



**UNIVERSITI TEKNIKAL MALAYSIA MELAKA**

**A STUDY OF COBALT CATALYST PREPARATION FOR  
CARBON NANOTUBE POWDER GROWTH BY USING  
ALCOHOL CATALYTIC CHEMICAL VAPOR DEPOSITION**

This report submitted in accordance with the requirement of the Universiti Teknikal  
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(Engineering Materials) (Hons.)

by

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## ABSTRAK

Tesis ini membincangkan tentang keunikan ciri Nanotiub karbon (CNTs) terutamanya dalam penggunaan superkapasitor (CNT digunakan dalam memfabrikasikan elektrod untuk meningkatkan fungsi elektrik), diikuti dengan segi langkah persediaan, kajian berparameter, dan pencirian pertumbuhannya, dimana ia diperbuat daripada pemangkin kobalt yang telah dihasilkan. Kajian bermula dengan penyediaan pemangkin kobalt dengan menggunakan kaedah sol-gel, dimana ia menggunakan kobalt acetate tetrahidrat dan pelarut 2-amino ethanol, diikuti dengan pertumbuhan sebenar Nanotiub karbon dengan menggunakan kaedah alkohol pemangkin pemendapan wap kimia (ACCVD). Setelah pemangkin kobalt telah disediakan, serbuk yang terhasil telah dicirikan dengan menggunakan mesin serakan X-ray (XRD), Optik Mikroskop (OM), dan Analisa Saiz Partikel (PSA), dan kemudian serbuk itu digunakan untuk pertumbuhan CNT di suhu 700, 750, 800, and 850 °C untuk mengkaji kesan suhu pada kualiti bahan berasaskan karbon yang dihasilkan melalui proses CVD. Bahan berasaskan karbon yang dihasilkan dicirikan melalui Spektroskopi Raman dimana puncak D-band dan G-band dari setiap serbuk yang dihasilkan diperhatikan. Hasil menunjukkan di dalam kajian ini, dengan menggunakan pemangkin kobalt yang dihasilkan, suhu terbaik untuk pertumbuhan CNT adalah 850 °C dengan kadar nisbah  $I_G/I_D$  ialah 1.052, dimana ia adalah tertinggi di kalangan yang lain. Tetapi, untuk memperoleh serbuk bahan berasaskan karbon yang dihasilkan adalah payah, jadi rekaan baru untuk ACCVD telah dikemukakan.

## ABSTRACT

The thesis discusses the Carbon Nanotubes (CNTs) unique properties especially for supercapacitor applications (use of CNT in fabricating electrode to induce electrical function), which triggers the idea to do this research, followed by the preparation step, parametric study, and from the prepared cobalt catalyst, its growth characterization is analyzed. The research started with the preparation of cobalt catalyst by using sol-gel method, which used of cobalt acetate tetrahydrate and 2-amino ethanol solvent, followed by actual growth of CNT by using the prepared catalyst in Alcohol Catalytic Chemical Vapour Deposition (ACCVD). Once the cobalt-based catalyst powders were prepared, the resulting powders were characterized by using X-ray Diffraction (XRD, Optical Microscopy and Particle Size Analyzer, and then tested to grow CNTs at 700, 750, 800, and 850 °C, where other parameters were fixed in order to determine the effect of CVD processing temperature on the quality of resulting carbon-based materials. The resulting carbon-based materials were analyze by using Raman Spectroscopy where D-band and G-band of each resulting powders were observed. It was found that in this research, by using the prepared cobalt catalyst, the best CVD processing temperature was 850 °C with  $I_G/I_D$  ratio were 1.052, which was the highest among the tested temperatures. But to obtain the resulting carbon-based powders were troublesome, so a new design of ACCVD furnace was proposed.

## **DEDICATION**

Dear beloved parents, this is dedicated to you.

## **ACKNOWLEDGEMENT**

Alhamdulillah, praise to Allah S.W.T, upon His blessings, I managed to complete my final year project. A number of people who have made significant contributions in the completion of this project deserved more than a thank from me. Their advices, insights and suggestions helped me a lot, especially from my supervisor, Assoc. Prof. Dr. Mohd Asyadi 'Azam Mohd Abid for his time, tolerance, and encouragement which without him, I may not finish my project. Not to forget Miss Nor Najihah Zulkapli and Miss Raja Nor Amalina for their supports, commitments and technical help by illuminating views on issues related to the project.

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# LIST OF ABBREVIATIONS, SYMBOLS & NOMENCLATURES

|                                |  |
|--------------------------------|--|
| %                              | Percent                                      |
| ACCVD                          | Alcohol Catalytic Chemical Vapour Deposition |
| °C                             | Degree Celcius                               |
| CNT                            | Carbon Nanotube                              |
| Co                             | Cobalt                                       |
| Co <sub>3</sub> O <sub>4</sub> | Cobalt (III) Oxide (IV)                      |
| CRT                            | Cathode Ray Tube                             |
| CVD                            | Chemical Vapour Deposition                   |
| D                              | Disordered                                   |
| DWCNT                          | Double-walled Carbon Nanotube                |
| DWNT                           | Double-walled Nanotube                       |
| FESEM                          | Field Emission Scanning Electron Microscopy  |
| G                              | Graphitic                                    |
| HR-SEM                         | High Resolution Scanning Electron Microscopy |
| MWCNT                          | Multi-walled Carbon Nanotube                 |
| MWNT                           | Multi-walled Nanotube                        |
| nm                             | nanometer                                    |
| RBM                            | Radial Breathing Mode                        |
| SEM                            | Scanning Electron Microscopy                 |
| SWCNT                          | Single-walled Carbon Nanotube                |
| SWNT                           | Single-walled Nanotube                       |
| UTeM                           | Universiti Teknikal Malaysia Melaka          |
| XRD                            | X-ray Diffraction                            |

# CHAPTER 1

## INTRODUCTION

The purpose of this project is to study the effect of 2-amino ethanol solvent on cobalt catalyst preparation for carbon nanotube (CNT) powder growth, by using chemical vapor deposition (CVD) technique. In this chapter, the definition details, and functions of catalyst in CNT growth will be generally briefed. The objectives, problem statements, and scope of this research will also be discussed.

### 1.1 Background

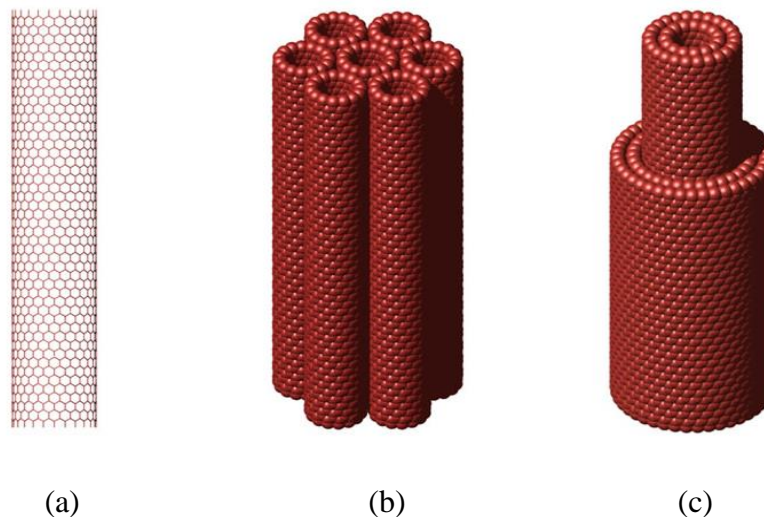
Throughout the past 15 years, CNTs have advanced into one of the most intensively studied materials of this decade (A. Jorio, M. S. and G. Dresselhaus, 2008). In general, CNTs can be characterized as a tube, rolled-up from a graphene sheet in nano-size scale ( $1 \times 10^{-9}$ ). This unique tube has shown a promising, set to revolutionize the technological landscape in the near future. This is due to their unique properties, in terms of structural, chemical, mechanical, thermal, optical, optoelectronic, and electronic, which increases the interest to study the CNT fundamental properties to be exploited to suit specific functions or applications (Berlanga et al., 2011; Katz & Willner, 2004). Some of the applications have grown rapidly, especially in industrial research laboratories, startup companies, large established corporations, and everything in between. For example, single-wall carbon nanotubes (SWCNTs) have broad impact in metrology, standardization and industrial quality control. SWCNTs provides special importance in nanometrology science where CNT is used as the probe tip material for atomic force microscopy (AFM) as CNT has a diameter as small as one nanometer, possess robust mechanical properties, and can be specifically functionalized with chemical and biological probes at the tip ends.

Although that being said, at the state of the art, the applications of CNTs are still limited due to the high processing cost and the presence of impurities. So, CNTs processing are still being studied and developed to produce high grade or quality CNTs in mass scale, at low cost. This is also occurs in CVD technique, which is the most preferable technique in CNT growth, where the CNTs growth optimal parameter control is still slacking. Based on trusted sources, CNT growth does greatly depend on the CVD process parameters, especially the processing temperature (Bronikowski, 2006; Sivakumar *et al.*, 2010).

### 1.1.1 Carbon Nanotubes (CNTs)

Solid state carbon can be differed into three crytalline forms, known as allotropes, and these allotropes are diamond, graphene and fullerene. Fullerene is a new class of material, formed by wrapping graphene sheets into spherical or cylindrical shapes. CNTs are fullerenes and their diameter can be as small as 1 nanometer (nm), and up to centimeters long (1-D nanomaterial).

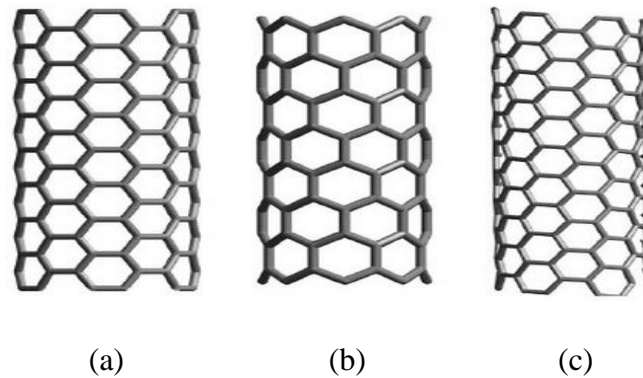
Below shows the representation of CNTs;



**Figure 1.1:** Representation of the CNTs,

(a) SWCNT, (b) Rope of SWCNT, and (c) MWCNT (P. Guay, 2014).

The chirality of CNT can be varied too, and they are shown Figure 1.2 below;



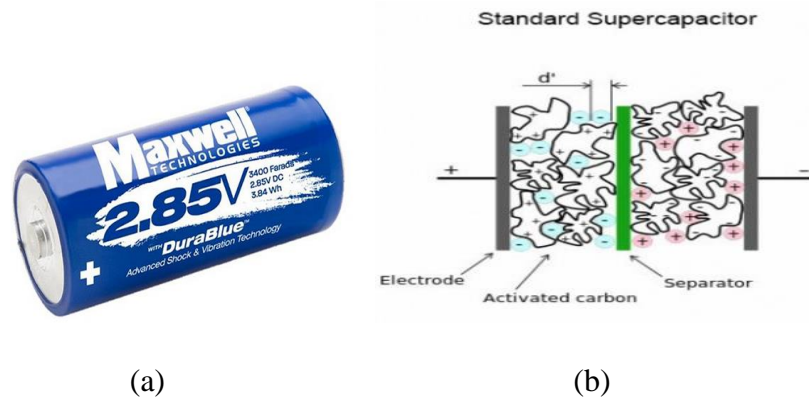
**Figure 1.2:** Structures of CNTs, (a) Armchair, (b) Zigzag, and (c) Chiral (B.P. Grady, 2004).

These two figures visualized that CNTs are available in varied representation and chirality, but no matter what their representations and structures, generally they can be categorized into two different groups, which are SWCNT and MWCNT (Dupuis, 2005; Sivakumar *et al.*, 2010). To be precised, SWCNT has one cylindrical tube structure of graphene with diameter of 1 to 2 nm, while MWCNT has two or more tube structures with diameter of 10 to 50 nm. Under well defined conditions, these SWCNTs or MWCNTs are formed spontaneously into seamless tubes, and exhibited a high level of atomic-scale perfection. Some of researchers focus on producing MWCNTs because these MWCNTs have significant commercial applications as fillers in polymers (B.P. Grady, 2011), and others in nanoelectronics devices and biomedical sensors. Table 1.1 will discuss the comparison between SWCNT and MWCNT.

To show an example, CNT is compared to metals. Due to the close relationship with graphene, this results in chemically inert porperties. At 1/6th of weight of steel, CNTs are twice stronger under tensional stress, and in ideal vacuum, CNT melts at 4000 °K (3726.85 °C), closed to graphite, which surpasses any metal. In terms of thermal properties, CNTs seem to be outstanding conductors of heat and seems to be biocompatible in various surroundings due to the relation to graphite (D. Tomanek, 2007).

These concludes that CNTs have appear as ideals for wide range of current or future applications due to their excellent characteristics, or properties. Below shows an application of CNTs;





**Figure 1.3:** (a) An example of a supercapacitor (Courtesy of Mouser Tech.), and (b) an illustration of standard supercapacitor (Courtesy of Wiki Commons).

Supercapacitors are made from various materials in many ways, from multilayer ceramics, ceramic disc, multilayer polyester film, tubular ceramic, axial and radial polystyrene, to CNTs. CNTs are used in the electrodes in supercapacitors and fuel cells because they are practical for the supercapacitors' design (Murdoch Uni, 2015). This is because CNTs have excellent nanoporosity properties, allowing tiny spaces for the polymer to sit in the tube and act as a dielectric. Due to unusual arrangements of conductive and insulating of CNTs, they may generate electronic fabrics with supercapacitor functionality. This is also due to the high conductive level of CNTs, combined with high surface-to-volume ratios.

Other applications of CNTs;

- i. Aircraft components (as composites).
- ii. Electron guns in Cathode Ray Tube (CRT).
- iii. Ballistic conductors of electrons and holes.
- iv. Additive to graphite component of Li-ion batteries.

However, among the many examples above, some inconsistencies were observed. For examples, CNTs possesses superconducting characteristic only after good contact with lead are made, and whether the CNTs will perform to the required specifications is still questionable (D.Tomanek, 2007). This is because critical steps are needed to properly grow CNTs. Although researchers have developed various kind of methods to grow them, limitations and restrictions occurred in most of the methods as they require intensive devising processes or aid of excellent properties materials. This results in restraining the applications of CNTs in other fields.

**Table 1.1:** Comparison between MWCNT and SWCNT (Rajkumar *et al.*, 2013).

| MWCNT |  | SWCNT |  |
|-------|--|-------|--|
| i.    | Composed of multi layers of graphene sheets.                               | i.    | Composed of single layer of graphene sheet.                                |
| ii.   | Able to be produced without presence of catalyst.                          | ii.   | Catalys is needed in production.   |
| iii.  | Homogenously dispersed with no apparent bundled formation.                 | iii.  | Not fully dispersed and form bundle structure.                             |
| iv.   | Contain high purity.   | iv.   | Having poor purity.  |
| v.    | Typical MWCNT content in prepared samples by CVD method is about 35-39wt%. | v.    | Typical SWCNT content in prepared samples by CVD method is about 30-50wt%. |
| vi.   | Low possibilities of defect.   | vi.   | High possibilities of defect during fictionalization.                      |
| vii.  | High structure complexity.   | vii.  | Low structure complexity.  |
| viii. | Cannot be twisted easily.  | viii. | Easily twisted and more pliable.   |

## 1.2 Problem Statement

Up to this day, many initial problems of CNT studies have been overcome, theoretically and experimentally. By creating a homogenous precursor solution from precursor material and solvent, a specific catalyst can be prepared for actual growth of CNT powders in CVD growth technique. To grow CNTs, the process is not simply as rolling a graphene sheet into tubular shape. Instead of that, the CNT powder must be grown, under tremendous supply of heat, from catalyst (the precursor powder) who acts as a seed. There are several type of catalysts, and in this work, the catalyst is a cobalt-based catalyst, made from cobalt acetate tetrahydrate (precursor material) and 2-amino ethanol solvent. Various techniques can be used to grow CNT from precursor solution or powder, and the most common methods are laser ablation, arc discharge and chemical vapor deposition (CVD).

Among these three, CVD is known for its capability to grow high quality CNTs in large scale, at low cost, using variety of substrates (if there is any), and high catalytic yield reaction. However, the optimal parameters are still undefined. Up to this day, researchers are still pondering, “what is the most optimum temperature for CNT growth in CVD?, and “what are the best material to be used to prepare catalyst for CNT growth?”. This shows that the CVD process is still slacking in growth parameter control to obtain the best quality of CNT growth, in terms of materials used in catalyst preparation. From a systematic investigation of studying the effect of growth temperature on the synthesis of CNTs by using CVD technique, it is known that CNTs can grow from 450 °C to 1000 °C (Unalan & Chhowalla, 2005). At low temperatures, the decomposition of hydrocarbon gas (non-alcohol method) would be limited, results in forming amorphous, highly defective carbon structures while at high temperatures, CNTs form in bundles and possess walls disorder (Kumar & Ando, 2010; Unalan & Chhowalla, 2005). For catalyst preparation, several researchers use various combinations of precursor material and solvent to make catalysts, and the results are varied.

Therefore, this work is existed in order to grow CNT powders from cobalt catalyst made from 2-amino ethanol to clarify the effect of using it and its temperature dependence in the CNT growth by alcohol catalytic CVD technique.

### **1.3 Objectives**

The objectives of this research project are;

- i. To characterize the cobalt-based catalyst powders synthesized from sol-gel process.
- ii. To investigate the effect of temperature on the cobalt-based catalyst powders in CNT powder growth by using ACCVD.
- iii. To characterize the structural property of carbon-based powders by using Raman Spectroscopy.

## 1.4 Scope

The main aim of this study is to investigate the effect of using 2-amino ethanol solvent on cobalt catalyst preparation for CNT powder growth by synthesizing the CNT powders from the processed precursor powder, and to investigate the effect of temperature on the cobalt-based catalyst for CNT powder growth by using alcohol catalytic CVD. This means that, to remove distractions from other factors, the research will be performed based on several scopes. For the first objective, 2-amino ethanol solvent and cobalt acetate tetrahydrate will be used to make cobalt catalyst, Then, the precursor material will be dried in oven for overnight at temperature above their melting points. Next, it will be calcined for 2 hours and a half at 700 °C before proceeding to CNT growth process, which would be the second objective of this work. For the third objective, the CNT powder growth from the resulting cobalt catalyst would be varied in temperature which are 700, 750, 800, and 850°C by using ACCVD technique. Lastly, for the last objective, the characterizations of CNT powders would be by using Raman Spectroscopy at 532 nm laser excitation.

## **CHAPTER 2**

### **LITERATURE REVIEW**

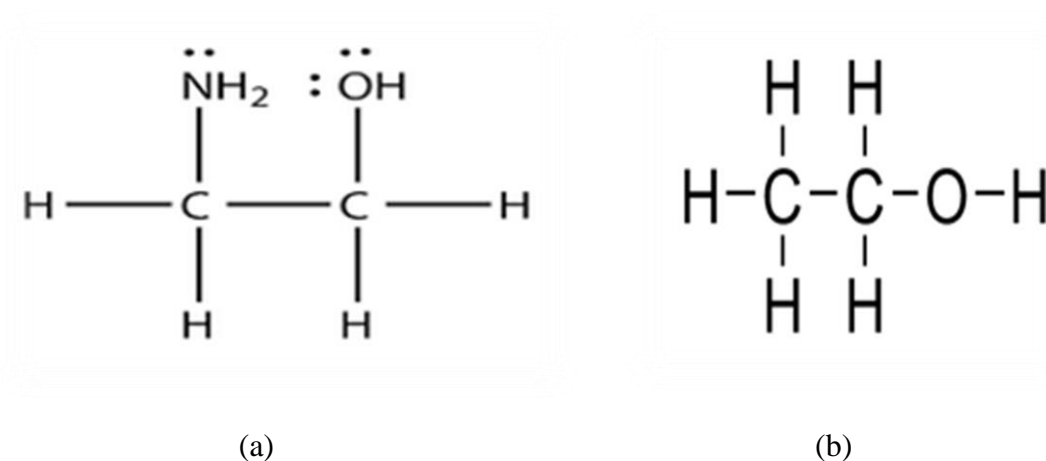
This chapter will describe the literature review regarding to the process of Carbon Nanotube (CNT) growth that started with the preparation of catalyst, made from specific solvent and precursor material, followed by the actual growth of CNT by using CVD technique, including the characterization techniques. First, reliable catalyst preparation was selected and the stable growth conditions were determined to ensure robust and reproducible result can be obtained, as these would be crucial regarding to the experimental observation of the grown CNTs. Besides that, the selection of transition metal would also be emphasized. Then, the chosen CNT growth technique is discussed with its detailed parameters that affect the growth of CNTs, especially the influence of processing temperature.

#### **2.1 The use of 2-amino ethanol as Solvent**

The use of 2-amino ethanol solvent in cobalt catalyst preparation is suggested based on previous research made by N. Azura (2015) where the results show that the CNT growth cannot be utilized 100% from cobalt catalyst that had been prepared. In addition, the researcher believed due to the low boiling point of ethanol ( $\pm 78\text{ }^{\circ}\text{C}$ ), a certain amount of ethanol evaporated under spin coating process, which made the volume of cobalt catalyst become lesser due to the unreacted volume of cobalt acetate tetrahydrate increased.

Based on M. A. Krest'yaninova *et al.*, (2013), 2-amino ethanol will react with precursor material better than ethanol due the the fact that 2-amino ethanol evidently strengthens the O-H•••N hydrogen bonds, with higher boiling point ( $\pm 170\text{ }^{\circ}\text{C}$ ).

So, once it reacts with cobalt acetate tetrahydrate, it will not be easily experience bond breaking, and maintain as uniformed cobalt catalyst, especially on substrate, which produces SiN (Lee, S. W *et al.*, 2014). However, since this work is to study the effect of 2-amino ethanol on cobalt catalyst preparation for CNT powder growth, no substrate will be used.



**Figure 2.1:** Chemical configurations of (a) 2-amino ethanol, and ethanol.

**Table 2.1:** Comparison of 2-amino ethanol and ethanol solvents in cobalt catalyst preparation (M. A. Krest'yaninova *et al.*, 2013)

| 2-amino ethanol solvent (C <sub>2</sub> H <sub>7</sub> NO)  | Ethanol solvent (C <sub>2</sub> H <sub>6</sub> O)  |
|---|--|
| “Evaporated/gone” after certain period of time, which resulting unreacted cobalt acetate tetrahydrate, which later affecting the quality of CNT produced. | Evidently strengthens O–H···N hydrogen bonds, can be used either on substrate or powder. |

At the state of the art, it is hard and almost impossible to find researchers that mentioned they have used 2-amino ethanol solvent in their catalyst preparation for CNT growth. So, there is an originality in this research where it could be the first attempt of using 2-amino ethanol as solvent in catalyst preparation, and it is expected the resulting cobalt catalyst will lead to high quality and high yield CNTs.

## 2.2 Transition Metals as Catalyst for CNT Growth

The main concern in this subtopic is the effectiveness of catalyst properties and its activity for CNT growth process. The catalyst interaction determines the morphology and the growth modes of CNTs in chemical vapour deposition (CVD) technique as in CVD, nanometer-size metal particles are crucial in order to allow hydrocarbon decomposition which then allows CNT growth. The efficiency of the catalyst will determine the CNT diameter and size, and also the composition of catalyst particles present in the final product (Magrez *et al.*, 2010).

In CVD techniques, the catalyst can be Fe, Co, Ni, Cr, V, Mo, Pt, Y, Mg, Si or their alloys (T. Izak *et al.*, 2008). Fe, Co, and Ni are the most used transition metals as catalysts in CNT growth due to their high solubility of carbon, and high carbon diffusivity, at elevated temperature (Kumar & Ando, 2010). Besides that, they possess high melting temperatures and low equilibrium-vapor pressure which allow them to be tested at various temperatures, on wide range of substrates; in other words, high efficiency formation, and wide growth windows (T. Maruyama *et al.*, 2015).

In fact, these transition metals are applicable in CVD techniques as they are nanoparticles in size. This is to ensure hydrocarbon decomposition at a lower temperature than the spontaneous decomposition temperature of the hydrocarbon, if hydrocarbon process is used (T. Oguri *et al.*, 2014).

In terms of adhesiveness, researchers found that Fe, Co, and Ni have larger adhesion strengths compared to other transition metals like Cu, Pd, and Au. This means that they are more efficient for supporting growth (F. Ding *et al.*, 2008). Moreover, these nano-sized transition metal particles can be used in CVD techniques as catalysts in the form oxide, metallic or mixture (Magrez *et al.*, 2010).

### 2.2.1 Cobalt Catalyst

In this research, cobalt is chosen as the catalyst to support CNT growth. Based on Seah *et al.*, (2011), in comparison, the results shows that Co is better in growing higher quality of CNTs than Fe and Ni. This is because of the superior solubility of carbon at elevated temperatures, the advanced diffusion rate, added with its high melting point, and low equilibrium-vapor pressure (Kumar & Ando, 2010). These characteristics are triggered by cobalt's oxidation-reduction properties, capability to form complexes by receiving or accepting atoms from other molecules, capability to demonstrate numerous valencies with easy electron transfer, and the presence of vacancies in cobalt's crystal lattice (Cobalt Development Institute).

In comparison to other transition metal catalysts, cobalt catalyst has the upper hand by having better performance under tested range of metallic concentrations and CVD parameters (Mohammad *et al.*, 2011). In producing CNTs by alcohol-based CVD, one of the important element in producing outstanding quality and density of CNTs is cobalt catalyst (Azam *et al.*, 2013; S. Inoue *et al.*, 2007). By using cobalt catalyst, the CNTs can grow on the seeds in the range of temperature in between 500°C to 900°C. In addition, it permits prefabricated undersized diameter in the range of 7 nm to 40 nm during the synthesization of solvent and precursor material (sol-gel process) which advances the quality of CNTs (Palacio *et al.*, 2014). By controlling the particle size, and the chemical nature of the cobalt catalyst, SWCNT, DWCNT, and MWCNT can be grown (Sivakumar *et al.*, 2010).

Besides that, the usage of cobalt as catalyst will allow standardized, and uniformed small diameter sizes during sol-gel process, which results in high quality CNT growth (Huh *et al.*, 2003; Dupuis, 2005). These conclude that cobalt is the most suitable transition metal to be used as catalyst, and the reason why researchers oftenly used cobalt catalyst to promote CNT growth (Huh *et al.*, 2005; Wei *et al.*, 2009; Mohammad *et al.*, 2011).