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