DEPOSITION OF GRAPHENE-LIKE CARBON ON COPPER FOIL USING METHANE

by

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LIST OF ABBREVIATIONS

0-D	Zero dimension
1-D	One dimension
2-D	Two dimension
3-D	Three dimension
CDM	Catalytic decomposition of methane
CNFs	Carbon nanofibers
CNTs	Carbon Nanotubes
CNWs	Carbon Nanowalls
CVD	Chemical Vapour Deposition
DFT	Density Functional Theory
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy
FG	Functionalized graphene
GO	Graphene Oxide
HOPG	Highly Oriented Pyrolytic Graphite
ICPCVD	Inductively Coupled Plasma Enhanced Chemical Vapour Deposition
MPCVD	Microwave Plasma Chemical Vapour Deposition
OCM	Oxidative coupling of methane
PECVD	Plasma Enhanced Chemical Vapour Deposition
PMMA	Poly(methyl methacrylate)
POM	Oxidation of methane
RCMGO	Reduced Chemically Modified Graphene Oxide
RF	Radio Frequency
RGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
SRM	Steam Reforming of methane
Syngas	Synthesis gas

TDM	Thermal Decomposition of methane
TEM	Transmission Electron Microscopy
TRG	Thermally Reduced Graphene
UHV-CVD	Ultra-high Vacuum Chemical Vapour Deposition
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

LIST OF SYMBOLS

Π	Pi
Ar	Argon
Å	Angstrom
CH_4	Methane
C_2H_4	Ethylene
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
$C_{12}H_{22}O_{11}$	Sucrose
$C_{13}H_{10}$	Fluorene
CO_2	Carbon Dioxide
Cu	Copper
CuO	Cupric oxide
Cu_2O	Cuprous oxide
H_2	Hydrogen
H_2S	Hydrogen sulphide
HCB	Hexachlorobenzene
He	Helium
Mlpm	Milli liter per minute
N_2	Nitrogen
Ne	Neon
Ni	Nickel
O_2	Oxygen
Pt	Platinum
Si	Silicon
Xe	Xenon

Pemendapan Karbon seperti Graphene pada Kerajang Kumprum menggunakan Metana

ABSTRAK

Graphene, allotrope karbon dua dimensi yang terdiri daripada satu lapisan atom karbon hibrid sp^2 yang disusun dalam konfigurasi heksagon. Sejak graphene ditemui pada tahun 2004, penyelidikan graphene telah meningkat dengan pesat kerana sifatnya yang unik dan luar biasa. Pelbagai kaedah telah dicadangkan untuk mensintesis lapisan graphene di mana kaedah yang paling menjanjikan adalah penggunaan pemendapan wap kimia (CVD). Walau bagaimanapun, masih terdapat banyak masalah mengenai kesan parameter tindak balas dan mekanisme pertumbuhan dalam pertumbuhan pemangkin menggunakan kaedah CVD. Contohnya, pemisahan lapisan graphene daripada substrat dan keseragaman lapisan graphene pada substrat. Dalam kajian ini, penguraian pemangkin metana digunakan untuk menghasilkan lapisan graphene pada kerajang kuprum. Parameter tindak balas dalam proses CVD termasuk tempoh masa, suhu tindak balas dan kadar aliran metana telah diubah untuk mengkaji kesan parameter ini pada sampel graphene. Pelbagai ujian pencirian termasuk Kemikroskopan Elektron Imbasan (SEM), Kemikroskopan Sinar-X Dispersive Tenaga (EDX), Belauan Sinar-X (XRD), Kemikroskopan Raman dan Kemikroskopan Fotoelektron Sinar-X (XPS) telah dijalankan pada sampel graphene yang dihasilkan. Aglomerasi karbon dapat dikesan di sempadan butiran substrat kuprum. Kandungan karbon pada sampel graphene meningkat apabila tempoh masa, suhu tindak balas atau kadar aliran metana meningkat. Ini menunjukkan bahawa lebih banyak atom karbon telah didepositkan pada kerajang kuprum apabila tempoh masa, suhu tindak balas dan kadar aliran metana meningkat. Sebaliknya, peratusan berat aglomerasi karbon di sempadan butiran adalah lebih tinggi daripada pusat butiran dalam semua sampel. Selain itu, keputusan XRD menunjukkan kehadiran puncak pembelauan untuk kuprum-oksida dan puncak grafit kecil pada $2\theta=26.5$ ° yang menandakan pembentukan karbon seperti graphene dengan kuantiti yang sangat rendah di bawah masa reaksi tinggi (90 and 300 saat), suhu reaksi tinggi (1050°C) dan kadar aliran metana (200-600mlpm). Di samping itu, keputusan XPS mengesahkan kehadiran spektrum C1s pada 284.8eV yang berasaskan kewujudan karbon hibrid sp^2 pada sampel. Dengan karbon hibrid sp^2 ini, dipercayai bahawa jumlah struktur seperti graphene yang sangat rendah telah disintesis yang diedarkan secara rawak di permukaan sampel kami. Walau bagaimanapun, tiada puncak Raman di D ($1350cm^{-1}$), G ($1580cm^{-1}$) dan 2D ($2700cm^{-1}$) dijumpai dengan menunjukkan tiada graphene pada sampel tetapi hanya puncak Raman kuprum-oksida dapat dikesan. Daripada keputusan di atas, sampel yang dihasilkan mengandungi lapisan graphene dalam kuantiti yang sangat kecil disebabkan dua batasan: tiada gas hidrogen dan kadar aliran metana yang tinggi telah digunakan. Tambahan pula, kehadiran spesies oksigen di dalam relau CVD telah menghalang pembentukan lapisan graphene dan akhirnya, pembentukan lapisan graphene tidak digalakkan pada substrat kuprum.

Deposition of Graphene-like Carbon on Copper Foil using Methane

ABSTRACT

Graphene, a two-dimensional carbon allotrope that is made up of single-layer sp^2 hybridized carbon atoms arranged in a hexagonal configuration. Since graphene was discovered in year 2004, graphene research has surged exponentially owing to its unique and remarkable properties. A variety of methods have been proposed to synthesize graphene layer of which the most promising method is using chemical vapour deposition (CVD). However, there still lie a lot of issues about effects of reaction parameters and growth mechanism in the catalytic growth using CVD method. For example, is the separation of the graphene from the substrate and uniformity of graphene layer on the substrate. In this study, catalytic decomposition of methane was employed for producing graphene layer on copper foil. The reaction parameters in CVD process including reaction times, reaction temperatures and methane flow rates were varied to study the impact of these parameters on the graphene samples. Various characterization tests including Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were carried out on the graphene samples produced. The agglomerations of carbon were observed at the grain boundaries of the copper substrate. The carbon content on the graphene sample increased when the reaction time, reaction temperature or methane flow rate were increased. This indicated that more and more carbon atoms were deposited on the copper foil when the reaction time, reaction temperature and methane flow rate were increased. On the other hand, the weight percentage of carbon agglomeration at the grain boundaries was higher than that of the centre of grains in all samples. Besides, XRD diffraction peak for the copper oxide and small graphite peak at $2\theta=26.5°$ were seen which signified very low quantity of graphene-like carbon structures were formed under high reaction times (90 and 300 seconds), high reaction temperature (1050°C) and methane flow rates (200-600mlpm). In addition, XPS results confirmed the presence of the C1s spectrum at 284.8eV which ascribed to the existence of sp^2-hybridized carbon on the samples. With this sp^2-hybridized carbon, it is confirmed again very low amount of graphene-like carbon materials were synthesized and distributed randomly on the surface of our samples. However, no Raman peak at D($1350cm^{-1}$), G($1580cm^{-1}$) and 2D($2700cm^{-1}$) were shown to represent the graphene on the sample but only the Raman peaks of copper oxide were detected. From above results, the produced samples contain very small amount of graphene layer due to two limitations: no hydrogen gas and high methane flow rate were used. Furthermore, the presence of oxygen species in the CVD furnace even further hinders the formation of graphene layer and eventually, the graphene layer was less likely to be formed on the copper substrate.

CHAPTER 1

INTRODUCTION

1.1. Catalysis

The term ‘catalysis’ elucidates the chemical reaction is influenced due to the participation of the additional material in the chemical reaction (Berzelius, 1836). The material with the said property is called catalyst which can greatly modify the rate of attainment of chemical equilibrium and maintain its original form. In general, catalysts can be divided into three main types, those are: heterogenous catalysts, homogenous catalysts and biocatalysts or enzymes.

Heterogenous catalysts are different from homogenous catalysts by the phases of the catalysts during the reaction. Heterogenous catalysts could exist in different phases, usually solid, as compared to reactants and products. Heterogenous catalysts are crucial in manufacturing and research fields as they were used in vast variety of chemical processes. For instance, catalytic cracking, production of acids, catalytic reforming, and hydrogenation.

In contrast, homogeneous catalysts are catalysts that are in the same phase as the reactants and products. There are some examples of heterogeneous catalysis: Lewis acids as homogeneous catalyst, general acid and base catalysis and porphyrin complexes (Van Leeuwen, 2004). By comparing heterogeneous and homogeneous catalysts, the former is usually more stable and slower in the degradation of the latter (Spessard & Miessler, 2010).

On the other hand, biocatalysts or enzymes are normally natural proteins that are produced by living organisms and they are used to perform chemical transformation on organic compounds. Biocatalysts are imperative to life because they speed up metabolic reactions to a very tremendous extent, without undergo any change in the biocatalysts in the process. Biocatalysts show some distinct advantages, such as, high specificity, highly biodegradable, high activity under moderate conditions, and are treated as natural products. However, biocatalysts are complex in molecular structures and costly in production costs are the definite disadvantages of the enzymes (Illanes, 2008).

Copper foil is commonly used as the metal catalyst to synthesize graphene films (X. Li, Colombo, & Ruoff, 2016) due to its low carbon solubility (Froumin, Frage, Aizenshtein, & Dariel, 2003). The catalytic activity of copper foil during the CVD is to facilitate the decomposition of carbon precursor and nucleation of graphene lattice (Mattevi, Kim, & Chhowalla, 2011). CVD is also one of the common methods to produce graphene film. Via CVD, the gas precursors react and decompose to adsorb on the surface of the substrate to produce the desired deposit which is graphene layer. Owing to the low carbon solubility in copper, the dominant growth mechanism of graphene on copper is surface adsorption, unlike the segregation and precipitation growth mechanism in high carbon solubility catalyst (X. Li, Cai, Colombo, & Ruoff, 2009).

1.2. Allotropes of Carbon

Allotropy is the attribute of elements to exist in two or more different forms in the same physical states. These allotropes are simply different in the structural configurations where the atoms are associated in different manner. However, allotropy only occurs with certain elements. In previous years, diamond and graphite are the only known allotropes of carbon until the discovery of fullerene in year 1985 (Kroto, Heath, O'Brien, Curl, & Smalley, 1985) and carbon nanotubes (CNTs) in year 1991 (Iijima, 1991). In year 2004, the discovery of graphene has further added to the existed allotropes of carbon.

Carbon atom consists of six electrons, which fill in the atomic orbitals of $1s^2$, $2s^2$ and $2p^2$. Thus, the electrons in the orbitals provide three viable hybridizations in carbon bonding, they are: sp, sp^2 and sp^3 hybridization configurations. Carbon hybridization bonding by sp configuration results in chain structures, sp^2 bonding gives rise to planar structures and sp^3 hybridization produces tetrahedral structures. Therefore, the formation of different allotropes of carbon owes to the different hybridizations in carbon bonding. Figure 1.1. shows a few allotropes of carbon and their atoms arrangement. For instance, diamond is formed where the carbon atoms are connected in a tetrahedral structure, graphite is made up of carbon atoms in sheets of hexagonal lattice and graphene consists of single sheet of graphite layer.

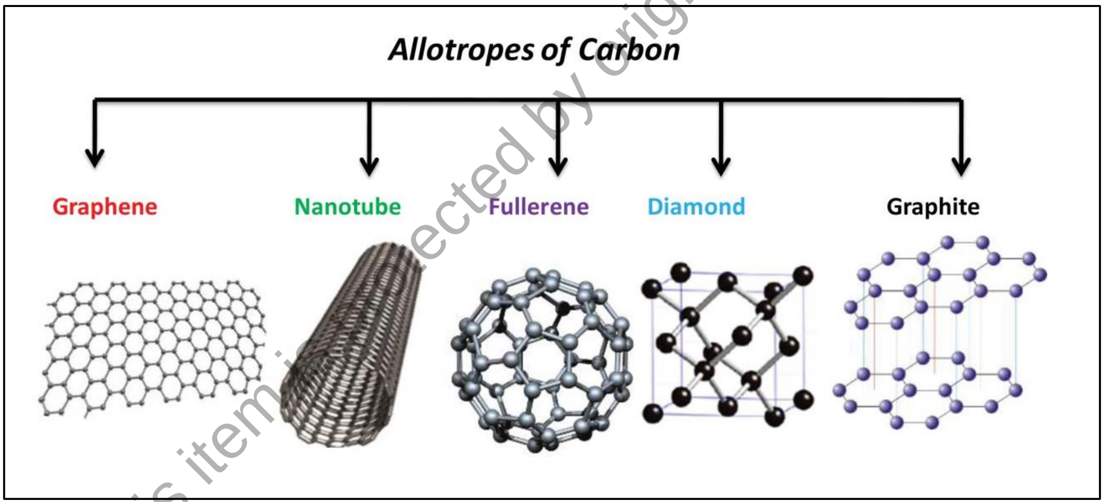

Figure 1.1: Allotropes of carbon (Tiwari et al., 2016).

1.3. Graphene

Graphene is a two-dimensional (2D) material found to be thermodynamically stable in nature. It was thought to be an impossible material to exist until two great scientists, Andrei Geim and Kostya Novoselov isolated graphene layer via a rather simple technique, by regular scotch tape (Novoselov et al., 2004). Since then, the graphene research has developed quickly due to graphene possesses peculiar properties. The extraordinary attributes have intrigued the interest of many researchers and scientists from all over the world and thus, it emerged to be a popular chapter in research field thereafter. The remarkable properties of graphene also show prospect to be used in several promising applications. For example, graphene can be applied in transparent conductive electrodes and photovoltaic cells due to its high optical transparency and high electrical conductivity.

As the simplest allotrope of carbon, graphene is made up of single two-dimensional carbon atoms arranged in hexagonal honeycomb lattice as shown in Figure 1.2. Graphene is the basic building block of other carbon allotropes. For instance, graphene can be wrapped up into fullerene (0-D), rolled up into carbon nanotube (1-D), and stacked up into many layers graphite (3-D). Due to its simplicity and one atom thick, it is the thinnest material known to man and has almost zero mass. Besides, its electrical conductivity of six orders of magnitude is higher than copper, flexible yet harder than diamond and optical transparent. The full potential of graphene will be explored and effectively be utilized by researchers and industrialists in the near future.

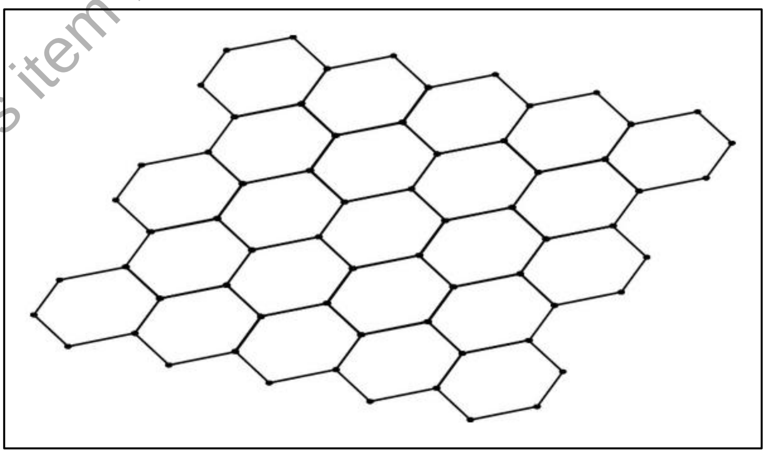

Figure 1.2: Structure of graphene (Jarosz, Skoda, Dudek, & Szukiewicz, 2016).

1.4. Natural Gas

Natural gas is generally considered a non-renewable fossil fuel which is found deep beneath the earth's surface. Natural gas is formed when decomposed plants and animals are exposed to extremely high geological stresses which transformed the organic compounds into natural gas. The transformation process is believed to take millions of years to happen. Natural gas contains a mixture of hydrocarbon gas that are made up mostly of methane, and also including minor amounts of other alkanes. The typical composition of natural gas is shown in Table 1. Natural gas is combustible and it gives off energy when it is burned. However, unlike other fossil fuels, natural gas is comparably cleaner during combustion and emits lower levels of harmful substances into the surroundings. Applications of natural gas is very broad in diversity, in which there are wide variety of ways to convert natural gas into value-added products, such as CNTs, graphene, and other carbon materials. Conversion of natural gas is usually expressed as methane conversion because methane is the primary component of natural gas (70-90%).

Table 1.1: Typical composition of natural gas (Abu Bakar & Ali, 2010).

Chemical Name	Chemical Formula	Percentage (%)
Methane	CH_4	70-90%
Ethane	C_2H_6	0-20%
Propane	C_3H_8	
Butane	C_4H_{10}	
Carbon Dioxide	CO_2	0-8%
Oxygen	O_2	0-0.02%
Nitrogen	N_2	0-5%
Hydrogen sulphide	H_2S	0-5%
Rare gases	Ar, He, Ne, Xe	Trace

1.5. Hydrogen

By viewing the problems of the future shortage supply of petroleum and the upsurge of the prices of petroleum-based fuels, the shifting of the supply of energy towards the alternative fuels sector has been concerned since many years ago. Moreover, the rising of the awareness of the greenhouse gas emissions has further increased the pace to move to another different source of fuels for energy. Consequently, it can be observed from Figure 1.3 that approximately half of the energy consumption globally by the end of the 21st century. This indicates that the shifting of the energy consumption to hydrogen as the alternative energy source is one of the choices for consideration by mankind. On the other hand, hydrogen gas is one of the important gases to be used to synthesize CNTs and graphene in chemical vapor deposition (CVD).

1.6. Methane Activation

Effective implementation of methane for various applications remains to be one of the continuing issues in catalysis. A wide variety of approaches including direct and indirect ways, have been developed for the conversion of methane to more valuable products. Figure 1.4 shows different approaches for methane activation. Oxidative coupling of methane (OCM) became prominent topics in methane activation research after Keller and Bhasin (1982) reported the direct conversion of methane into ethylene for the first time in year 1982. The reason to the fact that OCM became prominent is that OCM offers a cheaper and simpler path for higher hydrocarbon production from methane as compared with hydrocarbon produced by synthesis gas (syngas) approach.

This is followed by reforming of methane to synthesis gas (syngas) which can be carried out by a few methods, as shown in Figure 1.4, i.e. steam reforming of methane (SRM), partial oxidation of methane (POM), and CO_2 reforming of methane. These three reforming processes produce syngas with different CO/H_2 ratios, namely 1:3, 1:2 and 1:1. SRM processes methane at high temperature in a reformer in the presence of metal-based catalyst such as nickel. In addition, SRM represents the current trend for hydrogen production due to methane has the highest H/C ratio which can yield more hydrogen than others (P. Tang, Zhu, Wu, & Ma, 2014). On the other hand, POM process also requires high temperatures (1100 – 1200 K) to obtain the CO_2 and H_2, whereas POM has safety issue to industrial application due to the reaction is difficult to be controlled and would end up in local overheating. Lastly, CO_2 reforming of methane consumes two greenhouse gases (CO_2 and CH_4) and transforms them into valuable syngas. This process provides an effective way to employ low grade natural gases and reduces emission of CO_2 and CH_4 into the atmosphere. Furthermore, the syngas produced can be further processed into methanol which is favorable to be used in production of gasoline. The Fischer-Tropsch process (Vannice, 1976) is another alternative option to process syngas by converting syngas into hydrocarbon.

In addition, direct methane decomposition produces only H_2 and solid carbon without the addition of other substances like the reforming processes which were mentioned above. The carbon byproduct generated from the methane decomposition process is beneficial as they contain different types of valuable carbon, including CNTs, carbon black and graphene.