SYNTHESIS AND CHARACTERIZATION OF TWO-DIMENSIONAL TITANIUM CARBIDE MXENE Ti_3C_2

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by

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LIST OF ABBREVIATIONS

2-D	Two-Dimensional
3-D	Three-Dimensional
Al	Aluminum
Al_2O_3	Aluminum oxide
C	Graphite
CO_2	Carbon dioxide
Cr_2C	Chromium(II) carbide
Cr_2N	Chromium(III) nitrate
DFT	Density functional theory
DMSO	Dimethyl sulfoxide
DNA	Deoxyribonucleic acid
DOS	Density of state
F	Fluoride
HCL	Hydrochloric
HF	Hydrofluoric
HIP	Hot isostatic press
HP	Hot pressing
ICDD	International Committee of Diffraction Data
LIB	Lithium ion battery
MA	Mechanical alloying
MoS_2	Molybdenum disulfide
MSDS	Materials Safety Data Sheet
MSR	Mechanically-induced self-propagating reaction
O	Oxygen
OH	Hydroxide

Pb	Lead
PLS	Pressureless sintering
PPE	Personal protection equipment
Rn	Radon
Si	Silica
SiC	Silica carbide
SEM	Scanning electron microscope
Sn	Tin
SPS	Spark plasma sintering
STM	Scanning tunneling microscope
Ta_3N_2	Tantalum(III) carbide
TEM	Transition electron microscope
Ti	Titanium
TiC	Titanium carbide
TiH_2	Titanium hydrate
TiO_2	Titanium oxide
Ti_3C_2	Titanium carbide
Ti_3N_2	Titanium nitrate
Ti_3SiC_3	Titanium silica carbide
TMD	Transition metal dichalcogenides
UHV	Ultra-high vacuum
US EPA	United States Environmental Protection Agency
WS_2	Tungsten(IV) sulphide
XRD	X-ray diffraction

LIST OF SYMBOLS

α	Alpha
°	Degree
°C	Degree Celsius
σ	Electrical conductivity
°C/min	Degree per minutes
μ	Micrometer
ΔT	Temperature difference
θ	Theta
A	A-group elements (mostly from group 13 or 14)
A	Area of specimen
D	Distance between 2 probes
eV	Electronvolt
g	Gram
K	Thermal conductivity
kHz	Kilohertz
M	Early transition metal
M	Molar
ml	Milliliter
n	Numbers, can be 1, 2 or 3
nm	Nanometer
Pa	Pascal
pCi/l	Picocuries per liter
R	Resistivity
rpm	Rotation per minute
X	Carbon and/or Nitrogen

t	Thickness of sample
V	Volt
W	Power
wt.%	Weight percentage

Sintesis dan Perincian Bahan Dua-Dimensi Titanium Karbida MXene Ti_3C_2

ABSTRAK

Dalam kajian ini, logam peralihan karbida dua-dimensi (2-D) telah disintesis dari fasa berlapis MAX. Serbuk awal titanium hidrat (TiH_2), aluminium (Al) dan grafit (C) ditimbang mengikut nisbah stoikiometri 3:1.1:2, dan campuran ini dikisar selama 20, 40, 60 dan 80 jam pada kelajuan 300 rpm. Melalui kajian pembentukan fasa semasa proses, 60 jam adalah tempoh kisar yang optimum untuk menghasilkan sebatian Ti_3AlC_2 dengan keaslian tertinggi dengan 1 µm diameter serta kurang sebatian oksida. Sebatian yang optimum tersebut telah ditekan pada 40 MPa bagi membentuk pelet dengan 1 sm diameter dan 3 mm ketebalan dengan menggunakan acuan keluli tahan karat. Lapisan fasa MAX Ti_3AlC_2 disintesis melalui pembakaran tanpa tekanan dan pelet diletak dalam tapak alumina tanpa proses dehidrogenasi awal di bawah persekitaran argon pada 1350 ˚C selama dua jam dengan kadar pemanasan 10 ºC / minit. Pendekatan pengelupasan elegan digunakan untuk menghilangkan Al dari pendahulunya untuk membentuk struktur berlapis 2-D Ti_3C_2 dengan merendam Ti_3AlC_2 dalam larutan hidrofluorik (HF) selama 20 jam. Ciri-ciri morfologi dan struktur 2-D Ti_3C_2 ini juga dikaji. Imej SEM menunjukkan dua jenis morfologi yang terdiri daripada lapisan Ti_3C_2 dan aglomerat Al_2O_3 dengan grafit. Imej Ti_3C_2 berlapis dengan ketebalan 0.1-1.0 µm mengesahkan pengelupasan Ti_3C_2 yang berjaya. Corak XRD mendedahkan bahan ini mempunyai tiga fasa iaitu struktur rhombohedral Al_2O_3, grafit dan fasa Ti_3C_2. Pembentukan fasa Ti_3C_2 dalam corak XRD disebabkan oleh proses ultrasonik campuran dalam metanol menyebabkan pengelupasan MXene Ti_3C_2. Sifat konduktif haba fasa MAX dan fasa 2-D MXene dikaji dengan menggunakan kaedah aliran haba paksi mutlak dalam unit watt/meter kelvin (W/m.K). Pellet MAX phase dan 2-D Ti3C2 dengan ketebalan 1 mm ditempatkan di antara plat dan kekonduksian haba bahan telah direkodkan untuk 5 voltan berbeza yang dibekalkan. Konduktiviti elektrik kedua-dua fasa MAX dan 2-D MXene diukur dengan menggunakan kuar 2 titik untuk menentukan daya tahan elektriknya seterusnya mengira sifat konduktif elektrik untuk bahan tersebut. Hasilnya mendedahkan perbezaan antara nilai teori dan eksperimen kekonduksian termal dan elektrik Ti_3C_2 dan Ti_3AlC_2 disebabkan oleh tingkah penelusan semasa proses tekan-sejuk. Pengukuran kadar keluar Radon (Rn) dilakukan dalam monitor Rn untuk mengkaji kadar pernafasan Rn dalam pelbagai suhu dan kelembapan selama lima hari berturut-turut bagi menganggarkan tahap radiasi bahan. Pengukuran tahap Rn biasanya dinyatakan sebagai kepekatan Rn dalam unit picocuries per liter udara (pCi / L) dan Agensi Perlindungan Alam Sekitar (EPA) mengesyorkan nilai mestilah lebih rendah daripada 4 pCi / L untuk penggunaan industri. Kepekatan radiasi tertinggi dicatatkan pada hari ke-5 (1.2 pCi / L) yang lebih rendah daripada nilai yang disyorkan oleh EPA.

Synthesis and Characterization of Two-Dimensional Titanium Carbide MXene Ti_3C_2.

ABSTRACT

In this study, two-dimensional (2-D) transition metal carbide was synthesized from a layered MAX phase. The initial powders of titanium hydrate (TiH_2), aluminium (Al) and graphite (C) was weighed according to the stoichiometry ratio of 3:1.1:2. The mixture was ball-milled for 20, 40, 60 and 80 hours at 300 rpm to study the phase formation during the process. It found that the 60 hours was the optimum milling period to yield the highest purity of Ti_3AlC_2 with the diameter of 1 µm with the least oxide compound. The optimum ball-milled mixture was selected to cold-pressed for 40 MPa to form a pellet with the diameter of 1 cm and thickness of 3 mm by using the stainless-steel mould. A layered of MAX phase Ti_3AlC_2 was synthesized through pressureless sintering (PLS)and the pellet was placed in alumina cricuble without preliminary dehydrogenation under argon atmosphere at 1350 ˚C for two hours with the heating rate of 10 ºC/minutes. An elegant exfoliation approach was used to eliminates Al from its precursor to form a layered-structure of 2-D Ti_3C_2 by immersing Ti_3AlC_2 in hydrofluoric (HF) solution for 20 hours. Morphological and structural properties of this 2-D Ti_3C_2 also studied. SEM images shows two types of morphology consist of a layer of Ti_3C_2 and the agglomerates Al_2O_3 with graphite. The images of layered Ti_3C_2 with the thickness of 0.1-1.0 µm confirms the successful exfoliation of Ti_3C_2. XRD pattern reveals three phases in this material which is a rhombohedral Al_2O_3, graphite and Ti_3C_2 phases. The formation of Ti_3C_2 phase in XRD pattern was attributed to the ultrasonication the mixture in methanol leads to exfoliation of MXene Ti_3C_2. Thermal conductivity of MAX phase and 2-D MXene was studied by absolute axial heat flow method in unit of watt/meter kelvin (W/m.K). A pellet of MAX phase and 2-D Ti_3C_2 with the thickness of 1 mm was placed in between the plate and thermal conductivity of materials was recorded for 5 different voltage supplied. Electrical conductivities of both MAX phase and 2-D MXene was measured by using 2-point probe to determine its bulk resistivity thus calculate the electrical conductivity of materials. The result reveals differences between the theoretical and experimental value of the thermal and electrical conductivity of Ti_3C_2 and Ti_3AlC_2 due to percolation behaviour during cold-press process. Radon (Rn) measurement was carried out in established Rn monitor to study the rate of exhalation of Rn in various temperature and humidity for five consecutive days, thus estimates the radiation level of the materials. Measurements of Rn levels are normally expressed as the concentration of Rn in units of picocuries per liter of air (pCi/L) and US Environmental Protection Agency (EPA) recommend values is must be lower than 4 pCi/L to be considered average exposure for industry usage. The highest radiation concentration was recorded at day 5 (1.2 pCi/L) which is lower that the suggested value by US EPA.

CHAPTER 1: INTRODUCTION

1.1 Overview

Two-dimensional (2-D) materials are well known materials with unique properties in materials engineering perspective. 2-D materials can be defines as a material with single atomic plane, such as graphene, with only 0.34 nm thick of one atomic layer of carbon (Geim & Novoselov, 2007) as shown in Figure 1.1.

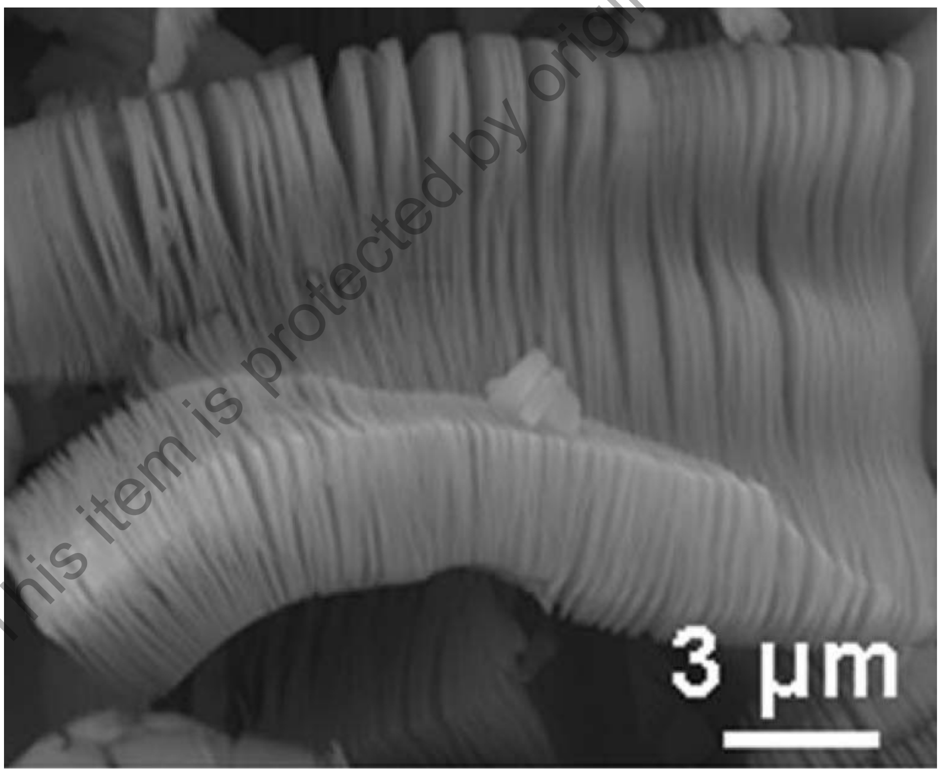

Figure 1.1: Scanning Electron Microscope (SEM) images of 2-D materials (Naguib et al., 2012).

Naguib et al. (2012) state that 2-D materials is known as a material with very high aspect ratio and thicknesses corresponding to a few atomic layers. In different studies, Bianco et al. (2013) state that the range of materials to be 2-D materials is 1 layer to 10 layers whereas higher than 10 layers is considered as 3-D materials. The most studied 2-D material is graphene, which is comprised of atomically thin layers of sp2-bonded carbon atoms connected by aromatic in-plane bonds. Graphene is the first example of 2-D materials with only one-atom thickness, isolated from graphite. It was found in 2004 by Novoselov et al., (2004). Since the outstanding electronic properties of graphene have been discovered, other 2-D materials such as hexagonal boron nitrides (Haubner et al., 2002), transition metal dichalcogenides (TMDs) (Miró et al., 2014) , metal oxides, and hydroxides, start to attract much attention.

Graphene shows tremendous attraction to researchers from different fields and has risen as the most exciting star in materials science during the past several years. Its exceptional properties, such as half-integer quantum Hall effect, ambipolar electric field effect, extremely high carrier mobility, high thermal conductivity, high specific surface area, and the highest strength ever measured, provide a fertile ground for the possible implementation of graphene in nano-devices for a large variety of applications, and a lot of recent reviews have been directed towards its synthesis, properties, and functionalized applications (Tang & Zhou, 2013).

A fascinating idea was proposed by Naguib et al. (2011) which is to prepare freestanding graphene-like carbides (and nitrides) not from their 3-D parent binary phases, but from ternary layered MAX phases (known also as nanolaminates), which include various 2-D-like layers of transition metal carbides (or nitrides) as building blocks (Shein & Ivanovskii, 2013). These 2-D materials are now known as ‘MXenes’; this term denotes their genesis from MAX phases (with the loss of the A component) and their similarity to graphene (Naguib et al., 2011).

MXenes is new 2-D nanosheet materials and gaining so much attention from materials engineer because its properties and unique behaviour and has similar lamellar structure with graphene. Most of materials engineers interested with this new material because of it's potential to be used with latest technologies and application.

Generally, 2-D materials are produced by removing A from MAX phases by chemical etching as shown in Figure 1.2. MAX phases are ternary carbide or nitrides with the chemical formula of $M_{n+1}AX_n$, where M is an early transition metal, A is an A-group element and X is either carbon or nitrogen. The value of n can be 1, 2 or 3 (Naguib et al., 2012).

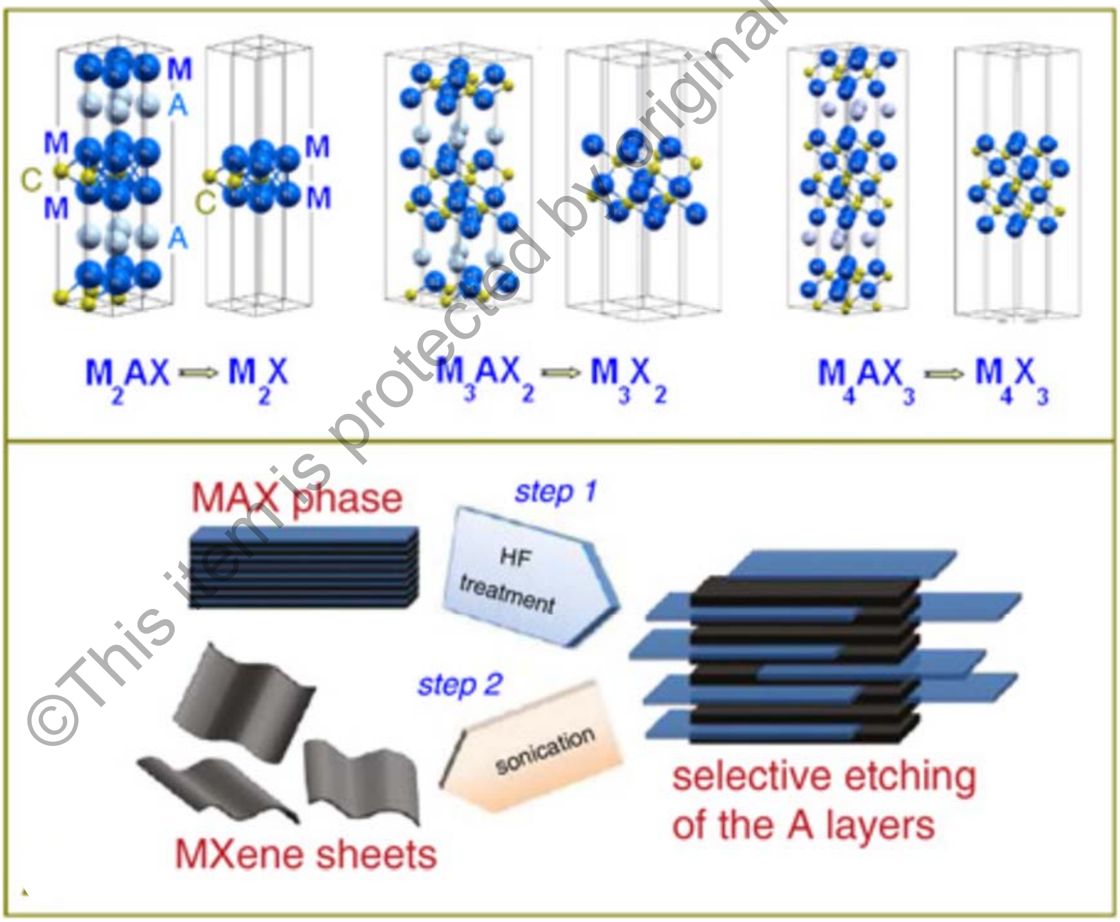

Figure 1.2: Atomic model of preparation of MXenes ($M_{n+1}X_n$) from MAX phases ($M_{n+1}AX_n$) via removing of A sheets (Shein & Ivanovskii, 2012)

1.2 Problem statement

It has been admitted that there is a lot of researchers study this material. Due to the diversity of this material, some of the properties is remain unclear. Most of the researchers faces a similar problem, which is to find the optimum solution to synthesis this material with high purity and low-cost method. To synthesis a high purity of MAX compound and MXene, a lot of critical parameter in each process need to be controlled and monitored from one to another since all the process is corelated. To synthesis MXene with the lower cost approach, some of the techniques and method need to be carefully modify due to the complexity of the process and related equipment. Most of the researchers, such as Ge et al., (2003) using hot press (HP) sintering method to produces high purity of MAX phase compound, but since there is a limitation in term of equipment and materials, a new methods and process is identify with similar purity of MAX phase and MXene.

Most of the thermal and electrical conductivity of MAX phase compound and MXene was reported by calculation using density functional theory (DFT). In this research, thermal and electrical properties of MAX phase and MXene will be reported in experimental procedures and the values between theoretical and experimental will be compared and discussed. Since there are limited studies discuss about the radon measurement emitted by MXene, it is important to study about this material's properties and proves there is no significant effect for using this material in industry by achieving the standard of United States Environment Protection Agency (US EPA).

1.3 Objectives of study

The objectives of this research are;

I. To optimized and synthesis the MAX phase and MXene compound (Ti_3C_2) using a pressureless sintering method and elegant exfoliation approaches

II. To investigate the morphological, phase, thermal and electrical properties of MAX phase and MXene (Ti_3C_2)

III. To determine the radiation characteristic of MXene (Ti_3C_2) in form of exhalation rate of Rn.

1.4 Scope of study

This work aims to synthesis two-dimensional titanium carbide (Ti_3C_2) using an elegant exfoliation approaches. There were certain limitation and scope during synthesizing and testing of this materials that need to be counts. First, the raw materials used in this study was limited to the titanium hydrate (TiH_2), aluminium (Al) and graphite (C) with the stoichiometry ratio of 3:1.1:2 based on previous study conducted by Naguib et al. (2012).

In this study, pressureless sintering (PLS) is used as the sintering method to produce MAX phase, Ti_3AlC_2. Sintering temperature was set up to 1350 ºC for two hours based on differential scanning calorimetry (DSC) technique. In elegant exfoliation approaches, 49 % hydrofluoric (HF) solution was used as an etchant to separates Al layers from Ti_3AlC_2 and form two-dimensional Ti_3C_2 MXene.

Scanning electron microscope (SEM) and X-ray diffraction (XRD) is used characterize the MAX and MXene. Its also utilised and investigate the purity of final product. This study aims to compare the thermal and electrical conductivity and the radon exhalation rate between MAX phase and MXene and discussed it with the value from theoretical calculation from other researchers.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter presents the literature review on the basic two-dimensional (2-D) materials and graphene as well its properties and applications. This chapter also reveals the different methods to synthesis MAX phase in bulk or fine powder form and synthesize MXene from its precursor, MAX phase. The morphology, phase, properties and application of both MAX and MXene also presented in this chapter.

There are three major topics were discussed in this chapter which are;

I. Background study of graphene and other two-dimensional materials

II. Background study of MAX phase, and

III. Background study of MXene

2.2 Graphene and other two-dimensional (2-D) materials.

The studies of exfoliation of three-dimensional (3-D) materials and its conversion to the 2-D materials was reported by Brodie (1859) using graphite as main materials. Moreover, Joensen et al (1986) also reported the exfoliation of 2-D molybdenum disulphide, MoS_2 from its precursor and the climax of this studies is when Novoselov et al. (2004) were successfully isolate the single atomic layer of graphene and reported it's ballistic electronic properties and conductivity. 2-D materials have becoming a major study for materials engineer since the outstanding electronic properties of graphene was discovered (Lei et al., 2015).

2-D material is a material with single atomic plane or monolayer plane material. In case of graphene, the thickness of one atomic layer of carbon is around 0.34 nm. For comparison, 100 atomic layers of carbon is defines as a thin film of graphite and characterized as 3-D materials (Geim & Novoselov, 2007). Moreover, Naguib et al. (2014) defines 2-D materials as crystal with very high aspect ratios and thickness corresponding to a few atomic layers. In different study, Bianco et al. (2013) stated that the range of materials to be 2-D material is 1 layer to 10 layers, and more than 10 layers were considered as 3-D materials. This statement was based on the electronic structure of graphene which changes from being a zero-gap semiconductor for a monolayer of graphene to the graphitic 3-D bulk electronic structure when exceeding 10 atomic layers.

Since the discovery of excellent properties of graphene such as its 2.3% absorption in the white light spectrum, high surface area, high Young's modulus, and excellent thermal conductivity (Xu et al., 2013), other 2-D compound such as metal chalcogenides (Chung & Kanatzidis, 2014), transition metal oxides (Walia et al., 2013) and transition metal carbides and/or carbonitrides, known as MXene (Naguib et al., 2012) has gained popularity in research by researcher and industry. All of these properties leads to the wide range of application on graphene, including high speed electronic (Lin et al., 2010) and optical devices (Liu et al., 2011), energy generation and storage (Kim et al., 2009; Liu et al., 2011; Zhu et al., 2011), hybrid materials (El-Kady et al., 2012; Yang et al., 2011), chemical sensor (Deng et al., 2011; Geim & Novoselov, 2007) and even Deoxyribonucleic acid (DNA) sequencing (Garaj et al., 2010; Xu et al., 2009) have all been reported.

The usual method to synthesis graphene is micromechanical exfoliation, also known as peel-off method, epitaxially grown on silicon wafers, chemical vapor deposition, intercalation of small molecules in a graphite lattice and its exfoliation by thermal shock and unzipped the one-dimensional carbon nanotubes (Pumera et al., 2010).

Figure 2.1 shows the possible arrangement of graphene as discussed by Pumera et al., (2010). A single layer of graphene existed in the form of six atom rings in the honeycombed network and can be conceptually viewed as a true planar aromatic molecule. This basic building block of C can either be wrapped to form zero dimensional fullerenes, rolled to form one dimensional carbon nanotubes or stacked up to form its parent element, three-dimensional graphite.

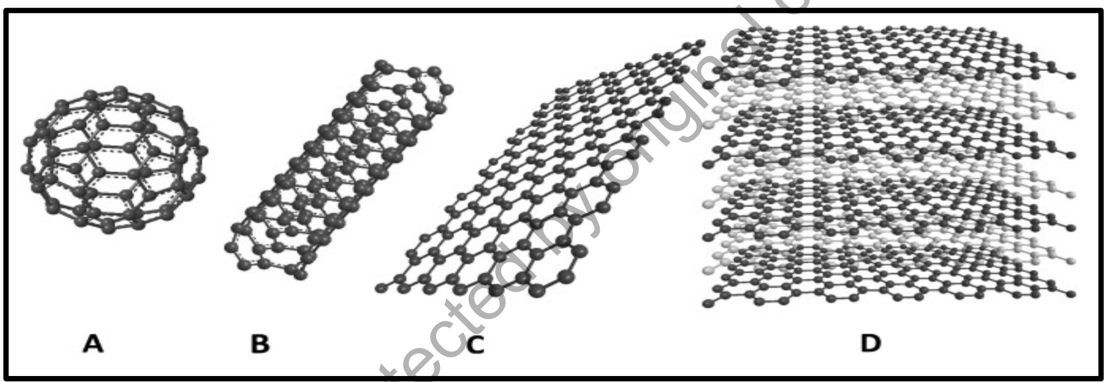

Figure 2.1: The possible ways which single layer of graphene can exist. (A) zero dimensional fullerenes, (B) one dimensional carbon nanotubes, (C) single layer of two dimensional graphene, and (D) stacked up of graphene to form three dimensional graphite (Pumera et al., 2010).

2.2.1 Available method to synthesizing 2-D materials

The synthesizing method for other 2-D materials are different depends on the phase of their 3-D parent binary phase or another ternary phase. There were 3 major methods to synthesis 2-D materials which is epitaxial growth, unconventional method and exfoliation technique (Jayasena & Melkote, 2015).

In epitaxial growth methods, 2-D materials were deposited on top of the substrate via physical vapor deposition or chemical vapor deposition techniques. By applying this