



SYNTHESIS AND CHARACTERIZATION OF
GRAPHENE GROWN BY OPEN FLAME DEPOSITION
TECHNIQUE

BY

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ABSTRACT

Ever since the discovery of graphene with its many unique properties, there has been demand for a production method that could cheaply produce high-quality and large-area graphene. So far, high-quality large-area graphene is grown through chemical vapor deposition either through thermal activation or plasma activation. Presently, there are many barriers to achieve mass production of such graphene. Current complexities in production method only allows batch production at extreme condition to achieve minimal defects in graphene. To achieve an economical method for high-quality large-area graphene production, simplification to the system is a must. Our group proposes to produce graphene through the flame deposition technique which unlike the conventional chemical vapor deposition (CVD) would drastically reduce energy consumption while still producing graphene of a reasonable quality. Amongst all deposition methods, CVD is one of the slowest compared to flame combustion which has the highest deposition rates without involving microwave plasma and direct current arc. We also aim to study the reaction kinetics involved in the production of graphene by this method. To achieve this, a normal horizontal CVD reactor was modified to allow flame deposition of graphene. Graphene deposits grown by flame deposition were characterized by Raman spectroscopy, sheet resistance and electrochemical impedance spectroscopy (EIS). Simultaneously, simulations on the chemical reactions were also performed to obtain information on the equilibrium concentrations of the gas species. It was shown that deposits obtained from the reactor that we designed were comparable to graphene grown flame deposition reported in literature. At its best, multilayer graphene with a monolayer ratio of 1.14 and defect ratio of 0.87 was successfully grown at 750°C through a 10 min reaction using a gas composition of 0.2 atm Ar, 0.3 atm CH₄, 0.5 atm O₂. Compared to literature using 0.07 atm H₂, 0.68 atm CH₄, 0.25 atm O₂, monolayer ratio was 600% higher and defect ratio increased slightly by 9%. Additionally, using equilibrium concentrations of predicted products obtained from simulations of chemical kinetics provided the initial mechanism pathways and a gas phase species that have a close correlation to the deposition rates. Both Arrhenius and van't Hoff analysis shows a single growth mechanism the range of 400°C to 1000°C which further corroborates this. Our investigations revealed that when compared to conventional CVD grown graphene, this technique produces few-layer graphene growth through a different pathway and highlights flame deposition technique as a viable method for graphene production.

خلاصة البحث

منذ تم اكتشاف الجرافين وخصائصه الفريدة، ازداد الطلب على نظام إنتاج بمقدوره إنتاج جرافين ذو جودة عالية وكمية كبيرة وبسعر رخيص. حتى الآن، يتم استخراج كمية كبيرة من الجرافين عالي الجودة من خلال الترسيب إما من خلال التنشيط الحراري أو تنشيط البلازما (Chemical Vapor Deposition) الكيميائي للبخار. حالياً، هناك العديد من الحواجز التي تمنع إنتاج ضخ لهذا الجرافين، وتسمح التعقيدات الحالية في نظام الإنتاج بإنتاج كمية في أقصى الظروف للحصول على أقل نسبة من العيوب في الجرافين. يجب تبسيط النظام لتحقيق أفضل طريقة اقتصادية لإنتاج الجرافين ذو الجودة العالية والكمية الكبيرة. مجموعتنا تقترح إنتاج الجرافين باستخدام فإنها تقلل من، (CVD) تقنية ترسيب الشعلة، والذي بخلاف التقنية التقليدية للترسيب الكيميائي للبخار استهلاك الطاقة بشكل جذري بينما تنتج جرافين ذو جودة معقولة. يُعد الترسيب الكيميائي للبخار واحداً من أبطأ طرق الترسيب، مقارنة بتقنية احتراق النار التي يحتوي على أعلى معدلات ترسيب دون الإستعانة ببلازما الميكروويف وقوس التيار المباشر. نحن نهدف أيضاً إلى دراسة حركية التفاعل المشتملة في إنتاج الجرافين في هذه الطريقة. تم تعديل مفاعل عادي لترسيب كيميائي أفقي للبخار ليسمح بترسيب شعلة الجرافين. تم تمييز الرواسب (sheet) و ورقة المقاومة، (Raman spectroscopy) الناتجة عن ترسيب الشعلة باستخدام مطيافية رامان في (electrochemical impedance spectroscopy) ومطيافية المعاوقة الكهروميكانيكية (resistance) في نفس الوقت، تم إجراء عمليات محاكاة للتفاعلات الكيميائية للحصول على معلومات حول توازن تركيزات أنواع الغاز. أظهرت النتائج أن الرواسب الناتجة عن المفاعل الذي صممناه، يشبه الجرافين الناتج من ترسيب الشعلة الذي ذكر في المؤلفات. تم تطوير الجرافين متعدد الطبقات في أفضل حالاته بنجاح بمعدل أحادي الطبقة 1.14 ونسبة الخلل 0.87 في درجة مئوية 750 من خلال تفاعل طالت مدته إلى 10 دقائق باستخدام تركيبة غاز تبلغ 0.2 ذرة أرغون، 0.3 ذرة ميثان، 0.5 ذرة أكسجين، مقارنة بالمؤلفات التي استخدمت 0.07 ذرة هيدروجين، 0.68 ذرة ميثان، 0.25 ذرة أكسجين، و أحادي الطبقة بنسبة أعلى 600٪ ونسبة العيوب زادت بشكل طفيف بنسبة 9٪. بالإضافة إلى ذلك، باستخدام توازن التركيزات من المنتجات المتوقعة التي تم الحصول عليها من محاكاة الحركية الكيميائية، تم التوصل إلى المسارات الآلية الأولية وأنواع مراحل الغاز التي لها آلية نمو أحادية تتراوح van't Hoff و Arrhenius علاقة وثيقة بمعدلات الترسيب. يظهر كلاً من تحليلي من 400 إلى 1000 درجة مئوية مما يعزز من هذا أكثر. كشفت التحقيقات التي أجريناها أنه عندما يتم مقارنة هذه التقنية مع الجرافين المنتج تقليدياً باستخدام الترسيب الكيميائي للبخار، فإن هذه التقنية تنتج نمواً قليلاً من طبقات الجرافين من خلال مسار مختلف وكذلك تؤكد على قابلية تطبيق تقنية ترسيب النيران لإنتاج الجرافين

APPROVAL PAGE

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DECLARATION

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Firstly, all praise to Allah SWT. Alhamdulillah, it is through his grace that this study has reached its end and yielded beneficial results. It is my utmost pleasure to dedicate this work to my dear parents and my family, who granted me the gift of their unwavering belief in my ability to accomplish this goal: thank you for your support and patience.

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LIST OF ABBREVIATIONS

2D	2-dimensional
AFM	Atomic force microscopy
APCVD	Atmospheric pressure CVD
BF	Bright field
C-C	Carbon-carbon bond
CE	Counter electrode
CEA	Chemical equilibrium with applications
C-M	Carbon-metal bond
CNT	Carbon nanotube
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DF	Dark field
DFT	Density functional theory
DSLR	Digital single-lens reflex
EEC	Equivalent electrochemical circuit
EIS	Electrochemical impedance spectroscopy
FD	Flame deposition
FESEM	Field emission scanning electron microscopy
FFT	Fast Fourier transform
FLG	Few layers graphene
ITO	Indium tin oxide
LEEM	Low-energy electron microscopy

LIF	Laser-induced fluorescence
LPCVD	Low pressure CVD
OM	Optical microscope
PCAH	Polycyclic hydrocarbon
RE	Reference electrode
SSA	Specific surface area
sccm	Standard cubic centimeter per minute
TEM	Transmission electron microscopy
WE	Working electrode

LIST OF SYMBOLS

ΔG_r°	Standard Gibbs reaction energy
ΔG_r	Gibbs reaction energy
P_{CH_4}	Methane partial pressure
P_{H_2}	Hydrogen partial pressure
P_{O_2}	Oxygen partial pressure
k_{-1}	Reaction constant (reverse)
A	Pre-exponential factor
\AA	Angstrom
Ag	Silver
Ag/AgCl	Silver/silver chloride
Ar	Argon
atm	Atmosphere
Au	Gold
C	Carbon
C(gr)	Graphite
C ₂ H ₂	Acetylene
C ₂ H ₄	Ethylene
C ₂ H ₆	Ethane
C ₃ HO	Propioloyl
CH	Methylidyne
CH ₃	Methyl group
CH ₃ O	Methoxy group

CH ₄	Methane
Co	Cobalt
CO	Carbon monoxide
CO ₂	Carbon dioxide
Cu	Copper
Cu ₂ O	Cuprous oxide
E_a	Activation energy
eV	Electronvolt
Fe	Ferum
Ga	Gallium
Ge	Germanium
H*	Hydrogen radical
H ₂	Hydrogen
H ₂ O	Water
HCHO	Aldehydes
HCOOH	Carboxylic acid
I_{2D}/I_G	Monolayer ration
I_D/I_G	Defect ratio
Ir	Iridium
J	Joule
$J K^{-1}mol^{-1}$	Joule per kelvin-mole
K	Kelvin
K_{eq}	Equilibrium constant
kg	Kilogram

kJ mol^{-1}	Kilo joule per mole
m	Meter
m^2	Square meter
$\text{m}^2 \text{ g}^{-1}$	Square meter per gram
Mo	Molybdenum
mV s^{-1}	Meter volt per second
N	Newton
N m^{-2}	Newton per meter square
N_A	Avogadro's number ($6.023 \times 10^{23} \text{ mol}^{-1}$)
NaCl	Sodium chloride
NaSO_4	Sodium sulphate
Nb	Niobium
Ni	Nickel
nm	Nanometer
O_2	Oxygen
$^{\circ}\text{C}$	Celsius
Pt	Platinum
P_x	Partial pressure of gas X
R	Gas constant (8.314)
Rh	Rhodium
Ru	Ruthenium
s	Second
S_h	Area of hexagon cell
Si	Silicon

SiC	Silicon carbide
SiO ₂	Silicon dioxide
T	Temperature
Ta	Tantalum
V	Vanadium
V	Volt
W	Tungsten
W m ⁻¹ K ⁻¹	Watt per meter-Kelvin
W_h	Weight of a hexagon cell
μ	Electron mobility
μm	Micrometer
ρ	Resistivity
k	Reaction constant (forward)

CHAPTER ONE

INTRODUCTION

This chapter provides a brief background on graphene. While it gained prominence in 2004, it has a long history which is introduced here. Its exceptional properties which were the reason it underwent such intense scrutiny are also introduced. A brief discussion of its present situation, challenges and its future could also be found here. Finally, in light of this, the aim of this research will then be explained.

1.1 RESEARCH BACKGROUND

How was graphene even worthy of a Nobel prize when Geim and Novoselov reported their study on it back in 2004. The reason for them winning such a prestigious award lies within the fact that they had proven conventional knowledge to be wrong and opened a yet undiscovered field in science, 2-D materials. Before its discovery, 2D materials of a single atomic thickness were deemed to be thermodynamically unstable. Such standalone 2D structures would have its melting point decreased so much that as it gets smaller, it would either decompose or segregate into agglomerates in order to achieve stability (Geim & Novoselov, 2007). Rather than forming free-standing graphene layers, the formation of soot, nanotubes and fullerenes would take place. Hence, having a free-standing monolayer graphene was considered an impossibility despite knowing that it exists within graphite and the very idea of graphene was just limited to a mere abstract idea. That was the accepted knowledge, at least until 2004.

The scientific world was greatly surprised when Geim and Novoselov reported on the successful synthesis of “graphitic sheets of thickness down to single-layer

graphene” and its exceptional electrical properties (Novoselov et al., 2004). Soon people discovered that other 2D structures from other materials such as boron nitride and molybdenum sulfide could also exist. On top of that, such materials actually display high crystallinity especially in the case of graphene which has extremely good electronic properties which goes against the preconceived notion of how 2D materials are impossible to have these qualities. They have, in essence, discovered a wholly new dimension in material science.

However, graphene has actually been observed for quite some time. Geim (2012) himself have noted various authors that have noted the existence of monolayer graphene without realizing its significance. In 1859, in the process of measuring the atomic weight of graphite, Brodie (1859) had repeatedly oxidized graphite powders and he noted that the resulting flakes were so thin that it was impossible to measure. He termed the product as “graphic acid”. Later, the compound was chemically reduced, and it was observed that the resulting material was graphitic as well, which he then named “graphon”. Now with proper hindsight, we know that what he actually did was a chemical exfoliation of graphite turning it into graphene oxide. In fact, the chemical exfoliation method he reported in his paper is now known as the Brodie method which alongside with Hummer, Staudenmeier, and Hofmann methods is one of the few common chemical exfoliation methods for graphene production. Such methods will be discussed later in the graphene production segment.

The benefit of modern analytical equipment in later years finally yielded an image of the material Brodie produced. Using TEM shown in Figure 1.1, Ruess and Vogt (1948) noted that dried “graphic acid” has a nano-order thickness flake-like structure. Boehm, Clauss, Fischer, & Hofmann, (1962) later observed the reduced flakes also have very thin flake structures with the possibility of it being a monolayer. At the