UNIVERSITI PUTRA MALAYSIA

***PHYSICOCHEMICAL PROPERTIES AND GROWTH KINETICS OF MULTILAYER GRAPHENE BY CHEMICAL VAPOR DEPOSITION FOR GAS SENSING APPLICATION***

MAY ALI MUSLIM

# PHYSICOCHEMICAL PROPERTIES AND GROWTH KINETICS OF MULTILAYER GRAPHENE BY CHEMICAL VAPOR DEPOSITION FOR GAS SENSING APPLICATION

By

**MAY ALI MUSLIM**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy**

**October 2017**

## DEDICATION

*In appreciation of their patience, love, sacrifices, and encouragement*

*I would like to dedicate my thesis to my dear father, my beloved husband Adel Kadhim and my sweetheart daughter Maryam*

*and*

*to the memory of my late mother*

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the Degree of Doctor of Philosophy

**PHYSICOCHEMICAL PROPERTIES AND GROWTH KINETICS OF MULTILAYER GRAPHENE BY CHEMICAL VAPOR DEPOSITION FOR GAS SENSING APPLICATION**

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**October 2017**

**Chairman : Associate Professor Suraya Abdul Rashid, PhD**
**Faculty : Engineering**

This research has employed CVD to obtain high quality and large surface area MLG films on Co-Ni/$Al_2O_3$ substrate for gas sensing applications. The effect of process conditions on the yield of the MLG films grown on the Co-Ni/$Al_2O_3$ substrate was investigated using RSM. The employed parameters were reaction temperature (700-800ºC), nominal catalyst (Co/Ni) composition (0.3-0.7), and ethanol flowrate (9-11ml/min) at a constant pressure. A total of 20 experimental runs were performed for the optimum growth condition of 77% yield of the MLG film. The optimal results show that the 800°C reaction temperature, a catalyst ratio of 0.3/0.7 with an ethanol flow rate of 11 ml/min were the best conditions for a scalable yield of large-area and high-quality MLG for gas sensing applications. The experimental test results show a correlation between the RSM predicted and experimental responses. The obtained MLG films was systematically characterized by using FESEM, EDX, HRTEM, RS, XRD, TGA and DTG, TEM analysis, FT-IR analysis and XPS analysis. All these characterizations confirm the excellent quality and number of layers of the MLG.

Furthermore, the growth kinetics of MLG was investigated by varying the reaction temperature and monitoring the partial pressure of the ethanol ($C_2H_5OH$) as well as that of hydrogen. The data obtained were fitted to the Langmuir-Hinshelwood kinetic model for the estimation of the reaction rate constants at different temperatures. The results showed that the reaction rate constant increased with temperature and the apparent activation energy of 13.72 kJ $mol^{-1}$ was obtained indicating a relatively fast rate of MLG growth. The parity plot obtained for the comparison of the predicted and observed rate of $C_2H_5OH$ consumptions showed an excellent agreement. This study is important for understanding the growth

kinetics of MLG in order to develop appropriate measures that can control the production of MLG thin films for use in the electronic industries.

Finally, the use of MLG thin films as a sensor material for gas sensing device has been demonstrated. The gas sensing characteristics of MLG films was investigated by measuring the resistance across the MLG film at different time while passing the gas mixtures. When different gases are introduced to the test chamber at a steady flowrate, the resistance increased and reached to a saturation level. The findings showed that the MLG-based sensor device was most sensitive to $NH_3$ gas and $H_2$ gases whereas it shows the least sensitivity to $CH_4$ gas. This study has demonstrated the suitability of the MLG as a material that can be employed as sensor device for gas sensing applications most especially $NH_3$ and $H_2$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

**SIFAT FIZIKOKIMIA DAN KINETIK PERTUMBUHAN LAPISAN GRAFIN OLEH PEMENDAPAN WAP KIMIA BAGI APLIKASI PENGESANAN GAS**

Oleh

**MAY ALI MUSLIM**

**Oktober 2017**

**Pengerusi : Profesor Madya Suraya Abdul Rashid, PhD**
**Fakulti : Kejuruteraan**

Penyelidikan ini telah menggunakan CVD untuk menghasilkan kawasan permukaan yang luas dan berkualiti tinggi filem MLG di atas substrat Co-Ni/$Al_2O_3$ untuk aplikasi penderiaan gas. Kesan keadaan proses terhadap hasil filem MLG yang tumbuh di atas substrat Co-Ni/$Al_2O_3$ diselidik menggunakan RSM. Parameter yang digunakan ialah suhu tindak balas (700-800$^oC$), komposisi pemangkin nominal (Co/Ni) (0.3-0.7), dan kadar aliran etanol (9-11ml/min) pada tekanan malar. Sebanyak 20 eksperimen telah dilakukan untuk mendapatkan keadaan pertumbuhan optimum bagi hasil 77% filem MLG. Hasil optimum menunjukkan yang suhu tindak balas 800 °C, nisbah pemangkin 0.3/0.7 dengan kadar alir etanol 11ml/min adalah kombinasi terbaik bagi hasil berskala permukaan-luas dan berkualiti tinggi MLG untuk aplikasi penderiaan gas. Ujian eksperimen menunjukkan terdapat korelasi antara tindak balas yang diramal dengan eksperimen. Filem MLG yang diperolehi telah dianalisis menggunakan FESEM, EDX, HRTEM, RS, XRD, TGA dan DTG, TEM, analisis FT-IR dan analisis XPS. Kesemua karakteristik ini mengesahkan kualiti dan bilangan lapisan MLG yang cemerlang.

Sebagai tambahan, pertumbuhan kinetik MLG diselidik dengan mempelbagaikan suhu tindak balas dan pemantauan tekanan separa etanol ($C_2H_5OH$) dan juga gas hidrogen. Data yang diperolehi disesuaikan dengan model kinetik Langmuir-Hinshelwood untuk menganggarkan kadar reaksi yang malar pada suhu yang berbeza. Keputusan menunjukkan bahawa kadar tindak balas malar meningkat mengikut suhu dan tenaga pengaktifan ketara 13.72 kJ mol$^{-1}$ diperolehi yang menunjukkan kadar pertumbuhan MLG yang pesat secara relatif. Plot pariti yang diperoleh untuk perbandingan kadar yang diramal dengan yang diperhatikan bagi penggunaan $C_2H_5OH$ menunjukkan kaitan yang sangat baik. Kajian ini penting untuk memahami kinetik pertumbuhan MLG untuk membangunkan langkah-

langkah yang sesuai yang dapat mengawal pengeluaran filem tipis MLG bagi kegunaan dalam industri elektronik.

Akhirnya, penggunaan filem tipis MLG sebagai bahan pengesan untuk peranti penderia gas telah dapat ditunjukkan. Karakteristik penderiaan gas filem MLG telah diselidik dengan mengukur rintangan pada filem MLG pada masa yang berbeza-beza sementara ia melepasi campuran gas. Apabila gas yang berbeza-beza digunakan di dalam kebuk uji pada kadar aliran yang tetap, rintangan meningkat dan mencapai tahap tepu. Hasil kajian menunjukkan bahawa peranti penderia yang berasaskan MLG sangat sensitif terhadap gas $NH_3$ dan gas $H_2$ tetapi kurang sensitif terhadap gas $CH_4$. Kajian ini menunjukkan kesesuaian MLG sebagai bahan yang boleh digunakan sebagai peranti penderia untuk aplikasi penderiaan gas terutamanya $NH_3$ dan $H_2$.

## ACKNOWLEDGEMENTS

In awareness that this work could not be accomplished without the God willing, hereby "Praise be to God, the Lord of the World."

Then, it is pleasure to give my deepest gratitude to my supervisor Associate Professor Dr. Suraya Abdul Rashid who has supported me throughout my work with her patience, knowledge, helpful discussions and encouragement during this research. Furthermore, I wish to thank my committee; Associate Professor Dr. Nizar Hamidon for his valuable knowledge, encouragement and advices. I would also like to extend my most sincere thanks to Dr. Faizah MD Yasin for her continuous support throughout this research.

My deepest gratitude goes to my father for his unflagging love and support throughout my life, this dissertation is simply impossible without you. There is a very important person that without him, his care and love I wouldn't achieve all I have had achieved. I am forever indebted to my husband, Adel Kadhim Alattar for helping me achieve my goal. I also want to acknowledge and thank the people whose live was most affected by this work, my sweetheart daughter Maryam.

In my daily work, I have been blessed with a friendly and cheerful group of fellow students. Alia, and Suzan, Vector and Frienda who have helped me. Thank you all for being great friends and brothers.

I am highly grateful to my two brothers, my nephews, my parents in law, my sisters in law and my brothers in law for their encouragement and love from thousands of miles away. I owe you all more than just my thanks. May Allah’s graces and blessings be forever yours.

I certify that a Thesis Examination Committee has met on 12 October 2017 to conduct the final examination of May Ali Muslim on her thesis entitled "Physicochemical Properties and Growth Kinetics of Multilayer Graphene by Chemical Vapor Deposition for Gas Sensing Application" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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This thesis was submitted to the Senate of the Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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I hereby confirm that:

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## LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| ANOVA | Analysis of Variance |
| MLG | Multilayer graphene |
| SLG | Single layer graphene |
| FLG | Few layer graphene |
| FET | Field Effect Transistor |
| CVD | Chemical Vapour Deposition |
| CCD | Central Composite Design |
| BBD | Box Behnken Design |
| HRTEM | High Resolution Transmission Electron microscopy |
| SAED | Selected Area Electron Diffraction |
| Nm | Nanometer |
| eV | Electron volte |
| θ | Bragg angle |
| h | Hour |
| min | Minutes |
| SEM | Scanning electron microscopy |
| EDX | Energy dispersive X-Ray |
| LH | Langmuir-Hinsherwood |
| TEM | Transmission electron microscopy |
| FTIR | Fourier transforms infrared spectroscopy |
| XRD | X-ray diffraction |
| TGA | Thermo gravimetric analysis |

| | |
|---|---|
| RSM | Response Surface Methodology |
| XPS | X-ray Photoelectron Spectroscopy |
| RS | Raman Spectroscopy |

CHAPTER 1

# INTRODUCTION

## 1.1 Background

The interest in graphene as an important material began in 1947 with the work of Wallace on the band structure of graphene (Wallace, 1947). Wallace's discoveries showed that graphene was a potential starting material for understanding the electronic properties of three-dimensional graphite. This discovery lead to the publication of the first TEM images of few-layer graphite by Ruess and Vogt in 1948 (Ruess and Vogt, 1948). As a follow up to this publication, the formation of single graphene layers was observed directly using electron microscope, as reported by Boehm et al. (Boehm et al., 1962). Two decades later, advancements in technology lead to the synthesis of single-layer graphene grown epitaxially on top of other materials. The synthesized epitaxial graphene was reported to consist of a single-atom-thick hexagonal lattice of $sp^2$-bonded carbon. It was not until 2004 that Novoselov and Geim managed to produce graphene flakes through mechanical exfoliation. There has been growing interest in the synthesis of graphene since the first published article in 2004 by Novoselov et al. (2011).

Graphene, a two-dimensional form of carbon with a honeycomb-like lattice arrangement, has been reported as the main building block for all categories of graphitic materials (G. Wang et al., 2008). Graphene exhibits a two-dimensional structure with distinct atomic and electronic properties, which justify its application in electronics and photonics (V. Singh et al., 2011). The growing interest in graphene applications as semiconductors in electronics can be attributed to its high carrier mobility (>100,000 $cm^2\ V^{-1}\ s^{-1}$) as well as saturation velocity (the maximum attainable velocity for a charge carrier in a semiconductor in the presence of a very strong electric field, i.e., $5\times10^7$ cm $s^{-1}$) (Lightcap, Kosel, and Kamat, 2010; Moon et al., 2012; Williams and Kamat, 2009). Furthermore, graphene has been reported to display excellent mechanical properties (stiffness and tensile strength), high thermal conductivity and high current carrying capacity (Lian et al., 2010; J. Yu, Liu, Sumant, Goyal, and Balandin, 2012). Similarly, the application of graphene in photonics is primarily due to its excellent optical properties over a wide range of wavelengths without constraints such as local defects (Bao and Loh, 2012; M. Liu, Yin, and Zhang, 2012; Zhipei Sun et al., 2010). Graphene, as a non-silicon-based material, has the potential to be a driving force in nanotechnology (Soldano, Mahmood, and Dujardin, 2010). Its applications will help develop integrated circuits at a smaller scale, comparable with that of silicon-based complementary metal-oxide-semiconductor (CMOS) technology (Xiangyu Chen et al., 2010; Lemme, Echtermeyer, Baus, and Kurz, 2007). In addition, graphene is characterized by excellent physicochemical properties, such as a theoretically large surface area, high intrinsic mobility, high Young's modulus and thermal conductivity as well as high optical transmittance (Terrones et al., 2010). Its high specific surface area makes it appealing as a support for the synthesis of metal-based catalysts. Graphene-supported catalysts have been reported in reactions such as biomimetic oxidation, photocatalysis, hydrous hydrazine decomposition, hydrogen production from a silicon photocathode and the enhanced electrocatalytic oxidation of methanol (Kaminska et al., 2012; Khalid et al., 2012; Zhao, Zhan, Tian, Nie, and Ning, 2011).

In most of the reported work on graphene synthesis, methods such as exfoliation and cleavage, chemical reduction of exfoliated graphite oxide and chemical vapor deposition (CVD) have been employed (Mattevi, Kim, and Chhowalla, 2011; Stankovich et al., 2007; Wang et al., 2009). The exfoliation mechanism entails a process whereby graphene can be peeled from bulk graphite, layer by layer (Yi and Shen, 2015). To achieve this, resistance from van der Waals attraction between adjacent sheets must be overcome. The application of mechanical exfoliation pioneers the discoveries of the excellent electronic and mechanical properties of graphene (Chen, Duan, and Chen, 2012). However, one major challenge of the exfoliation technique is the low graphene yield obtained from this process (Qian et al., 2009). Graphitic materials can also be obtained from the chemical reduction of graphene oxide (Gilje et al., 2007; Stankovich et al., 2007). Reducing agents, such as hydrazine hydrate, are usually employed at a controlled temperature (Robinson et al., 2008). Often times, the reducing agent is very toxic and hence poses health risks to the environment (Marcano et al., 2010).

In addition, the use of extremely strong reducing agents (e.g., lithium aluminum hydride) has been problematic due to side reactions with dispersing solvents for graphene oxide (Dreyer et al., 2015). Among the several methods reported in the literature, the CVD synthesis of graphene is a promising method for the large-scale production of graphitic materials (Mattevi et al., 2011). Reports have shown that the diffusion of the carbon into the metal thin film is the main growth mechanism (Wei et al., 2009). Although graphene (also known as single-layer graphene) has excellent properties for several applications, there is growing interest in applications of multi-layer graphene (MLG) in the field of materials science and engineering. MLG can best be defined based on its applications and physical properties. According to its electrical properties, a material is considered to be MLG if it is thin enough for its carrier density to be tuned by the electrostatic gating. Additionally, based on its thermal properties, if the material has a Raman spectrum distinct from that of the bulk graphite, such material is considered to be MLG (Shahil and Balandin, 2012). Finally, MLG is a graphene thin film with weak van der Waals interactions between its layers that shows superb electronic properties with high potential for sensing applications.

CVD is one of the most suitable methods for the formation of MLG films for gas sensing applications. Since the use of a catalyst is essential for MLG growth by CVD, the choice of the catalyst to be used is crucial. Previous studies have investigated MLG film growth on metal catalysts such as Co, Ni, W, Ti and Ru (Seah, Chai, and Mohamed, 2014). The results from these studies showed that Co and Ni displayed suitable growth with improved film qualities (in terms of crystallinity) under high-temperature conditions. Nevertheless, in the temperature range of 600-700 °C, the surface morphology of the Ni catalyst was found to be severely degraded due to agglomeration during CVD. To prevent this agglomeration, the use of bimetallic catalysts has been proposed. Ueno et al. (2013) employed a Co-W bimetallic catalyst for MLG growth by CVD. An MLG film with high crystallinity and without any agglomeration was obtained using $C_2H_5OH$ as the carbon source. The use of $C_2H_5OH$ as the carbon source for graphene synthesis is advantageous compared to other carbon sources, such as $CH_4$ and $C_2H_4$. $C_2H_5OH$ is less expensive, readily available and less flammable than $CH_4$ or $C_2H_2$. Moreover, $C_2H_5OH$ is a good hydrogen carrier candidate, which implies that $H_2$ is not required when using $C_2H_5OH$ as the carbon source in CVD (Jiang et al., 2013).

Moreover, dielectric substrates, such as alumina ($Al_2O_3$), are good choices for use in CVD because of their strong chemical reactivity with carbon atoms and their applicability to high-temperature-demand applications (Chai et al., 2011; Villacampa et al., 2003). This dielectric substrate can be used in combination with metal substrates, such as Ni and Co, that are known to have high carbon solubility. Due to the high solubility of carbon on these metal substrates, these substrates play significant roles in the formation of epitaxial or MLG growth, which are required for gas sensing applications due to the production of a large surface area for gas adsorption (Chai et al., 2011; Villacampa et al., 2003). Thus, the similar lattice structure of Ni and Co to that of graphene, along with their high carbon solubility, is extremely favorable, and these atoms play a significant role in controlling defect generation during graphene growth by reconstructing graphene sheets using annealing defects (Jiang et al., 2014; Yu et al., 2008; Villacampa et al., 2003). However, the growth of MLG using a bimetallic Co-Ni catalyst on an $Al_2O_3$ substrate via CVD has not been reported to the best of the author's knowledge. In the present study, the $Al_2O_3$ substrate serves as a support for the Co-Ni bimetallic catalyst. One important feature of the Co-Ni catalyst for MLG synthesis is it tendency to facilitate high carbon solubilization. Moreover, the kinetics of MLG growth on the Co-Ni/$Al_2O_3$ catalyst via CVD has also not been investigated. Therefore, this study aims to investigate the synthesis, characterization, optimization and kinetics of MLG growth on the Co-Ni/$Al_2O_3$ catalyst via CVD. The synthesized MLG was employed in gas sensing applications.

## 1.2 Problem statement

Recently, MLG growth on metals and alloys has been the main focus of studies involving gas sensing applications (Liu et al., 2010; Shahil and Balandin, 2012). However, in depth analysis on the effect of the process conditions, such as CVD temperature, catalyst ratio and hydrocarbon flowrate, on the MLG synthesis has not be given full attention in literature. Research has shown that these parameters play significant roles in the MLG growth. Hence, the investigation of these process conditions viz. their interaction effects on the MLG growth will enable the control of MLG yields and quality.

Moreover, reports have shown that the growth of graphene on metallic substrates by CVD is usually dominated by crystallization from the substrate surface, which is initially supersaturated with carbon adatoms (Celebi et al., 2013). This implies that growth is independent of hydrocarbon addition after the nucleation phase. In the present study, it is postulated that MLG growth can be controlled via the adsorption-desorption dynamics and the kinetic processes of the catalytic dissociation and dehydrogenation of the carbon source (ethanol) on the bimetallic Co-Ni catalysts. To date, kinetic studies on the synthesis of graphene have been performed using metal catalysts such as Cu (Celebi et al., 2013; Nano, Shu, Chen, and Academy, 2012), SiC (Tromp and Hannon, 2009) and Ru (Dong and Frenken, 2013). It is therefore important to investigate the kinetics of MLG growth on a Co-Ni catalyst by CVD in order to determine the rate controlling mechanism that govern the MLG growth.

This study proposed the use of the synthesized MLG films as a sensor material for gas-detecting applications towards ammonia ($NH_3$), hydrogen ($H_2$) and methane ($CH_4$) gases. Although, there is a well-established method of gas detection such as the electrochemical detection techniques. However, the electrochemical detection technique has the disadvantage of narrow or limited temperature range, short or limited shelf life, cross sensitivity of other gases, and shorter life span compared to the solid-state resistive-type metal oxides sensors which is the focus of this study. The choice of the $NH_3$, $H_2$, and $CH_4$ gases used in this study is hinged on the risks associated with the usage of the gases as well as their health hazards when exposed in little concentration. $NH_3$ which is extensively used as feed stock for the production of fertilizer and other valuable chemicals can cause serious health risk in a long-term exposure greater than 7 h. Moreover, $H_2$ and $CH_4$ gases are classified as highly flammable gases when they come in contact with a source of ignition. It is therefore desirable to develop a selective and sensitive $NH_3$, $H_2$, and $CH_4$ gas sensor which is one of the main focus of this study.

Furthermore, studies have shown that gas sensing plays significant role in several applications, such as, environmental monitoring, medical diagnosis, industrial production and safety. Even though solid-state gas sensors possess advantages such as small size, low power, high sensitivity and low cost for detecting very low concentrations of a wide range of gases in the range of parts-per-million (ppm), one of the major constraints of their applications is their instability and limited measurement accuracy. Hence, this study is positioned to tackle these challenges by employing high-quality MLG synthesized on a Co-Ni/$Al_2O_3$ substrate via CVD as a potential material for gas sensing applications.

## 1.3 Objectives of the Study

The objectives of this study are as follows:

i. To investigate the physicochemical properties of MLG grown on a Co-Ni/$Al_2O_3$ substrate.

ii. To investigate the effect of CVD process parameters such as the temperature, catalyst ratio and ethanol flowrate on the MLG yield as well as obtain the optimum conditions for maximum MLG yield using RSM.
iii. To investigate the kinetics and mechanism of MLG thin film growth by the tail-gas-based CVD process.
iv. To determine the performance of MLG in gas sensing applications.

## 1.4 Scope of the Study

i. Synthesis of Co-Ni/$Al_2O_3$ substrates with varying Co: Ni ratios using the drop casting method.
ii. The growth of MLG on the Co-Ni/$Al_2O_3$ substrate by CVD and subsequent characterization by X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) Raman spectroscopy (RS), Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscope (FESEM), High-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED) and $N_2$-physisorption analysis.
iii. Parameters such as the CVD temperature, catalyst ratio and ethanol flow rate were investigated at 700-800 $^oC$, 0.3-0.7 and 9-11 ml/min, respectively using RSM and DoE to determine the optimum conditions that gave the maximum MLG yield.
iv. The kinetic measurements were performed over the temperature ranged of 700-800 $^oC$ under atmospheric condition.
v. The Langmuir-Hinshelwood kinetic model was employed to estimate parameters such as activation energy and the rate constants.
vi. The suitability of the as-synthesized MLG for gas sensing applications was evaluated using $NH_3$ $CH_4$, and $H_2$ gasses.
vii. The dynamic response of the MLG to different concentration of the $NH_3$ (0.06-1%), $CH_4$ (0.06-1%), and $H_2$ (1%-2%) gasses was measured as a function of resistance and current.

## 1.5 Thesis layout

This thesis is divided into seven chapters. Chapter 1 is the introduction of the thesis and gives background on the study of graphene and multi-layer graphene synthesis and their applications. Additionally, the problem statement, objectives and scope of the study are also presented. In chapter 2, a detailed literature review on graphene, multi-layer graphene, synthetic methods, applications, kinetics and optimizations is reported to identify knowledge gaps and the novelty of this study. In chapter 3, the detailed materials and experimental methods for synthesis and characterization of the catalyst and MLG are presented. Additionally, the results obtained from the experimental procedures are discussed. In chapter 4, the method, results and discussion of MLG optimization by RSM are discussed in detail. Chapter 5 presents the methods, results and discussion on the growths kinetics and mechanism of MLG. In chapter 6, the methods, results and discussion on the application of MLG for gas sensing applications using $NH_3$, $CH_4$ and $H_2$ are presented. Finally, chapter 7 includes a summary, the general conclusions and recommendations for future research.

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