

**AN INVESTIGATION ON THE SYNTHESIS AND  
CHARACTERIZATION OF FLEXIBLE 3D  
GRAPHENE FOAM**

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**UNIVERSITI SAINS MALAYSIA**

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CHARACTERIZATION OF FLEXIBLE 3D  
GRAPHENE FOAM**

by

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**Thesis submitted in fulfilment of the requirements for the  
Bachelor's Degree of Engineering (Honours) (Aerospace Engineering)**

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## ENDORSEMENT

I, Syamil Bin Ahmad Huzaifah hereby declare that all corrections and comments made by the supervisor and examiner have been taken consideration and rectified accordingly.



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Date: 10 July 2021



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Date: 10 July 2021



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Name: ASLINA ANJANG AB RAHMAN

Date: 10/07/21

## DECLARATION

This thesis is the result of my own investigation, except where otherwise stated and has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any other degree.

*Syamil*

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(Signature of Student)

Date: 10 July 2021

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## LIST OF SYMBOLS

$\omega_G$	Band position in wavenumbers
$n$	Number of graphene layers present

## LIST OF ABBREVIATIONS

0D	Zero Dimensional
1D	One Dimensional
2D	Two Dimensional
3D	Three Dimensional
CNT	Carbon Nanotube
CNWs	Carbon Nanowalls
CVD	Chemical Vapor Deposition
FWHM	Full Width at Half Maximum
GO	Graphene Oxide
OSP	On-site Polymerization
PAH	Polycyclic Aromatic Hydrocarbon
PECVD	Plasma Enhanced Chemical Vapor Deposition
PMMA	Poly(methyl methacrylate)
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
VSGAs	Vertically Standing Graphene Arrays



**CHEMOMETRICS AND PATTERN RECOGNITION METHODS**  
**WITH APPLICATIONS TO ENVIRONMENTAL AND QUANTITATIVE**  
**STRUCTURE-ACTIVITY RELATIONSHIP STUDIES**

**ABSTRACT**

Carbon materials, with their many different allotropes, have played important roles in our everyday lives as well as the advancement of material science and engineering. Since 2004, 2D graphene materials with their unique and interesting features have received significant attention after the discovery of 0D C<sub>60</sub> and 1D carbon nanotube. 2D graphene is a single atomic layer of sp<sup>2</sup> bonded carbon atoms which crystallizes in a honeycomb/hexagonal structure. It has an outstanding electrical property due to its two-dimensional shape, as well as a very high carrier mobility that is symmetrical for electrons and holes. Over the last decade, 3D structures have been produced out of graphene sheets which give rise to a new type of graphene materials called 3D graphene which had better and improved electrical conductivity, easy of functionalization, and large area.

In this final year project, the synthesis of 3D graphene foam on copper foam was produced using methane (CH<sub>4</sub>) as a carbon source through chemical vapor deposition (CVD) process. The effect of some CVD parameters on the growth of 3D graphene on copper foam template such as growth temperature and growth time were manipulated. Afterwards, the sample was coated with poly(methyl methacrylate) (PMMA) to preserve the 3D graphene during transfer process. Then, the copper matrix was removed using nitric acid (HNO<sub>3</sub>). Next, the PMMA coating was removed by heating the samples in a Carbolite furnace. Afterwards, the 3D graphene samples

produced were characterized by Raman spectroscopy and Thermogravimetric Analysis (TGA).

Based on the  $I_D/I_G$  ratio, the sample produced at 1000°C, 40 minutes growth time has the fewest number of defects while the sample produced at 800°C, 40 minutes growth time has the highest number of defects. As the growth temperature increased from 800°C to 1000°C, the  $I_D/I_G$  ratio decreased which indicates that the graphene synthesized at 1000°C has fewer defects and better crystallinity than graphene synthesized at 800°C. Based on the  $I_D/I_G$  ratio approximates that all the graphene samples produced were multi-layered. Based on the  $I_{2D}/I_G$  ratio, the sample produced at 1000°C, 10 minutes is single layer graphene while the rest of the samples are few-layered graphene.

The final mass percentage of 3D graphene and PMMA-coated 3D graphene sample is 18.46% and 13.84%, respectively. The remaining mass was the residue that was left behind which indicates that the 3D graphene was not completely pure and can be considered as low purity. Apart from that, a greater amount of heat energy is required to burn carbon nanotubes (CNT) compared to 3D graphene. This suggests that CNT is more heat resistant and have higher thermal stability than 3D graphene.

## ABSTRAK

Karbon dan pelbagai alotropinya, telah memainkan peranan penting dalam kehidupan seharian kita dan juga dalam kemajuan sains material dan kejuruteraan. Sejak tahun 2004, bahan graphene 2D dengan ciri unik dan menariknya telah mendapat perhatian yang besar setelah penemuan 0D C<sub>60</sub> dan 1D karbon nanotube. 2D graphene adalah lapisan tunggal karbon atom terikat sp<sup>2</sup> yang mengkristal dalam struktur sarang lebah / heksagon. Ia mempunyai sifat elektrik yang luar biasa kerana bentuknya dua dimensi, serta mobiliti pembawa yang sangat tinggi yang simetri untuk elektron dan lubang. Selama dekad yang lalu, struktur 3D telah dihasilkan dari lembaran graphene yang menimbulkan jenis bahan graphene baru yang disebut 3D graphene yang mempunyai kekonduksian elektrik yang lebih baik, banyak kegunaan, dan permukaan yang lebih luas.

Dalam projek tahun akhir ini, sintesis busa graphene 3D pada busa tembaga dihasilkan menggunakan metana (CH<sub>4</sub>) sebagai sumber karbon melalui proses pemendapan wap kimia (CVD). Pengaruh beberapa parameter CVD terhadap pertumbuhan graphene 3D pada templat busa tembaga seperti suhu pertumbuhan dan masa pertumbuhan dimanipulasi. Selepas itu, sampel dilapisi dengan poli(metil metakrilat) (PMMA) untuk mengekalkan 3D graphene semasa proses pemindahan. Kemudian, matriks kuprum dikeluarkan menggunakan asid nitrik (HNO<sub>3</sub>). Seterusnya, lapisan PMMA dikeluarkan dengan memanaskan sampel di relau Carbolite. Selepas itu, sampel 3D graphene yang dihasilkan dicirikan oleh Raman spektroskopi dan Thermogravimetric Analisis (TGA).

Berdasarkan nisbah I<sub>D</sub>/I<sub>G</sub>, sampel yang dihasilkan pada suhu 1000°C, masa pertumbuhan 40 minit mempunyai jumlah kecacatan paling sedikit sedangkan sampel

yang dihasilkan pada suhu 800 ° C, masa pertumbuhan 40 menit mempunyai jumlah kecacatan tertinggi. Apabila suhu pertumbuhan meningkat dari 800°C hingga 1000°C, nisbah  $I_D/I_G$  menurun yang menunjukkan bahawa graphene yang disintesis pada 1000°C mempunyai lebih sedikit kecacatan dan kristalinitas yang lebih baik daripada graphene yang disintesis pada 800°C. Berdasarkan nisbah  $I_D/I_G$ , boleh dikatakan bahawa semua sampel graphene yang dihasilkan ialah berlapis-lapis. Berdasarkan nisbah  $I_{2D} / I_G$ , sampel yang dihasilkan pada suhu 1000 ° C, 10 menit adalah graphene lapisan tunggal sementara sampel yang selebihnya adalah graphene berlapis-lapis.

# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Carbon is an essential element for humankind due to its contribution in the advancement of our modern civilization. The first carbon nanostructure discovered is fullerene or  $C_{60}$  which is a zero-dimensional (0D) nanoparticle discovered by Kroto and his associates in 1985 followed by Kratschmer and his associates in 1990 (Sur, 2012). The second important carbon nanostructure is carbon nanotubes (CNT) which is a one-dimensional (1D) nanomaterial of  $sp^2$  bonded carbon founded by Iijima in 1991 (Iijima, 1991). After comprehensive research on CNT and their analogues, a two-dimensional (2D) carbon nanostructure called graphene, which is the composing unit of graphite, has received unparalleled attention ever since Geim and Novoselov et. al first isolated them experimentally in 2004 (Novoselov et al., 2004).

Graphene is a flat, single atomic layer of  $sp^2$ -bonded carbon atoms tightly arranged in a 2D hexagonal lattice, and is a basic building block of all other dimensional graphitic materials (Figure 1.1) (Geim & Novoselov, 2007). Graphene can be wrapped to form 0D fullerenes, rolled to form 1D nanotubes, or stacked to form 3D graphite.

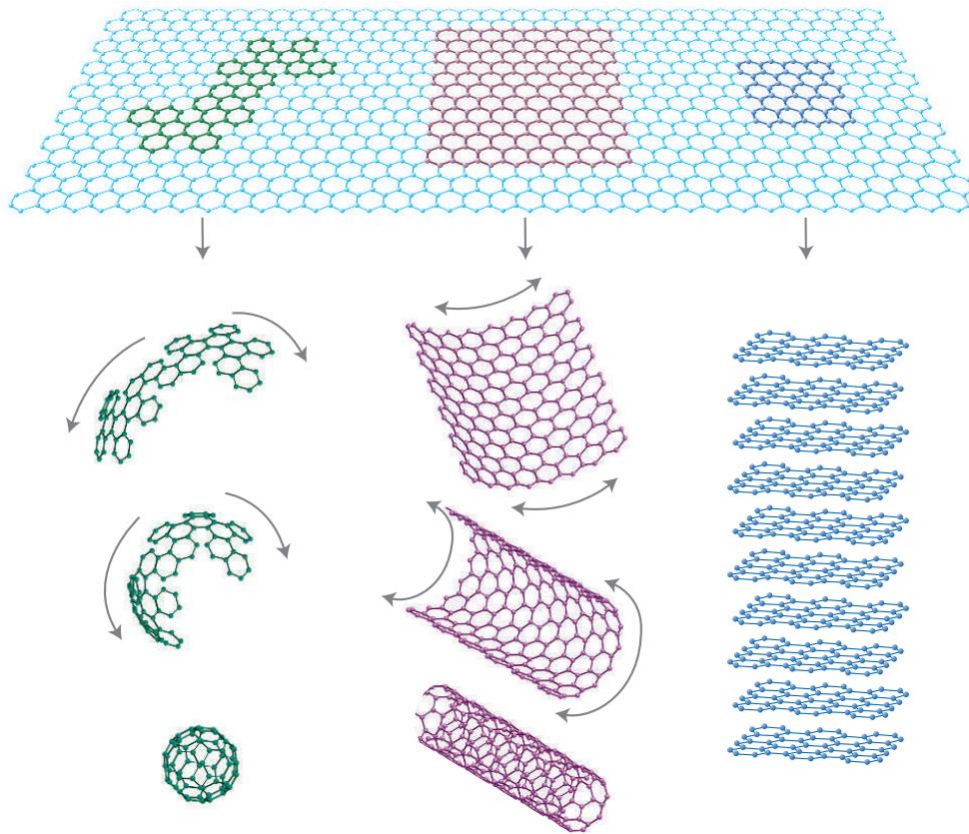


Figure 1.1 Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite (Geim & Novoselov, 2007).

Graphene is the thinnest material with an extraordinarily large specific surface area due to its honeycomb-like network of  $sp^2$  hybridized carbon atoms arranged in a single plane with a long range  $\pi$ - $\pi$  conjugation (Zhuxing Sun et al., 2020). Graphene has sparked interest in many fields such as materials science, medicine, chemistry, physics, and mechanics due to its unique and impressive physical and chemical properties (Huang et al., 2020; Yang & Wang, 2020). Ever since the 2D carbon nanostructure first scientific discovery, it has drawn a lot of attention from researchers because of its unusual structures and many intriguing properties, such as strong mechanical strength, massive electron mobility, and outstanding thermal conductivity, high elasticity, optical transparency, high electrical conductivity, large surface area, high Young's modulus and strength, excellent light transmission, and chemical stability

(Zhuxing Sun et al., 2020). Graphene started gaining attentions mainly because of its ambipolar field effect (Novoselov et al., 2004), anomalous quantum Hall effect, giant intrinsic carrier mobility, high sensitivity to external charge, and so forth (Zhuxing Sun et al., 2020).

Theoretically, graphene has been studied since 1947 (Sur, 2012), but it was only discovered by British physicists Andre and Novoselov by isolating sheets of graphene from graphite using adhesive ‘Scotch’ tape in 2004 (Novoselov et al., 2004). Ultimately, Andre Geim and Konstantin Novoselov were awarded and granted the Nobel Prize in Physics 2010 for their pioneering work and groundbreaking research on the two-dimensional material graphene. For several years, graphene was just a term used to describe the properties of different carbon-based materials. One explanation for this is that no one expected graphene to exist in its free state, and it was thought to be thermodynamically unstable at finite temperatures in terms of the creation of curved structures like soot, fullerenes, and nanotubes.

Nonetheless, the hurdles and obstacles in producing high quality (single layer and defect free) graphene restricted its widespread use in physical devices (Zhuxing Sun et al., 2020). On the other hand, this has fueled the growth of graphene-based research in chemistry, resulting in the development of new methods of synthesizing graphene materials with various properties and broader range of applications (Novoselov et al., 2012).

## **1.2 Problem Statement**

2D graphene films and/or flakes have been widely studied and used in electronics and photonics up to this point, but the industrial application of large-scale

graphene-based materials remains a significant challenge. The main issue when used in large-scale production for various practical applications, such as electrode materials in energy storage and conversion systems is that 2D graphene layers appear to restack and lose their distinct properties, which causes in performances that falls well short of theoretical values (Huang et al., 2020). An effective solution to this problem is to create the 2D layers into well-organized and interconnected 3D structures that can preserve the excellent properties of the 2D graphene materials while still being easily used without the need for restacking.

Many studies in recent years have concentrated on the design and fabrication of self-supporting and/or freestanding 3D graphene materials to utilize the intrinsic properties of graphene, resulting in the publication of some well-engineered ultra-thin graphite films/foams. It was discovered that by transforming 2D graphene sheets into 3D porous structures, the specific surface area and mechanical properties can be greatly improved while maintaining high electrical conductivity and chemical stability (Huang et al., 2020).

Since 2009, many graphene-sheet-based 3D architectures, such as macroscopic graphene hydrogel, graphene foam, graphene sponge, microscopic flower-like graphene, and porous graphene framework, have been synthesized from three different materials which are graphene oxide (GO), hydrocarbons, and inorganic carbon compounds (Zhuxing Sun et al., 2020). Firstly, 3D graphene has been synthesized from GO by methods such as hydrothermal reduction, chemical reduction, laser casting, and 3D printing. Secondly, it has also been synthesized from hydrocarbons via chemical vapor deposition process, and on-site polymerization processes. Thirdly, 3D graphene has been synthesized from inorganic carbon compounds as well based on a sequence of



alkali-metal-involved chemical reaction methods. The applications of graphene materials have expanded to a much broader with the advancement of these 3D graphene architectures such as batteries, supercapacitors, sensors, solar cells, solar-thermal conversion facilities, conductors, catalysis, thermal management systems, environmental decontamination, and so on (Zhuxing Sun et al., 2020).

Despite the rapid growth and development of 3D graphene materials over the last decade, with a plenty of new synthesis methods and application areas explored, an understandable definition and categorization for 3D graphene architectures has yet to be established. In short, there is still a lack of a detailed and complete overview of the 3D graphene (Zhuxing Sun et al., 2020).

Chemical vapor deposition is regarded as the most promising technique of producing graphene film in largescale (Al-Hilfi, 2018). Since Somani's first successful attempt at CVD graphene growth in 2006 (Somani et al., 2006), there has been a significant research effort to develop large areas of graphene for industrial applications. Despite the fact that a 30-inch single layer graphene was created using the CVD process, the mechanism of graphene formation is still unknown (Al-Hilfi, 2018).

Hence, a study focusing on the role of some variable parameters used during the CVD growth of 3D graphene on copper foam substrate is needed. In this paper, an investigation on how the effect of growth temperature and growth time affects the number of layers and presence of defects of the synthesized 3D graphene foam was conducted. Developing an understanding of the role of some variable parameters used during the CVD growth of 3D graphene on copper foam will not only assist in a better knowledge of the growth mechanism of 3D graphene, but it also controls the number of graphene layers which is an important aspect in electronic applications.

### **1.3 Objectives**

1. To develop 3D graphene foam using chemical vapor deposition method.
2. To study the effect of growth temperature and the growth time during CVD process on the presence of defects of 3D graphene produced.
3. To study the effect of growth temperature and the growth time during CVD process on the number of layers of 3D graphene produced.
4. To study the purity and thermal stability of the 3D graphene produced.

### **1.4 Scope of Work**

For this final year project, the method used to produce 3D graphene foam is chemical vapor deposition method. There are two parameters used during the CVD growth of 3D graphene on copper foam substrate catalyst which includes the growth temperature in the reaction chamber, and the growth time. The flow rates of methane are kept constant for all growth temperature and growth time.

Even though graphene foam CVD growth has been published in several publications (Banciu et al., 2017; Paronyan et al., 2017), the samples presented in this paper have been specifically tailored to our synthesis setup. This final year project used a simple, scalable, and cost-efficient method to synthesize 3D graphene foam on copper foam using methane,  $\text{CH}_4$  as a carbon source through chemical vapor deposition process. The effect of some CVD parameters on the growth of 3D graphene on copper foam template such as growth temperature and growth time were manipulated. After that, the sample was coated with poly(methyl methacrylate) (PMMA) as a post-growth stabilizer of the graphene foam to preserve the structure of graphene foam during transfer process. Then, the copper matrix was removed using nitric acid,  $\text{HNO}_3$  to remove the copper matrix. Next, the PMMA coating was removed by heating the

samples in a carbolite furnace. Afterwards, the 3D graphene samples produced were characterized using Raman Spectroscopy and Thermogravimetric Analysis (TGA).

## **1.5 Significant of Research**

The significance of this final year project is that this research can be referred by others when they wanted to produce 3D graphene foam using chemical vapor deposition method. This is because this research gives the reader the information about the presence of defects and number of layers of 3D graphene produced based on the growth temperature (800°C and 1000°C) and growth time (10, 20, 40 minutes).

## **1.6 Thesis Outline**

This thesis is subdivided into five main chapters as stated below:

Chapter 1 gives a brief introduction and explained about carbon nanostructure especially 2D graphene, its surprising ground-breaking discovery, and remarkable properties. This chapter also brought out readers about the advantage of 3D graphene over 2D graphene, and various methods of producing 3D graphene particularly chemical vapor deposition. The manipulated variable parameters of CVD process and the significant of this research were also discussed at the end of Chapter 1.

The related literature is reviewed in Chapter 2, to present the general definition, classifications, and brief history of 3D graphene. The review also covers three methods currently used to synthesize 3D graphene from graphene oxide, hydrocarbons, and inorganic compounds.

Chapter 3 contains the method of study of the dissertation. In further depth, the experiment setup such as choosing the substrate, CVD system, gas flow rate calibration

of the experiment are explained in this chapter. This chapter also describes the experimental procedure in detail of the 3D graphene synthesis via CVD, 3D graphene transfer by removing the copper substrate using nitric acid, and 3D graphene characterizations using Raman spectroscopy and Thermogravimetric Analysis (TGA).

Chapter 4 covers the results of the experiments and discussion by identifying and analyzing the G, D, and 2D band of Raman spectra as well as graph of mass percentage against temperature of 3D graphene foam samples. The aim of this chapter is to summarize the data obtained, interpret the data, and report the findings. The characterization methods used was able to determine the presence of defects, number of layers, purity, and thermal stability of the 3D graphene produced in different growth temperature (800°C and 1000°C) and growth time (10, 20, 40 minutes).

Finally, Chapter 5 summarize my dissertation and proposes some future work. This chapter will present the significant of this research as the foundation for the future production of a better 3D graphene foam. The conclusion is stated and drawn based on the parameter correlation in the experiments. Some of the future research suggestions are made to further experiment as well as some ideas to improve the synthesis of 3D graphene foam.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 3D Graphene Materials

Despite the advent of numerous 3D structures made up of graphene layers, many important questions remain unanswered, including: What is "3D graphene"? and Is graphite considered a "3D graphene material"?

This chapter provides the definition and classifications of "3D graphene materials". Moreover, the function and significance of 3D graphene materials in the carbon family as well as the history of 3D graphene materials, are briefly discussed.

##### 2.1.1 General Definition

It is important to understand the meaning of "graphene," "graphene layer," "2D graphene crystals," and "2D graphene materials", before defining 3D graphene materials.

When an isolated graphene was thought and believed to be unattainable, Hans Peter Boehm and colleagues described "graphene" as a hypothetical last member of infinite size of the polycyclic aromatic hydrocarbon (PAH) series in 1986 (Zhuxing Sun et al., 2020). As stated in previous chapter, graphene is a single layer of carbon atoms tightly packed into a 2D hexagonal lattice crystal structure with  $sp^2$  hybridization (Novoselov et al., 2004). Both of these meanings are similar. The term "graphene layer" is widely used to describe the sheet of  $sp^2$  hybridized carbon within a carbon material. The term "graphene layer" has been widely used to describe the sheet of  $sp^2$  hybridized carbon within a carbon material. For instance, graphite consists of graphene layer. The electronic spectrum of single layer, bilayer, and few-layer (3–10 layers) graphene are used to distinguish and classify them as three distinct forms of "2D graphenes", while

structures above 10 graphene layers are regarded as thin graphite films. This is due to the fact that only monolayer and, to a reasonable extent, bilayer graphene exhibit simple electronic spectrum of zero-overlap semi metals or zero-gap semiconductors with a single electron–hole mode. The electronic structure which consists of multiple charge carriers gets more complicated and complex gradually as the number of layer increases more than two, until it reaches 10 layers, which is the limit of graphite (Zhuxing Sun et al., 2020).

An ideal graphene is chemically inert and a zero-band gap semiconductor. Disordered graphene sheets having edge defects, topological defects, heteroatom dopants or functional groups, were widely investigated with the purpose of opening its band gap as well as expanding its usage and implementation in luminescence, catalysis, electrochemical reactions, electronic devices, and so on. This gave rise to a new series of materials known as "graphene-like materials," "disordered graphene," "porous graphene," and other names such as "graphane" for hydrogenated graphene. All of the graphene-based materials, including the previously described 2D graphene crystals are classified as members of the larger family of “graphene materials” or “2D graphene materials” (Zhuxing Sun et al., 2020).

At the moment, 3D graphite materials lack an exact and precise definition, making it confusing and unclear about whether graphite can be considered as a 3D graphene material. As a matter of fact, the purpose of researchers working and developing on 3D graphene architectures is to understand the high-performance and stable graphene materials using a smart 3D arrangement of graphene-based layers instead of graphite-like configuration, which results in a drastic loss of unique properties of few-layer graphene such as surface area, etc.(Zhuxing Sun et al., 2020). Thus, it is

possible to distinguish between 3D graphene materials and 3D structured graphene materials that are not graphite in nature. In order to preserve the basic characteristics of graphene materials, it is preferable for the graphene walls of a 3D graphene material to have 10 or fewer graphene layers. Figure 2.1 shows the relationships between graphene, 2D graphene materials, 3D graphene materials, and graphite.

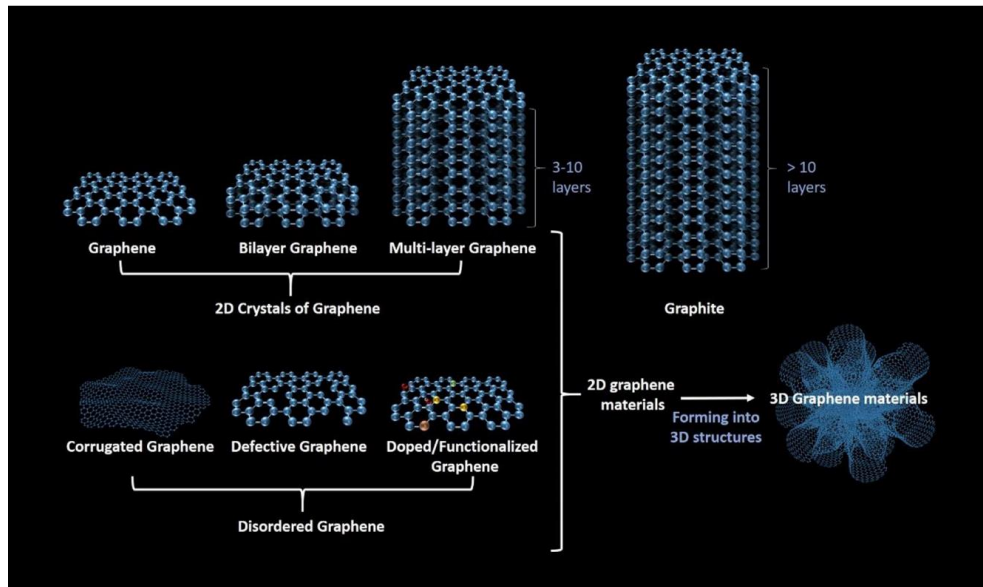


Figure 2.1 Diagram of the relationships between graphene, 2D graphene materials, 3D graphene materials, and graphite (Zhuxing Sun et al., 2020).

## 2.2 Classifications

According to Figure 2.2, 3D graphene materials can be categorised into several different forms based on the currently published research.

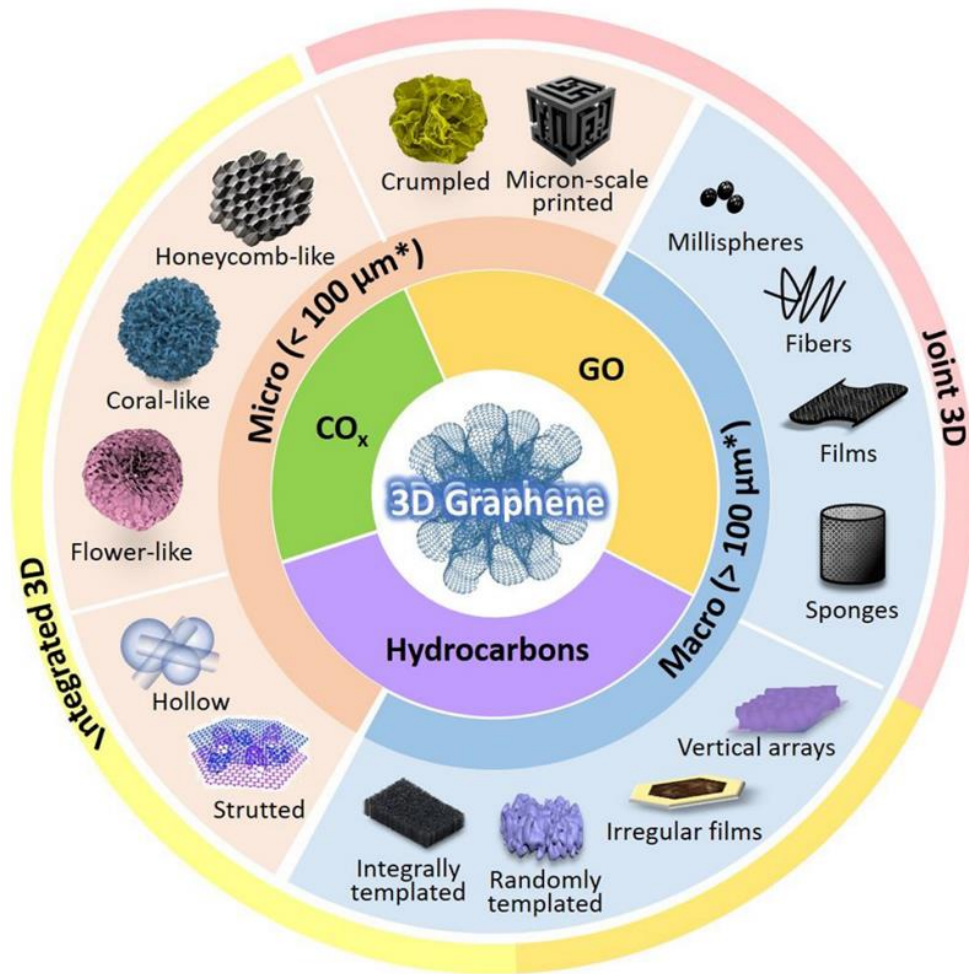


Figure 2.2 Various forms of 3D graphene materials are depicted in this diagram. Microscopic graphene materials have a length of less than  $100 \mu\text{m}$  in all three dimensions, whereas macroscopic graphene materials have a length of more than  $100 \mu\text{m}$  in one or more dimensions (Zhuxing Sun et al., 2020).

3D graphene architectures can be divided into two categories with regards to engineering scales. First category is macroscopic 3D graphene materials, or also known as 3D graphene macrostructures, with a length of more than  $100 \mu\text{m}$  in one or more dimensions. They include the macro 3D graphene millispheres, fibers, films, and monoliths like aerogels, sponges, and foams. Second category is microscopic 3D graphene materials, or also known as 3D graphene microstructures, with a length of less than  $100 \mu\text{m}$  in all dimensions. They appear as powders in macro-scale but have 3D structures in micrometer-scale or nanometer-scale (Zhuxing Sun et al., 2020).



There are two types of 3D graphene constructions can be distinguished based on the forms of connections. The first type is joint 3D graphene architectures, where several single sheets of graphene are mainly interconnected through van der Waal's forces. Second type is integrated 3D graphene networks, where the chemical bonds connect and bind the carbon atoms continuously. The integrated 3D graphene structures exhibit better integrity with improved conductivity, and mechanical strength, in comparison to the joint 3D graphene materials, when mass density is kept constant.

3D graphene materials can be classified into three main groups based on the synthesizing precursors, that is, 3D rGO (reduced GO), hydrocarbon, and inorganic carbon compounds. The vast majority of 3D graphene materials produced from GO precursors are jointly structured and macro monoliths (Zhuxing Sun et al., 2020). Although there are few micro 3D rGO structures, they are gaining a lot of interest. Hydrocarbons can be used to produce 3D graphene macro/micro structures by using the appropriate of substrates. In general, hydrocarbon-synthesized 3D graphene materials in a single substrate is integrated into a micro structure or macro network. 3D graphene foams produced using in situ formed gaseous templates or lots of granular templates may be integrated or joint (Zhuxing Sun et al., 2020). Similar thing may be made for the randomly standing graphene films or vertically aligned graphene arrays produced through laser or plasma treatment of hydrocarbons. The 3D graphene architectures produced from inorganic carbon compounds were recently reported to be integrated and typically micrometer in size (Zhuxing Sun et al., 2020).

### **2.3 Brief History**

Ruoff and colleagues used vacuum filtration to produce free-standing paper-like film of GO with a thickness of 1–30  $\mu\text{m}$  in 2007, thinking that macroscale free-standing

paper-like materials are significant for technological applications (Zhuxing Sun et al., 2020). The GO sheets are automatically tiled into a paper like film during the directional flow, exactly like CNTs when they form into bucky paper. However, the GO film outperformed and was better than the bucky paper formed from CNT in terms of resilience. This paper-like film composed of densely stacked GO layers can be reduced thermally or chemically to form a porous rGO film. Moreover, Ruoff and co-workers also used chemical reagent like hydrazine hydrate and reduced exfoliated GO sheets to form microscopic 3D graphene materials with poor arrangement which are also considered as randomly crumpled, aggregated, and thin graphitic sheets (Zhuxing Sun et al., 2020).

Until 2009, after carbon aerogels was widely and extensively developed, Wang and Ellsworth published 3D graphene aerogel produced from graphite oxide/water dispersion by freeze-drying them followed by annealing at temperature of more than 200°C (Zhuxing Sun et al., 2020). In 2010, Shi and colleagues used hydrothermal process on GO at temperature of 180°C to self-assembled 3D graphene hydrogels. They used the generated rGO hydrogel as an electrode in a supercapacitor device without using any binder or conducting agent. Almost around the same time, Liu and Seo's co-workers used a simple concentrated vacuum method followed by reduction of high temperature to obtain rGO sponges. The hydrothermal self-assembly 3D graphene can be considered as breakthrough in engineering of macroscopic 3D graphene and attracted a lot of attention, possibly due to the simple synthesis process and high probability to obtain graphene-based composites and functionalized/modified graphene monoliths (Zhuxing Sun et al., 2020).

Afterwards, both the synthesis and applications of rGO 3D architectures and composites attracted a lot of attention. Several techniques to produce 3D graphene macrostructures from GO have been successively developed, such as the most recent 3D printing technology, wet spinning, ice templating, solvothermal reaction, mild chemical reduction, in-plane pore/defect engineering, tape casting, laser scribing, and electrochemical construction (Zhuxing Sun et al., 2020).

Although the majority of the early 3D graphene materials were produced from GO, most of these materials relied on GO self-assembly, which is an unpredictable and somewhat random process with stochastic pore distributions. On top of that, a large number of 3D rGO architectures exhibited fairly poor intrinsic conductivities due to inadequate GO reduction in the majority of synthesis techniques (Zhuxing Sun et al., 2020). While new techniques and attempts are being made to manipulate the reduction and formation of GO to 3D rGO with desired properties, Cheng and colleagues published a report in 2011 on the use of chemical vapour deposition (CVD) technique as bottom-up solution to 3D graphene. The technique generally relies mostly on the catalytic breakdown of hydrocarbons on 3D templates. A macroscopic structure of graphene with a foam-like continuous network can be obtained by using methane as the carbon source, porous nickel foam as a sacrificial template, after a thorough template-etching process using inorganic acid. The CVD grown 3D graphene foam is an integrated 3D monolith of perfectly interconnected graphene structure that enables and gives it an outstanding electric conductivity, as opposed to the structure of 3D graphene produced from GO which consists of many small sheets. Furthermore, the 3D graphene material may also be very light, and by varying the reaction time and the flow rate of carbon source, the number of layers of graphene can be easily controlled. A variety of templates such as metals, dielectrics, semiconductors, and in situ formed gases have

been investigated using the bottom-up templated method have been investigated (Zhuxing Sun et al., 2020).

## **2.4 3D Graphene Assembling Based on GO**

GO is the usual form of chemically modified graphene. It is widely used component to make 3D graphene materials, particularly 3D graphene macrostructures (Z. Chen et al., 2019; Kim et al., 2017). 3D rGO is an essential member of the 3D graphene family due to its versatile and simple synthesis technique, as well as its ability to achieve a wide range of pore morphologies (Z. Chen et al., 2019). Generally, the production of 3D graphene materials from GO involves two steps which is the fabrication of the 3D shapes and the reduction of GO. Both steps can be carried out either simultaneously or consecutively.

### **2.4.1 Self-Assembling of GO**

The 3D self-assembling of GO usually occurs by the gelation of their suspensions which is further facilitated by the subsequent drying process. The coexistence of functional groups that contains oxygen and the graphene basal plane gives GO an amphiphilic property. Correspondingly, there are two kinds of forces between the suspension's layers, that is, binding attractions due to hydrogen bonding, hydrophobic effect,  $\pi$ - $\pi$  interaction, etc. as well as electrostatic repulsions due to hydration and functional groups (Z. Chen et al., 2019). Generally, the attraction and repulsion force that exists are balance. The gelation of GO sheets into 3D networks occurs when the balance force breaks due to weakened repulsion forces or enhanced binding interactions. Electrostatic repulsion could be reduced by varying the surface chemical states, for example, by reducing the pH value of the suspension to decrease

the degree of ionization of carboxyl groups. The attractions among the sheets can be effectively improved by increasing the concentration of GO.

#### **2.4.2 Reduction of 3D GO Assembly**

The purpose of reducing GO is to eliminate the functional groups that contains oxygen and recover the graphene layers. Usually, it is easy to remove the in-plane hydroxyl and epoxy groups on GO. On the other hand, it is hard to remove the ester, carboxyl, and carbonyl groups located at the defective parts or at the boundaries (Z. Chen et al., 2019). The surface groups on the GO sheets in 3D GO frameworks might change significantly throughout the reduction process. When the GO is reduced, it is possible to enhance the  $\pi$ - $\pi$  interaction. At the same time, the removal of functional groups causes the disorders, defects, wrinkles, and curvatures to appear in the rGO sheets, which makes the produced 3D graphene having porous structure.

#### **2.4.3 Concurrent Reduction and 3D Construction**

Generally, a fairly high concentration of GO suspension is used to simultaneously reduced and 3D assemble the GO. When the repulsion force between the sheets is reduced and functional groups on the GO are eliminated by the reducing agent/atmosphere, the nearby and adjacent sheets in the suspension interconnect with each other, which results in the creation of a 3D network. However, the huge distance between the nearby sheets will prevent the sheets from forming contacts if the concentration is insufficient, which leads to only rGO suspension, instead of a 3D rGO monolith.

Throughout the reduction process, parallel stacking of rGO may possibly happen when the binding interactions increases up to some extent. It is unlikely for large rGO sheets to stack in parallel orientation because of its limited mobility as well as the

presence of interlayer solvent molecules or reduction products. However, parallel stacking may occur for small-sized GO because of the fairly weak repulsion forces, as well as its inability to encapsulate water molecules.

#### **2.4.4 Strategies for Synthesis of 3D rGO**

Several techniques have been explored and created to produce 3D rGO over the last decade. There are many effective methods to simultaneously reduced GO and produce 3D rGO, such as chemical, electrochemical, thermal, hydro/solvothermal, and photon-induced reduction. Freeze-casting is an effective method by using growing ice as the in-situ template to adjust and modify the inner 3D structure of GO or rGO gels. The effective methods in moulding GO sheet into a variety of forms, includes 3D printing, wet spinning, and anti-solvent and capillary compression, which are subsequently reduced to form 3D rGO structures.

#### **2.5 3D Graphene Construction from Hydrocarbons**

Although GO was the most direct precursor for the synthesis of 3D graphene materials, particularly macroscopic 3D graphene materials, the integrity of 3D graphic structures produced from GO is rather low. Furthermore, it is hard to control their microscopic geometries and random stacks of the interlayer. On the other hand, the production of integrated 3D graphene structures with controlled micro- and macroscopic 3D morphologies is possible using bottom-up methods with 3D substrates as templates and hydrocarbons as precursors.

Various bottom-up synthesis methods for 3D graphene materials using various hydrocarbons have been developed. The most famous and popular technique is the chemical vapor deposition (CVD) method (K. Chen et al., 2018; Z. Chen et al., 2019). An ideal method to produce vertically aligned graphene arrays is plasma-enhanced

chemical vapor deposition (PECVD) (K. Chen et al., 2018; Georgakilas et al., 2016; Wu et al., 2016). 3D graphene materials with various characteristics can be effectively obtain by performing on-site polymerizations for solid or liquid state precursors, with catalytic or in-situ generated gaseous templates through laser irradiation or treatment at elevated temperature (Zhongxin Sun et al., 2018).

### **2.5.1 Chemical Vapor Deposition (CVD)**

Chemical vapour deposition (CVD) is a method for converting a gaseous precursor into a solid substance on a heated substrate (Zhuxing Sun et al., 2020). CVD is the most commonly used bottom-up synthesis method to produce interconnected 3D graphene networks on 3D structured substrates (K. Chen et al., 2018; Z. Chen et al., 2019).

#### **2.5.1(a) General Transformation Steps**

The 3D graphene growth process through CVD method is similar to 2D graphene. In general, the CVD method for the synthesis of 3D graphene is conducted at 500–1100°C with volatile or gaseous hydrocarbon as the carbon source which flows into a quartz tube that contains a 3D porous catalytic or noncatalytic substrate for 5–10 min, and cooled down quickly to room temperature (K. Chen et al., 2018). The method consists of five main steps. First step is the gaseous precursor is transported onto the substrate. Second step is dissociation or dehydrogenation of the hydrocarbon. Third step is diffusion or dissolution of carbon atoms into or on the substrate. Fourth step is graphenization, also known as nucleation of graphene by surface collision or segregation. Fifth step is epitaxial growth of graphene either vertically or occasionally in plane, with active carbon species at its edge (Huaping Wang & Yu, 2016).

Active carbon species diffuse and bind to graphene edges after nucleation, resulting in an epitaxial growth process (Zhuxing Sun et al., 2020). Once two grains collide and combine, the disorientation between them causes the formation of grain boundary, which could lead to ripples and wrinkles on the graphene sheets. Although these structures are defective, they can cause the 3D graphene materials obtained to change its mechanical properties and have diverse 3D structures (Cao et al., 2018).

### **2.5.1(b) Choice of Carbon Sources**

Until now, various volatile and gaseous hydrocarbons as source of precursors for CVD grown 3D graphene materials were investigated. The size of carbon nuclei produced during CVD process is influenced by the amount of carbon atoms in the hydrocarbon precursors. Due to its stability and robustness, methane ( $\text{CH}_4$ ) is the most common carbon source for CVD, which helps to facilitate the homogenous and uniform growth of graphene layers (Zhuxing Sun et al., 2020). Nonetheless, to obtain high-quality graphene using methane requires a relatively high reaction temperature ranging from 900–1050°C. Because of their lower dissociating energies, carbon compounds like ethylene ( $\text{C}_2\text{H}_4$ ) and acetylene ( $\text{C}_2\text{H}_2$ ) with high carbon contents may be broken down at a lower temperature around 750°C. Alcohols such as methanol ( $\text{CH}_3\text{OH}$ ) and ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) have also attracted a lot of interest because they are safer and less expensive. Since the molecular structure of benzene ( $\text{C}_6\text{H}_6$ ) is analogous and similar to the basic unit of graphene, the energy required for graphene growth is considerably low around ~300°C when benzene is used (Xu et al., 2016). In addition, to enhance their functionality, foreign elements can be effectively doped in the 3D graphene materials using hydrocarbons with heteroatoms such as oxygen, nitrogen, sulphur, phosphorus, etc., as carbon source (Zhuxing Sun et al., 2020).