pollard et al. 2014). It also was found that the 2D band sharpened while the D band diminished indefinitely as the growth temperature was increased from 650 to 850 ^{o}C. The D band, mode or peak is caused by the disordered structure of graphene. Reduced intensity of the band represents graphene of higher quality. On the other hand, 2D band is closely associated with graphene crystallinity and the sharpening of the band represents for smaller FWHM. The fitted Lorentzian changed from many layers to just one Lorentzian at 850 ^{o}C indicating a good quality monolayer graphene. These findings indicated that the number of bonds in the precursor was less significant than the growth temperature for graphene formation with alcohol.

Dong et al. (2011) were able to synthesize large area, continuous graphene films by APCVD using pentane (C_5H_{12}) or ethanol. The liquid precursors were conveyed through the reaction chamber by using H_2/Ar gas mixture. It was found that graphene grown from ethanol has lower sheet resistance and lower defect density than the one grown from pentane. Besides ethanol, benzene (C_6H_6) is one of the most popular and effective liquid precursors for graphene synthesis. Li et al. (2011b) used benzene as liquid hydrocarbon source and obtained monolayer graphene flakes at a very low reaction temperature of 300 ^{o}C. Benzene molecules were suggested to only need dehydrogenation before it can inter-connect with each other on top of Cu to form graphene. However, no graphene was found due to insufficient energy at 200 ^{o}C, probably temperature was too low to remove hydrogen and form any graphene. This

finding implies that benzene basic structure has an instrumental impact towards the process of graphene synthesis.

John et al. (2011) used ethanol to produce graphene on commercially available stainless steel by using APCVD. Mono-, bi- and tri-layer graphene were formed over a large area verified by optical microscopy and Raman spectroscopy. However, there were a number of oxide species adsorbed on the grown graphene. Choi et al. (2013) used benzene as carbon source to produce monolayer graphene at a very low growth temperature of 300 ^{o}C. By using density functional theory (DFT) and transition state theory (TST) calculations together, the dehydrogenation times (t_D) were calculated. At 300 ^{o}C, the t_D for graphene growth using benzene was estimated to be around 6.5 s while at 200 ^{o}C it was around 20 min. The long t_D rules out the prospect of graphene synthesis at such a low temperature since the molecules must adsorb on the metal catalyst to create carbon-carbon bonds with other dehydrogenated precursor molecules or carbon active species.

A recent publication by Seo et al. (2017) was touted to have find the solution for low cost synthesis of graphene. Here soybean oil was used as the carbon source for graphene synthesis while the main emphasis was on exploiting the ambient-air as the filler for the CVD reaction. Normally, highly purified compressed gases such as N_2, Ar and H_2 were used to create a highly controlled environment for graphene growth. However, single to few layers of continuous graphene films were converted from this renewable natural precursor. It was here again demonstrated that the CVD technique is significant since it opens a new avenue to other types of renewable. There have been several other complex carbon precursors reported in the field of graphene synthesis such as waste chicken fat (Rosmi et al. 2016), commercial palm oil (Salifairus et al. 2016) and refined cooking palm oil (Jalani et al. 2016). Among them, waste chicken

is very promising as carbon precursor for graphene growth. It represents a huge portion of the waste from the poultry processing industries. The technology to convert waste materials to high quality product is always a good way to maximize a process earning potential with existing resources.

Han et al. (2014) used benzene to grow graphene on Cu(111) face in an ultra-high vacuum chamber via CVD. Benzene was purified by cycles of a freeze-pump-thaw method and then dosed into the chamber via a leak valve. XPS characterizations showed that the C=C sp^2 bonding is predominantly preserved with an energy gap of 0.8 eV. In order to modulate electrical properties of graphene, the ability to dope graphene is critical. Conventional CVD method using melamine or ammonia at high growth temperature produced N-doped graphene with high defect density, low carrier mobility and low doping level. On the other hand, Xue et al. (2012) demonstrated the synthesis of highly N-doped graphene at temperature as low as 300 ^oC by using pyridine (C_5H_5N) as carbon precursor (Xue et al. 2012). The doping process depends on formation of carbon-nitrogen bonds competing with carbon-carbon bond creation. High temperature region was found to suppress the doping of nitrogen to favor C=C bond formation (Zhang et al. 2011a). The use of pyridine as carbon precursor allowed the synthesis of graphene at low temperature (Xue et al. 2012). Like for benzene, dehydrogenation pathway of pyridine easily provides active species being then able to deposit onto the metal substrate chosen. Effective dehydrogenation temperature for pyridine is indeed lower than that of its hexahydric ring decomposition temperature (620-650 ^oC) (Johns et al. 1962). If a temperature above 650 ^oC is used, the hexahydric ring decomposes and supplementary energy is needed for C and N atom active species to combine again which is a redundant and a wasteful endeavor. Lastly, a recent study by Jang et al. (2015) showed synthesis of high quality monolayer graphene with optical