THESIS APPROVAL

GRADUATE SCHOOL, KASETSART UNIVERSITY

Master of Engineering (Chemical Engineering)
DEGREE

Chemical Engineering	Chemical Engineering
FIELD	**DEPARTMENT**

TITLE: Metal-loaded Multi-walled Carbon Nanotubes Based Gas Sensor for LPG Detection

NAME: Miss Phichamon Viboon

THIS THESIS HAS BEEN ACCEPTED BY

THESIS ADVISOR
(Associate Professor Metta Chareonpanich, D.Eng.)

THESIS CO-ADVISOR
(Associate Professor Phungphai Phanawadee, D.Sc.)

DEPARTMENT HEAD
(Associate Professor Paisan Kongkachuichay, Ph.D.)

APPROVED BY THE GRADUATE SCHOOL ON

DEAN
(Associate Professor Gunjana Theeragool, D.Agr.)

THESIS

METAL-LOADED MULTI-WALLED CARBON NANOTUBES BASED GAS SENSOR FOR LPG DETECTION

PHICHAMON VIBOON

A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Master of Engineering (Chemical Engineering)
Graduate School, Kasetsart University
2008

Phichamon Viboon 2008: Metal-loaded Multi-walled Carbon Nanotubes

Phichamon Viboon 2008: Metal-loaded Multi-walled Carbon Nanotubes Based Gas Sensor for LPG Detection. Master of Engineering (Chemical Engineering), Major Field: Chemical Engineering, Department of Chemical Engineering. Thesis Advisor: Associate Professor Metta Chareonpanich, D.Eng. 65 pages.

In this study, multi-walled carbon nanotubes were synthesized via the chemical vapor deposition (CVD) technique using anodic aluminum oxide (AAO) film as a template and 10% acetylene gas in nitrogen gas as a carbon source for 150 minutes. The carbon nanotubes on anodic aluminium oxides composites (CNTs/AAO) were synthesized by using the growth temperatures of 750°C and 1,000°C. The layers of obtained CNTs/AAO were 64 and 117 with the growth temperature of 750°C and 1000°C, respectively. After that, the obtained multi-walled carbon nanotubes were modified by loading reactive metals including platinum (Pt), ruthenium (Ru) and Nickel (Ni) into their framework structures for the LPG detection. The result revealed that the number of layer of CNTs/AAO composites influenced the amount of metal loaded inside the structure. Ruthenium gave the highest amount of metal particle. The morphology and structure of the obtained multi-walled carbon nanotubes were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The surface area and pore volume were characterized by N_2-Adsorption (Autosorb-I) technique. The effects of LPG on an electrical property of metal-loaded carbon nanotubes-based gas sensor were investigated using electrical resistance measurement technique. The Ni-CNTs/AAO-1000 product revealed the highest performance for LPG detection as it had a large significant change of resistance even small amount of nickel was loaded inside the structure of CNTs/AAO.

__________________________ __________________________ ____/____/____

Student’s signature Thesis Advisor’s signature

ACKNOWLEDGMENTS

First of all, I would like to express my sincere thanks and respect to my advisor, Associate Professor Metta Chareonpanich, for her continuing support and assistance, invaluable counsel and encouraging me to complete this study. I am so sincerely grateful to my co-advisor, Assoc.Prof. Dr.Phungphai PHANAWADEE for his useful suggestions, and interesting ideas in my thesis work.

I am very thankful to all staff members at the Department of Chemical Engineering, Kasetsart University for administrative help and indispensable instrument used in this work. Furthermore, I am also grateful to the Technical Services, National Metal and Materials Technology Center (MTEC) for TEM analysis. King mongkut's University of Technology Thonburi for ICP-OES instrument. In addition, I would like to thank my fellow graduate students for assisting me with my thesis. A special thanks to all my friends for their help, care and suggestions in so many ways.

Finally, I would like to express my deep gratitude to my parents for their love, concern and understanding at all times. My family has been greatest source of encouragement and inspiration for me.

I gratefully acknowledge financial support from Kasetsart University Research and Development Institute (KURDI), The National Excellence Center for Petroleum, Petrochemicals and Advanced Materials, National Nanotechnology Center (NANOTEC) and Center of Nanotechnology Kasertsart University.

Phichamon Viboon
September 2008

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

Figure **Page**

LIST OF FIGURES (Continued)

Figure **Page**

LIST OF FIGURES (Continued)

METAL-LOADED MULTI-WALLED CARBON NANOTUBES BASED GAS SENSOR FOR LPG DETECTION

INTRODUCTIONS

Carbon nanotubes (CNTs) are a kind of allotrope carbon that one atom thick sheet of graphite rolled up into the cylinder. They can be classified into two types which are multi-walled carbon nanotubes (MWCNT) and single walled carbon nanotubes (SWCNT). CNTs were discovered during the direct of synthesis of buckminsterfullerene (C60) and other fullerenes in 1985. The study of carbon nanotubes becomes a widespread development on several industries including the applications such as electronic devices, fuel cells and catalysis. Several researchers have been focused on carbon nanotubes utilization because of their unique properties (Zhiai Xu *el al*., 2004). Carbon nanotubes can be either metallic or semiconductor depend on synthesis process and their structures. In addition, CNTs have a high mechanical, chemical strength, and elastic deformability.

Several methods have been used for preparation of carbon nanotubes. Arc discharge and laser ablation are traditional methods for producing carbon nanotubes. There are some limitations for both of these methods because of a high cost of preparation and random sizes. Chemical vapor deposition (CVD) is a technique for deposition of materials on various substrates**,** i.e., carbon fibers, filaments, and tubular carbon materials. Recently, CVD has been used to synthesize a variety of nanostructure materials, including carbon nanotubes and nanowires. This method becomes the best alternative for large-scale production of carbon nanotubes due to the relatively low growth temperature, high yield and the high purity of carbon nanotubes that can be achieved (Daenen *el al.,* 2003).

According to the unique electronic and structural properties of CNTs, various application such as catalyst, energy storage and gas sensing applications have been found. In gas sensing application, the interaction between CNTs and the gas molecule are involved. Electron donating and withdrawing molecules can either transfer electrons or attract electrons from CNTs, respectively and giving them more charge carriers or holes which can be changed the conductivities of CNTs (Lu *el al.*, 2004). The specific types of gases such as NO_2, NH_3 or phenol show good electron donor or acceptor properties of which can promote the significant changes of CNT conductivities. In the contrary, gas molecules that show no or very small electron donor or acceptor properties such as methane, LPG and carbon monoxide, will therefore promote no or small changes of CNT conductivities. (Varghese *el al.,* 2004).

Recently, metal nanoparticles doped onto CNTs provide a way to obtain novel composite materials with useful properties for gas sensing and catalyst application. Various methods have been used to synthesize metal nanoparticles onto CNTs, i.e., electrodepositing, incipient wetness impregnation and supercritical fluid loading. Among these techniques, incipient wetness impregnation is easy and useful. Regarding this method, the metal-containing solution is directly added to a catalyst support with the same volume as the pore volume of catalyst (Fu *el al.*, 2007).

The objective of this research is to study the synthesis of carbon nanotubes by chemical vapor deposition (CVD) method using anodic aluminum oxide (AAO) as a template and modify carbon nanotubes by loading reactive metals such as platinum (Pt), ruthenium (Ru) and nickel (Ni) into their framework structures using wet impregnation method. Types of metal and the amount of metal loading were the studied variables. The morphology and structure of the obtained multi-walled carbon nanotubes were investigated using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The surface area was characterized by N_2-adsorption technique. The amount of metal loaded on CNTs was characterized by inductively coupled plasma (ICP). The effect of LPG on an electrical property of metal-doped carbon nanotubes-based gas sensor was investigated using electrical resistance measurement technique.

OBJECTIVES

1. To study the carbon nanotubes synthesis by chemical vapor deposition (CVD) method using AAO as a template.
2. To modify the carbon nanotubes composites (CNTs/AAO) by loading reactive metals (platinum, ruthenium and nickel) into their framework structures using the wet impregnation method.
3. To investigate the electronic and adsorption properties of carbon nanotubes and metal loaded carbon nanotubes (Pt, Ru and Ni-MWNTs/AAO composites)
4. To study the response and sensitivity of Pt, Ru and Ni-MWNTs/AAO compositions for the LPG detection by an electrical resistance measurement.

Benefits

1. High quality, uniform, highly ordered carbon nanotubes produced by chemical vapor deposition in anodic aluminum oxide were obtained.
2. High dispersive platinum, ruthenium and nickel in the structure of CNTs/AAO composites were prepared by using wet impregnation method.
3. High sensitivity of platinum, ruthenium and nickel-CNTs/AAO composites were obtained.

LITERATURE REVIEW

Carbon is one of the most abundant elements in the universe. It has four valence electrons. Carbon can form various structures with entirely different properties using these valence electrons. The versatility of carbons can be obtained from its ability of rehybridization among sp, sp^2 and sp^3. Three well-known allotropes of carbon are diamond, graphite and amorphous carbon.

Graphite is based on sp^2 hybridization of carbon electrons, whereas carbon in isotropically strong diamond has sp^3 hybridization. The structure of fullerenes and related derivatives was discovered in late1990s. These structures are recognized as a different phase from the graphite even though such structures maintain the architecture of sp^2. Figure 1 represents the architecture of three different bulk solid phases of carbon (Kuchibhatla *et al.*, 2007).

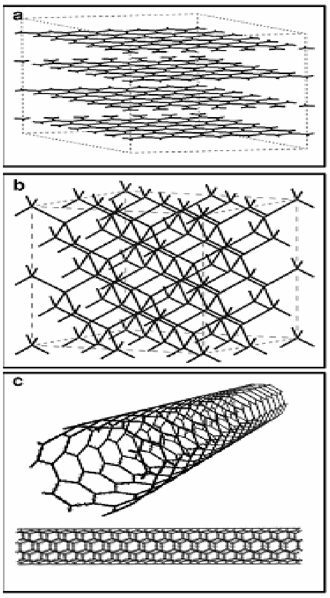


Figure 1 The architecture of three differnct forms of carbon: (a) graphite (b) diamond (c) carbon nanotubes

Source: Kuchibhatla *et al.* (2007)

Structure of Carbon Nanotubes

Carbon nanotubes are a kind of allotrope carbon that one atom thick sheet of graphite rolled up into the cylinder and built from sp^2 carbon unit. These hollow cylindrical tubes of graphitic carbon are characterized by a single tube wall or a large amount of ordered tube walls. Their length can be varied from a few hundred nanometers to several hundred microns, where as the diameter can be varied from 0.37 nm to 100 nm. Bonding in the nanotubes is essentially formed through sp^2 hybridization (Niyogi *et al.,* 2002). There are two types of carbon nanotubes which are single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs).

Single-walled carbon nanotubes (SWNTs) are consisting of a honeycomb network of carbon atoms. They can be considered as a long wrapped graphene sheet. A SWNT is best described as a rolled-up tubular shell of graphene sheet. The body of the tubular shell is mainly made of hexagonal rings (in a sheet) of carbon atoms, whereas the ends are capped by dome-shaped half-fullerene molecules (Meyyappan, 2005) as shown in Figure 2.

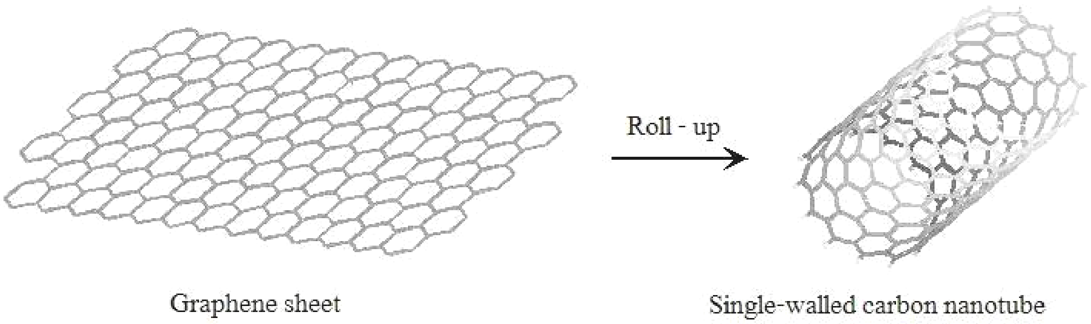


Figure 2 Sheme of graphene sheet rolled up to produce SWCNTs

Source: Sathreanranon (2005)

Multi-walled carbon nanotubes (MWNTs) can be cylinders of various diameters arranged concentric to each other with a constant spacing of 0.34-0.36 nm between them. They are consisting of multiple layers of graphitic sheets rolled in to their structure to form a tube shape (Figure 3). The length and diameter of these structures differ a lot from those of SWNTs and, of course, their properties are also significant different.

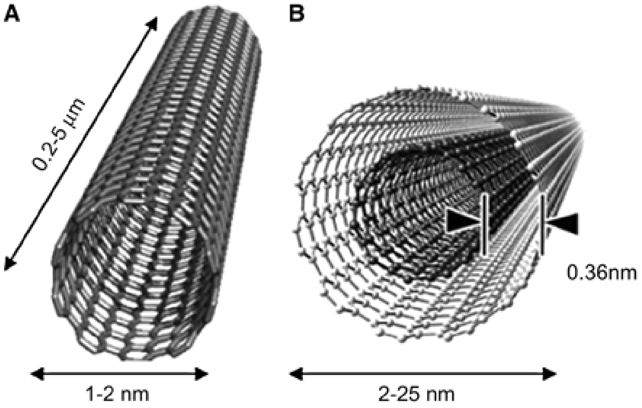


Figure 3 Structure of MWCNTs

Source: Charles (2005)

Carbon nanotubes may be either metallic or semi conducting, depending on the sheet direction which the graphene sheet is rolled to form a nanotubes cylinder. Carbon nanotubes prepared experimentally are observed to be closed at both ends. This involves the introduction of pentagonal topological defects, a minimum of six on each end of each cylinder in the tube (Sathreanranon, 2005). Thus, the tubes are essentially made of cylinders attached to half of large fullerene-like structure at the end. Types of carbon nanotubes depend on how the two-dimensional graphene sheet is rolled up (Figure 4). When the sheet rolled up in the direction of a1 axis or a2 axis, zigzag nanotubes (Figure 5b) or armchair (Figure 5a) are obtained, respectively. In the contrary, chiral nanotubes (Figure 5c) are formed when graphene sheet roll up in other axis such as c_n axis. Diameters of zigzag and armchair nanotubes are constant but that of the chiral nanotubes have different sizes depending on the roll up direction of graphene sheet (Harris and Peter, 1999).

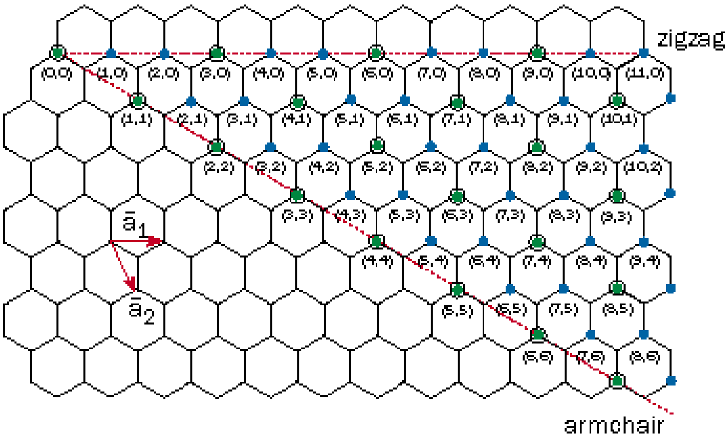


Figure 4 Characteristics of graphene sheet and roll up of graphene sheet for carbon nanotubes formation

Source: Daenen *et al.* (2005)

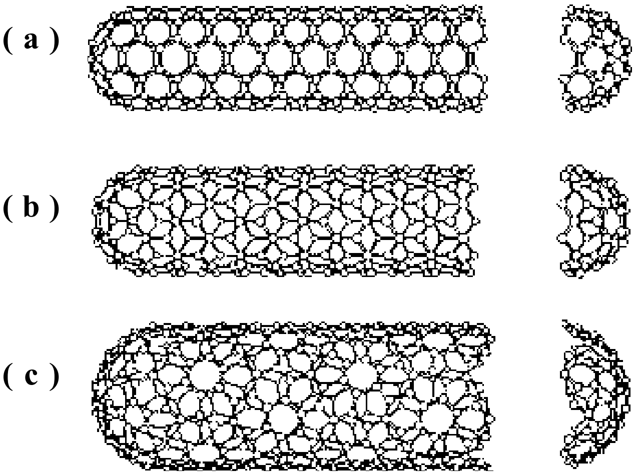


Figure 5 Characteristics of carbon nanotubes (a) Armchair (b) Zigzag (c) Chiral

Source: Daenen *et al.*

Synthesis of Carbon Nanotubes

Carbon nanotubes can be synthesized by several methods, which can be classified into 3 groups as follows: arc discharge into graphitic electrode, laser vaporization, and chemical vapor decomposition (CVD) on template by using hydrocarbon as the precursors. Methods of the carbon nanotubes synthesis are concluded as shown below.

1. Arc Discharge into Graphitic Electrode

An arc discharge evaporation method can create carbon nanotubes similar to that used for fullerene synthesis. In arc discharge, a vapor is created by an arc discharge between two graphite electrodes, place end to end and separated by approximately 1 to 4 mm (Meyyappan, 2005). The electrodes are installed in a water cooled chamber. Inert gas (helium or argon) is filled through the reactor at low pressure (between 50 and 700 mbar). After anodic graphite electrode is filled with the transition metal (Fe, Co, Ni, Y or Mo), the direct current of 50 to 1,000 Amp driven by approximately 20 Volts creates a high temperature discharge between the two electrodes. Consequently, the carbon atoms in carbon anode are vaporized and formed carbon products, depositing on the carbon cathode as shown in Figure 6. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposits form on the carbon electrode (Ebbesen *et al.,* 1992). This method can produce several forms of carbon such as carbon nanoparticles, amorphous carbon, graphitic carbon, SWCNTs and MWCNTs with defect few structural. Typical yields for arc discharge are approximately 30 % (Cui *et al.,* 2000).

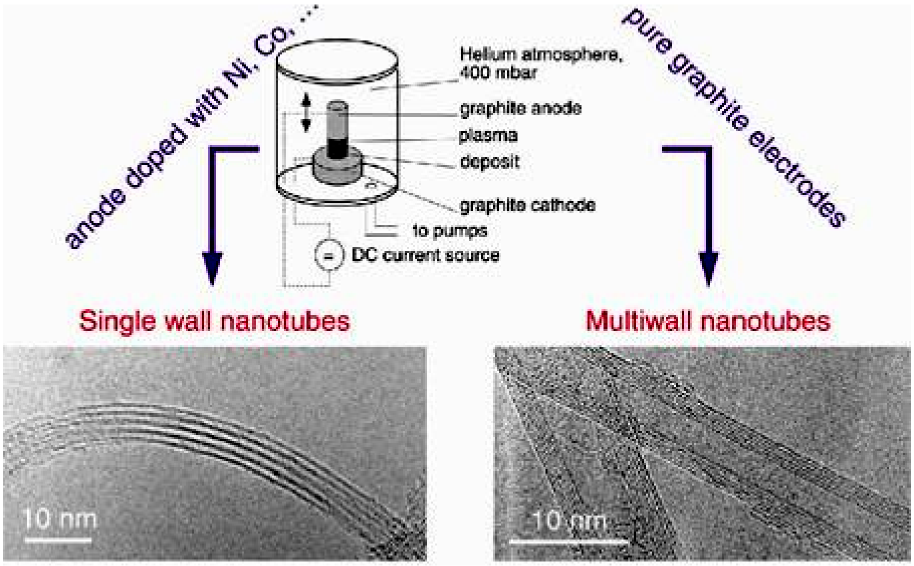


Figure 6 Experimental setup of an arc discharge apparatus

Source: Daenen (2005)

2. Laser Ablation

Another method to grow carbon nanotubes was demonstrated in 1995 by Smalley's group using laser ablation (Smalley *et al.,* 1995). The laser vaporisation apparatus is shown in Figure 7. The synthesis could be carried out in a horizontal flow tube which is heated to 1,200 °C by a tube furnace. Inert gas (helium or argon gas) is flowed to tube in order to control pressure at 500 Torr. A pulsed (Yudasaka *et al.,* 1999) or continuous (Maser *et al.,* 1998) laser enters the tube and strikes a target consisting a mixture of graphite and a metal catalyst such as cobalt or Nickel. The main difference between continuous and pulsed laser is that, the pulsed laser demands a much higher light intensity (100 kW/cm^2 with pulsed laser compared to 12 kW/cm^2 with continuous laser). Carbon nanotubes condense from the laser vaporization plume and deposit on a collector outside the furnace zone.

Laser ablation is almost similar to arc discharge, since the optimum background gas and catalyst mix is the same as in the arc discharge process. This might be due to very similar reaction conditions needed, and the reactions probably occur with the same mechanism (Daenen, 2005). This method can produce both SWCNTs and MWCNTs depending on composition of the target. The target consists of a mixture of graphite and metal catalyst is used for SWCNTs synthesis while pure graphite target is used for MWCNTs synthesis.

Carbon nanotubes formed by the laser ablation technique have large diameter range that can be controlled by varying the reaction temperature. The yield of this process is high as 70%, however it requires expensive lasers (Cui *et al.,* 2000).

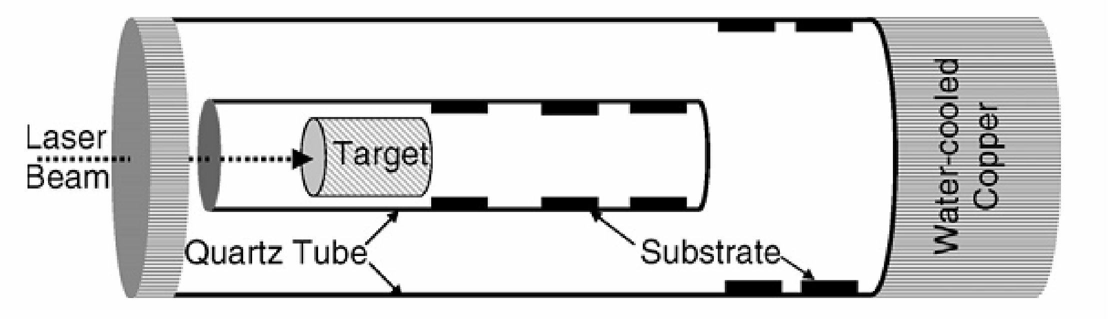


Figure 7 Schematics of a laser ablation set-up

Source: Kuchibhatla *et al.* (2007)

3. Chemical Vapor Deposition

The arc discharge and laser ablation methods are the traditional methods for obtaining nanotube materials. Nevertheless, both of them are not suitable for mass production of carbon nanotubes because of the limitation to scale up the process.

Chemical vapor deposition (CVD) is a heterogeneous reaction process used to synthesize CNTs from volatile precursors (Kuchibhatla *et al.*, 2007). This method is achieved by putting a carbon source in the gas phase and using an energy source, such as a plasma or a resistively heated coil, to transfer energy to gaseous carbon molecules. The temperature for the synthesis of nanotubes by CVD is generally between 650-900 °C (Ren *et al.,* 1998).

Normally, gaseous carbon sources used in CVD consist of methane, carbon monoxide and acetylene. The energy source is supplied in order to crack the carcon source molecule into reactive carbon atoms. Then, the carbon atom are passed through the substrate, which was heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) for a period of time (Hernadi *et al.,* 2000). At suitable condition, carbon nanotubes were formed on the substrate surfaces. The schematic of CVD process is shown in Figure 8. The carbon products were formed as SWCNTs or MWCNTs depending on types of metal catalyst and reaction conditions. In the last decade, various techniques for carbon nanotubes synthesis with CVD technique have been developed, such as plasma enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, vapor phase growth, aero gel-supported CVD, and laser-assisted CVD.

The CVD process is the best alternative to large-scale production of carbon nanotubes due to the relatively low growth temperature, high yields and the high purities that can be achieved (Kuchibhatla *et al*., 2007). This method can be categorized by the energy sources, i.e., plasma-enhanced chemical vapor deposition (PECVD), and thermal CVD.

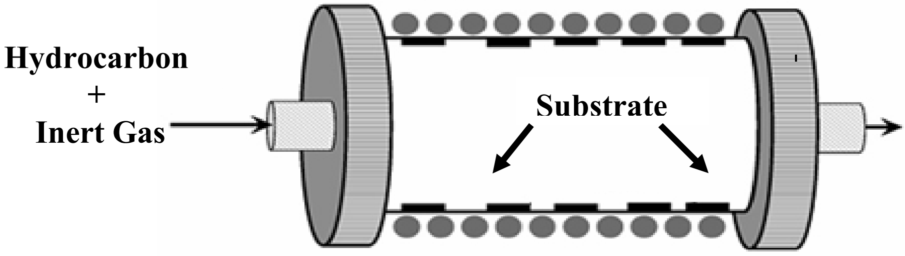


Figure 8 Schematic illustration of the CVD process

Source: Kuchibhatla *et al*. (2007)

A conventional heat source such as inductive heater, furnaces or infrared (IR) lamp can be used for thermal CVD. The thermal CVD apparatus for CNT growth was very simple. It consisted of a quartz tube of 12 mm diameters, inserted into a tubular furnace capable of maintaining a constant temperature over a 25 cm long zone (Kuchibhatla *et al.*, 2007)

Plasma source was used in plasma-enhanced chemical vapor deposition (PECVD). The PECVD method generated a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. Figure 9 shows a diagram of a typical plasma CVD apparatus with a parallel plate electrode structure (Daenen *et al.*, 2005). This method was used to avoid the elevated temperatures of thermal CVD which might be detrimental for devices (Kuchibhatla *et al.*, 2007).

As shown in Figure 9, a substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metals (such as Fe, Ni and Co) are placed on substrate (such as Si, SiO_2 or glass substrate) which the electrical energy is generated a glow discharge (plasma) and transferred into a gas mixture. This transforms the gas mixture into reactive radicals, ions, neutral atoms and molecules, and other highly excited species. A carbon source such as C_2H_2, CH_4, C_2H_6 and CO is supplied to the chamber during the discharge (Daenen *et al.*, 2005)

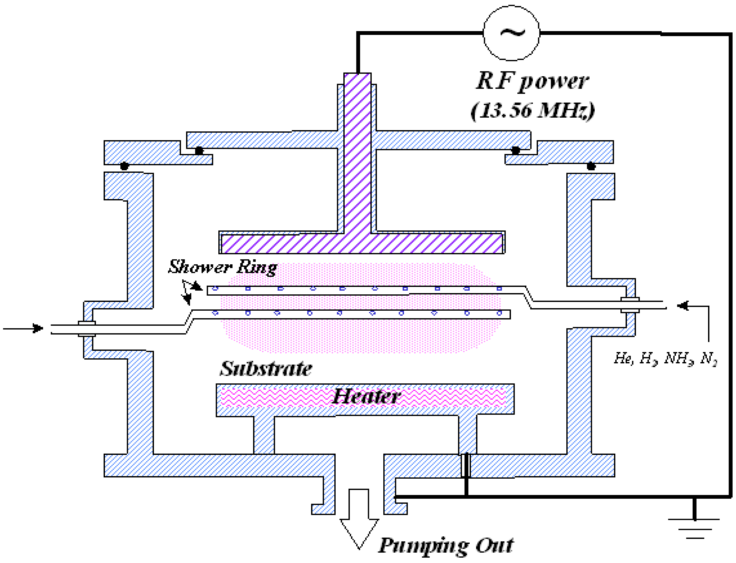


Figure 9 Schematic illustration of the PECVD process

Source: Daenen *et al*. (2005)

Properties of carbon nanotubes

The unique and powerful properties of carbon nanotubes are listed below.

1. Thermal properties

The thermal properties of carbon nanotubes display a wide range of behaviors which are related both to their graphitic nature and their unique structure and size. Kim et al. (2001) demonstrated that at room temperature thermal conductivity for an individual multi-walled carbon nanotube was 1,000 W/m.K greater than that of natural diamond and the basal plane of graphite

2. Optoelectronic properties

Defect free nanotubes have a direct band gap and well-defined band which is ideal for optical and optoelectronic applications (Meyyappan, 2005). As a result, no momentum transfer is needed to induce interband transitions and therefore direct light absorption and emission is possible (Avouris *et al.*, 2005).

3. **Chemical properties** (Meyyappan, 2005)

The unique properties including small radius, large specific surface and rehabilitation potential make CNTs very attractive in chemical and biological applications because of their strong sensitivity to chemical interaction.

Carbon nanotubes are hydrophobic and therefore, they do not show wetting behavior for most aqueous solvents. CNTs provide a capillary pressure that some of the solvents (such as HNO_3, ethanol and peroxides acid) can be filled inside their structures. CNTs have been used for molecular adsorption. Strong adsorption and charge transfer of oxygen to CNTs have been observed at room temperature.

4. **Electronic properties** (Nueangnoraj and Huskhunphisarn, 2006)

There has been considerable practical interest in the conductivity of carbon nanotubes. Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. Metallic carbon nanotubes can have an electrical current density 1,000 times greater than metals such as silver and copper.

However, there is no change in current across different parts of metallic single-walled carbon nanotubes, while the behavior of ropes of semiconducting is different, as a result the transport current changes immediately at various positions on the carbon nanotubes.

5. Mechanical properties

Carbon nanotubes have an extremely high Young's Modulus in a range of 1,500 – 5,000 GPa, which is approximately 5 times higher than steel and are very resistant to damage from physical forces (Harris, 1999). The tensile strength can be as high as 50 GPa, which is approximately 50 times higher than high-carbon steel (Treacy *et al.*, 1996).

Modifications of carbon nanotubes

Recently, surface modifications of CNTs become a significant enhancement for their properties and increase effective application purpose. The attachments of metal nanoparticles to CNTs provide the hybrid materials. These hybrid materials have found several applications in catalysis, nanoelectronic and gas sensor (Sun *et al.*, 2006). Metal particles are deposited directly onto the surface of CNTs. The surface of CNTs acts as templates which metal particles are interacted and formed hybrid materials (Georgakilas *et al.,* 2007), which the metal particles act as reactive sites for the adsorptions of target molecules (Esponosa *et al.*, 2007).

As long as, the investigation CNTs are relatively inert support, many researcher have been conducted the investigation in order to find the method to achieve optimal interaction between the support and metal or metal oxides (Fu *et al.,* 2003). Salts of noble metals are commonly used as precursors of metal nanoparticles which are obtained by a reduction process. These metal nanoparticles can be deposited onto the CNTs surface mostly through van der Waals interaction (Georgakilas *et al.,* 2007). Noble metals (Pt, Au, Ag, Pd, Ru, Rh and Cu) have been used extensively in a several application such as catalysis, optical device and gas sensing applications.

Palladium, platinum nickel and ruthenium are often used for catalytic combustion of methane and these metals are also used for hydrogenation reaction. Platinum and ruthenium have been utilized as fuel cells catalyst (Zho *et al*., 2007). Nickel shows excellent catalytic activities toward thermal decomposition of ammonium percolate (Zhang *et al.,* 2007). The researchers have been observed that nickel nanopaticles facilitate the chemisorption of hydrogen on CNTs and used for reversible hydrogen storages. CNTs are one dimensional carbon materials that the structure and morphology act as a specific template in preparing metal nanoparticles-CNTs monohybrid (Ma *et al*., 2006).

. Various methods have been used to synthesize metal nanoparticles onto the surface of CNTs, i.e., electrodepositing, incipient wetness impregnation, supercritical fluid (Fu *et al.,* 2007), electron beam evaporation and deposition/precipitation (Fu *et al.,* 2003), microwave, and template-synthesis method. The latter method leads to increase the dispersion of metal nanoparticles in the structure of carbon nanotubes (Yu. *et al.,* 2006). The metal-loaded methods are briefly explained as follows.

1. Wetness impregnation

Wetness impregnation is achieved by adding the metal-containing solution to the catalyst support. Metal salt is dissolved in the suitable solvent. The volume of this solution is the same as pore volume of support. This method requires less equipment and inexpensive. There are a lot of solvents have been used for impregnation such as distilled water, acetone and ethanol (Xue *et al.,* 2001).

Figure 10 shows an example for preparation of a Pt/Al_2O_3 catalyst by using impregnation method. Chloroplatinic acid (H_2PtCl_6) is usually used as a platinum precursors. Chloroplatinic acid is dissolved by a desired amount of solvent. The amount of solvent is equivalent to the pore volume of the alumina support. The solution is added to alumina supports. Then, the obtained catalyst is evaporated for removing the solution inside the pore and reduced by using hydrogen gas (Satterfield, 1991). A metal is then formed by reductions of the oxide or chloride by using reducing agents i.e., hydrogen gas (H_2), sodium borohydride ($NaBH_4$), hydrazine (N_2H_4) and formic acid (HCOOH) (Tsai Jeng, 2005).

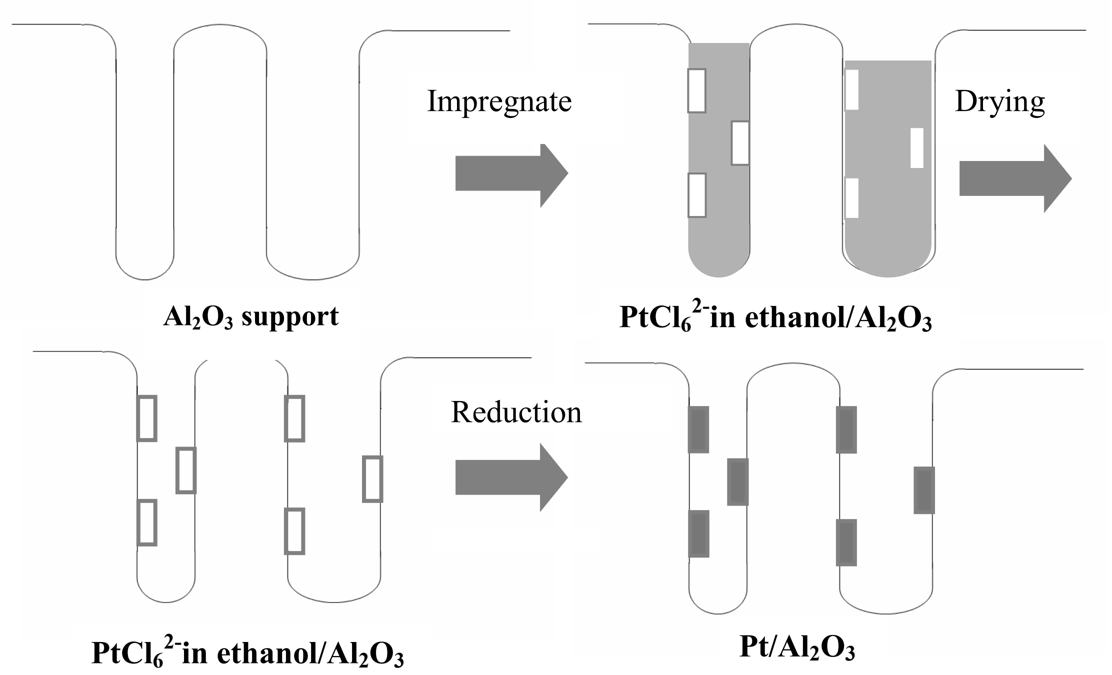


Figure10 Preparation of a Pt/Al_2O_3 catalyst by using impregnation

Source: Ruangpornvisuti (2004)

In 1996, T.W.Ebbesen *et al.* prepared the silver nanoparticles on acid treated CNTs. The results found that there was a small particle size distribution in the structure of MWNTs. The particle sizes of silver nanoparticles were about 10 nm. However, untreated CNTs found smaller amount of silver particle than that of acid treated CNTs and the particles were still 10 nm. The reason can be explained that CNTs do not possess a high amount of functional group on their surface, the silver nanoparticle can not be attached to the structure of CNTs (Fu *et al.,* 2003).

Silver particles loaded carbon nanotubes (Ag/CNTs) were also investigated by Ma *et al* in 2006. Silver were coated onto CNTs by using wet impregnation method. Silver nitrated ($AgNO_3$) was used as a silver precursor. The reduction of silver ions was undertaken in *N,N* dimethyl formamide (DMF) solution. CNTs were crushed by using ball milling with ammonium bicarbonate before silver loading. The result revealed that the conductivity of Ag/CNTs increased from 5.2 s/cm with CNTs only to 30.5 s/cm with Ag/CNTs.

The influence between the amount of metal salts and metal deposited size was found by Chen *et al* (1999). The sizes of copper salt were decreased from 25 nm to 10 nm when copper amount decreased from 2 of 1 wt%. Xue *et al.* (2001) studied the growth of palladium, platinum, silver and gold. The amount of metal salts was fixed at 2 wt%. The experiment was achieved by dispersing MWNT with the diameters of roughly 20 nm with distilled water and acetone in an ultrasonic bath. The metal salts were added and the mixture were heated until all the solvent was evaporated. The products were reduced to metals by using hydrogen gas. The result showed that the size of palladium, platinum, silver and gold were 7, 8, 8 and 17 nm, respectively. The same experiment was repeated by using palladium and the support was changed from CNTs to activated carbon. As the result, CNTs were found to be the unique templates for controlling the size of metal nanoparticles.

In 2003, Yin *et al.* studied the loading of ruthenium (Ru) on CNTs support using impregnation. Potassium ion was used for modification of Ru/CNTs. The Ru/CNTs catalysts were prepared by wetness impregnation using acetone as a solvent. The obtained catalyst was dried and calcined at 55 ^{o}C for 5 h and 550^{o}C for 2 h, respectively. The amount of Ru loading in the catalysts was 5 wt%. They found that the dispersion of ruthenium was high with the particle size around 3-10 nm. The Ru/CNTs was a good catalyst for ammonium decomposition. CNTs were highly graphitized, the electron transfer from support to ruthenium is very efficient. The enhancement in the desorption of nitrogen atom which was the kinetic controlling step in NH_3 decomposition is slow. The comparison of different supports (activated carbon, MgO, Al_2O_3 and carbon nanotubes) for ruthenium catalysts were also studied by Yin *et al.* (2004). Among these supports, CNTs was the best support material for Ru catalysts NH_3 decomposition. High dispersion of ruthenium catalyst on CNTs supported was found due to the restriction to the growth of Ru particles in the CNTs.

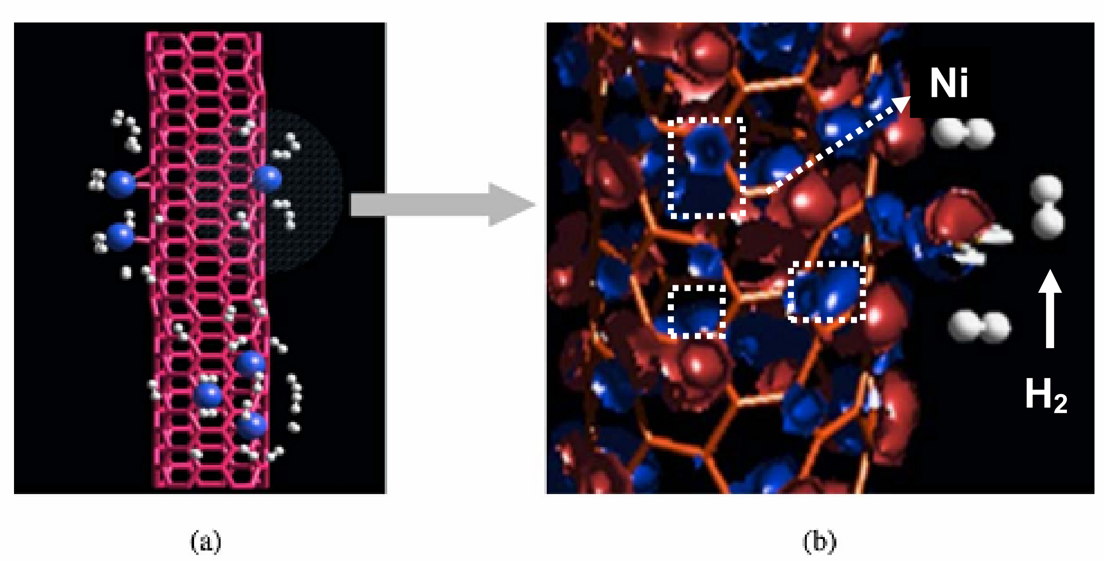
Garcia *et al.* (2006) studied the effect of metal precursors and surface modifications of carbon nanotubes. Ru/CNTs were applied for the treatment of high strength wastewater with aniline using wet air oxidation. Catalysts were prepared by using impregnation methods (excess solution and incipient wetness impregnation) and different ruthenium precursors (ruthenocene, ruthenium and ruthenium trichloride). The surface of MWNTs were modified their surface by using including nitric acid oxidized (MWCNT-COOH) and Na_2CO_3 ion exchanged (MWCNT-COONa) methods. The influence of the impregnation technique was found to be negligible. The surface of MWNTs and metal precursor influenced the catalyst properties including the catalyst selectivity for aniline removal. Ru/MWCNT-COOH showed the highest of aniline conversion.

Platinum supported carbon nanotubes (Pt/CNTs) were one of the most widely used materials, especially for fuel cell applications (Li *et al.* (2006). Pt/CNTs show good results in term of activity and selectivity in a large variety of reaction (Bittencourt *et al.*, 2008). In 2006, Li *et al.* studied the effects of the Pt deposition method and the support over Pt dispersion on CNTs by using wet impregnation. Chloroplatinic acid (H_2PtCl_6) and isopropyl alcohol were used as Pt precursors and solvent, respectively. After that, the catalysts were reduced by hydrogen gas at 500^{o}C. The particle sizes of Pt were approximately 9.8 nm. The obtained Pt/CNTs were used as catalyst for fuel cell.

Zhou *et al.* (2007) studied platinum supported multi-wall carbon nanotubes (Pt/MWNTs) for hydrodearomatization (HDA) of toluene. The platinum catalyst was loaded on MWCNTs. This mixture of H_2PtCl_6 in HCl was added dropwise to the CNTs followed by reduction with 5% H_2/N_2. The results showed a good dispersion of platinum on carbon nanotubes support. Pt/MWNTs exhibited the highest activity for toluene reaction.

Zhang *et al.* (2002) studied the preparation of nickel supported carbon naotubes (Ni/CNTs) for cracking of n-heptane. Ni/CNTs were prepared by impregnation. Nickel nitrate and alcohol were used as a nickel precursors and solvent for Ni/CNTs preparation. The carbon nanotubes were impregnated with nickel nitrate solution under stirring for 5 h, dried at 50 ^{o}C for 15 h and heated in vacuum at 136 ^{o}C for 2 h. The result showed a good dispersion of Ni and the high cracking activity for of n-heptane.

Lee *et al.* (2006) studied hydrogen storage and adsorption mechanism of Ni-dispersed CNTs based on theoretical (density functional theory method) and experimental (impregnation method) studies. Each Ni atoms dispersed on the surface of carbon nanotubes found to store the hydrogen molecules. The result observed that each Ni atoms dispersed on the surfaces of CNTs was found to store up to five hydrogen molecules with hydrogen adsorption enthalpy change of 0.26 eV/H_2 which is consistent with the 0.32 eV/ H_2 from the experimental results. Figure 11 shows that the adsorption by the first H_2 molecule occurred to induce the charge on Ni atom and was then followed by adsorptions on Ni atom by the other H_2 molecules with the help of the ionized charge on Ni atom. The results revealed that one of H_2 molecules have a H-H bonds length of 0.83 Å, while others have H-H bond length of 0.73-0.74 Å. For adsorption of the first H_2 molecule, the Ni-C bond distance was elongated to 1.99 Å and the Ni-H bond distance was 1.6 Å. The Mulliken atomic charges for Ni and H atoms was 0.11 e^- and 0.05 e^-, respectively.



(a) (b)

Figure 11 (a) H_2 molecules adsorbed around Ni atom dispersed on the surface of carbon nanotubes. (b) View for molecular orbital for 5 H_2 molecules adsorbed on the CNTs

Source: Lee *et al.* (2006)

Li *et al.* (2006) studied bimetallic Pt-Ni supported on carbon nanotubes for the liquid phase hydrogenation of cinnamaldehyde (CMA) to hydrocinnamaldehyde (HCMA). The Pt–Ni catalysts supported on CNTs were prepared by wet impregnation. Tetraammineplatinum (II) chloride ($Pt(NH_3)_4Cl_2$) and tetraamminenickel (II) chloride ($Ni(NH_3)_4Cl_2$) were used as metal precursors. The loading compositions of platinum and nickel were 0.50 wt% and 0.17 wt%, respectively. The particle size of the Pt-Ni/CNTs were 3-4 nm. The results show that the strong interaction between Pt and Ni improved the increase of activated hydrogen number. This was because of the hydrogen spillover from reduced Pt^0 onto CNTs promoted the increase of the catalytic activity and selectivity of CMA to HCMA.

2. Decomposition and reduction technique

This method is achieved by dissociating the metal salt (metal precursors), which leads to the formation of metal nanopaticles on the catalyst support. The metal loaded catalysts are dried and calcined at the optimal temperatures. After obtaining the nanotube-metal oxide or chloride product, the reducing agent is used for converting them to metal form.

The interaction between carbon materials and four transition metals such as Co, Ni and Fe was studied by Zhong *et al.* (2002). Nitrates of cobalt, nickel and iron were used as cobalt, nickel and iron precursors respectively. The procedure were proceeded through the decomposition of their nitrates at 600^oC in air for 1.5 h and followed by reduction in hydrogen at 600^oC for 1 h. The metal loaded on carbon nanotubes formed a continuous structure and the particles size was approximate 5-10 nm.

In 2006, Ayala *et.al* studied the alternative route for coating the outer walls of multiwall carbon nanotubes with metals such as nickel. Nickel compounds could be associated into nanoscale particles. The experiment was achieved by dehydration of nickel nitrate in the solution with deionized water and heated it at 500^oC. The reaction is shown below.

$$2Ni(NO_3)_{2(s)} \rightarrow 2NiO_{(s)} + 4NO_2 + O_{2(g)} \qquad (1)$$

The addition of NiO+ nanotubes were carried out by homogeneously dispersing nickel nitrate with nanotubes power using mild sonication was undertaken reduction nickel oxide to metallic nickel by using hydrogen gas as shown in equation 2.

$$NiO_{(s)} + H_2 \xrightarrow{650^{\circ}C} Ni + H_2O \qquad (2)$$

3. Thermal Evaporation Technique

Figure 12 shows the apparatus for thermal evaporation technique. Basically, this apparatus performs inside a vacuum container. The materials such as tungsten, silver and copper is heated typically to its melting point and deposited on positioned substrates. A high current flowing through the crucible heats up and causes evaporation. Various substrate materials have been used for thermal evaporation technique, i.e., alumina, halides and silicon. This method is commonly used for forming nanowires.

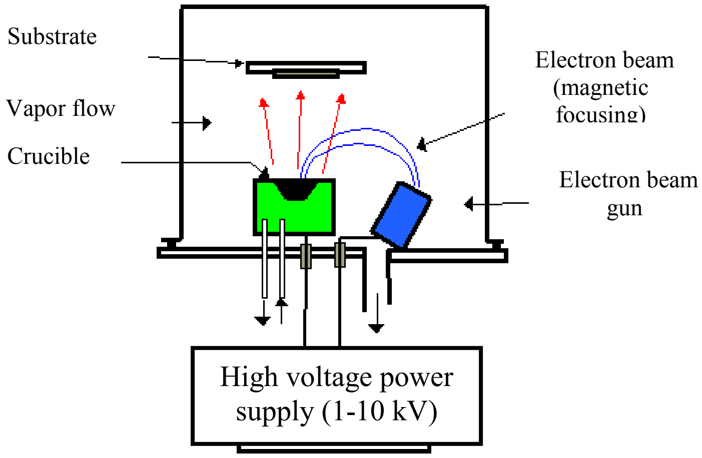


Figure 12 Thermal evaporation equipment for thin film despositions

Source: The university of Texas *at el,* paso (www.ece.utep.edu)

The interaction of transition metals was studied by Zhang *et al.* (2000). The various metals including titanium, nickel and palladium were loaded onto the single wall carbon nanotubes by using electron beam evaporation for producing carbon nanowires. The interaction between metal and carbon naotubes had the great effect on the forming of nanowires. Titanium and nickel were strongly interacted with the sidewall of nanotubes. These reactions were related to partial covalent bond. However, gold and silver led to weakly interaction with carbon nanotube through van der Waals forces.

Lu *et al.* (2004) studied the loading of palladium nanoparticles on carbon nanotubes (Pd/CNTs). A 10 nm thick metallic Pd was sputter-coated onto a pile of SWNT powder and mixed well with the SWNTs. The amount of palladium loaded was 1 wt%. The Pd/CNTs was dispersed in distilled water (0.1 mg Pd/SWNTs in 10 mL water). The solution was sonicated and dropped into the interdigitated finger for methane detection. Figure 13 shows the interdigitate finger width of 10 μm and SEM images of Pd nanoparticles.

Silver and gold loaded carbon nanotubes for gas sensing applications were studied by Espinosa *et al*. (2007). Multi-walled carbon nanotubes were deposited with gold or silver nanoclusters by thermal evaporation technique. After that, decorated MWCNTs were dispersed in an organic medium (glycerol) and dropped the MWCNTs onto silicon micro-machined sensor substrates and dried at 170°C for 1 h in order to remove organic medium. Finally, the deposited films were annealed at 400°C for 2 h. The resulting sensors were shown to be sensitive to NO_2 when operated at room temperature and significantly more selective than sensors based on MWCNTs without metal nanoclusters attached to their surface.

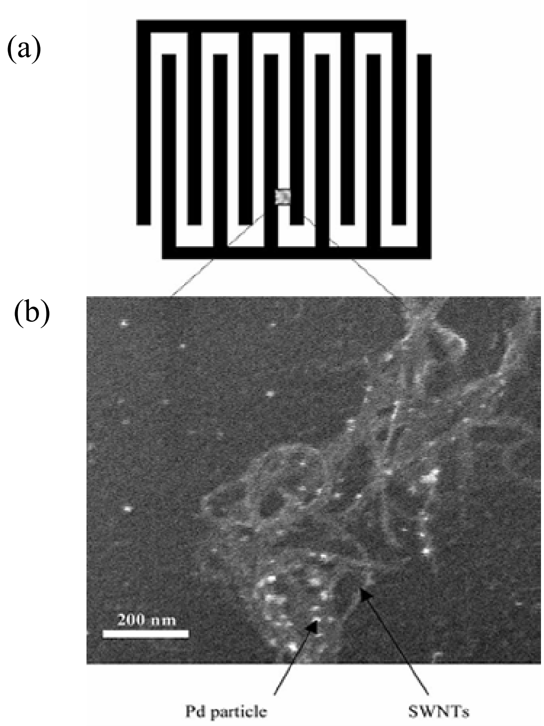


Figure 13 (a) Interdigitated fingers with a finger width of 10 μm and a gap distance of 8 μm (b) SEM image of Pd/SWNT bundles dispersed on the interdigitated fingers. The bright spots are Pd particles with measured average size of 10 nm.

Source: Lu *et al.* (2004)

Platinum has been used as an active metal loading onto CNTs with the same technique as mention above. Bittencourt *et al*. (2008) studied the amount of platinium loaded into carbon nanotubes. The desposited amount was calibrated in situ by a quartz microbalance and was reported as the nominal thickness of a hypothetical continuous layer of desposited metal given in angstroms.

Thermal evaporation technique gives a high dispersive, small particle of metal loaded onto the support and less of chemical substance. However, this method required an expensive equipment and high power consumption than those of method of preparation mention above. A wide variety of source materials for evaporation may be used including metal, alloys and semiconductor.

4. Electrochemical method

4.1 Cathodic deposition

This method is a standard of electroplating that two metal electrode are dipped into an electrolyte solution and on application of an external field across the electrodes. Metal ions from the solution are deposited on the cathode as a thin film. In order to charge balance, the anodic metal gradually dissolves in the electrolyste

4.2 Electrolyte deposition

This is similar to cathodic deposition except that it takes place in the absence of an applied external field. It is commonly used for the deposition films. Both this method and cathodic deposition have the drawback that their uses are limited mainly to the deposition of metallic films on to the electronically substrates conducting.

4.3 Anodic oxidation

This is an electrolytic method for producing oxide films on the surface of metal such as aluminium (Al), tallium (Ta), and titanium (Ti). These metals from the anode that dips into the liquid electrolyte such as salt or acid solution. Oxide ions are attracted to the anode to form a thin layer. An equilibrium thickness usually depends on the magnitude of the applied field. Anodic layers may also be formed by exploration of the metal to glow discharge. Figure 14 shows a schematic diagram of an electrolytic cell for the electrodeposition of metal "M" from an aqueous solution of metal salt "M^+,A^-"

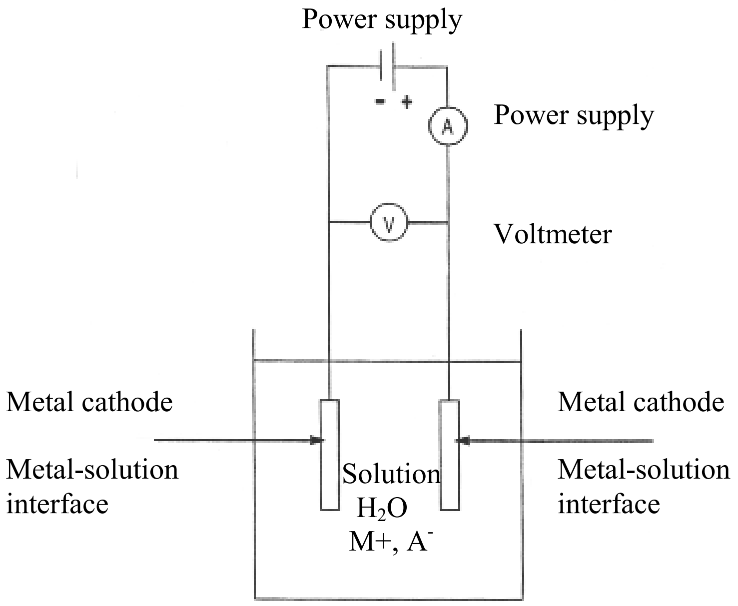


Figure 14 A schematic diagram of an electrolytic cell for the electrodeposition of metal "M" from an aqueous solution of metal salt "M^+,A^-"

Source: Mubeen *et al.*, 2007

Electrodeposition method is simple, low cost of preparations and can be operate under ambient operating condition. This method can be used to deposit various metals and metal oxides to prepared semiconductor. Electrodeposition has ability to control the properties of desposited materials such as size and density by simply altering the deposition parameters such as electrolyte, despostion time and potential (Mubeen *et al.*, 2007).

Wang *et al.* (2004) prepared Pt and Pt-Ru nanoparticles by electrodepositing method. The deposition and electrochemical studies of catalysts were carried out using an electrochemical working station at 37°C. The Pt and Pt–Ru catalysts were electrodeposited onto CNTs by potential-step deposition method using 7.7 mM H_2PtCl_6, and 7.7 mM H_2PtCl_6 mixed with 7.7 mM $RuCl_3$ aqueous solutions, respectively. The potential increased from 0.2V (the open-circuit potential of the CNT electrode) in the deposition bath solution (The potential was -0.25V) with a pulse width of 0.001 s. The results showed uniformly on the surface of CNTs.

Mubeen *et al*. (2007) prepared palladium nanoparticles decorated single-walled carbon nanotubes for hydrogen sensor application. The result indicated that there was site specific deposition of Pd nanoparticles on SWNTs. Palladium nanoparticles on SWNTs was performed using three electrode cell configurations. The electrochemical cell was performed by adding a 3 μL of Pd electrolyte solution on the top of the SWNT network and platinum and Ag/AgCl wires were inserted into the electrolyte. The annealed SWNT network along with the gold electrodes served as the working electrode while platinum wire and Ag/AgCl wire served as the counter electrode and reference electrode respectively. The amount of palladium on SWNTs was examined by varying the deposition potential from -0.7 to-1.0 V vs Ag/AgCl. The optimal Pd electrodeposing is -0.8 V

Applications of carbon nanotubes

Carbon nanotubes are of great potentail material for an applications in ultra fine devices, because of their unique electrical characteristics and their extraordinary fine structure on a nanometer scale. The potential applications of carbon nanotubes are briefly explained as follows.

1. Energy storage

Nueangnoraj and Huskhunphisarn (2006) Because of their cylindrical and hollow geometry, carbon nanotubes have been predicted that they can store a liquid or gas in the inner core. Many experimental reports showed that carbon nanotubes could be used in fuel cell or energy storage application. The advantages of considering them as energy storage are their small dimensions, smooth surface topology and perfect surface characteristics. Nutzenadel *et al.* (1999) demonstrated that single-walled carbon nanotubes could electrochemically store hydrogen. The hydrogen storage capacity was analyzed by means of electrochemical galvanostatic measurement in potassium hydroxide (KOH) electrolyte as shown in Figure 15. During the charging process, water in the electrolyte would be dissociated and the work electrode adsorbed the atomic hydrogen. During the discharge process, the atomic hydrogen in the electrode would recombine with the hydroxide ions (OH^-) in the electrolyte to form water. The amount of hydrogen desorbed can be measured by measuring the electric charge (Zuttel *et al.,* 2002). The advantage of hydrogen as the energy source is that its combustion product is water. In addition, hydrogen can be easily generated.

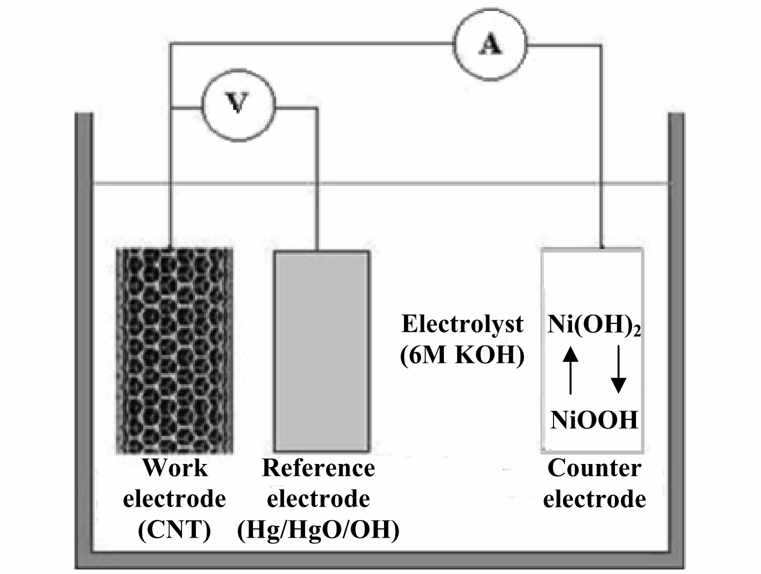


Figure 15 Schematic diagram of a charge-discharge cyclic apparatus for the hydrogen storage capacity analysis

Source: Daenen *et al.* (2005)

2. Gas sensing application

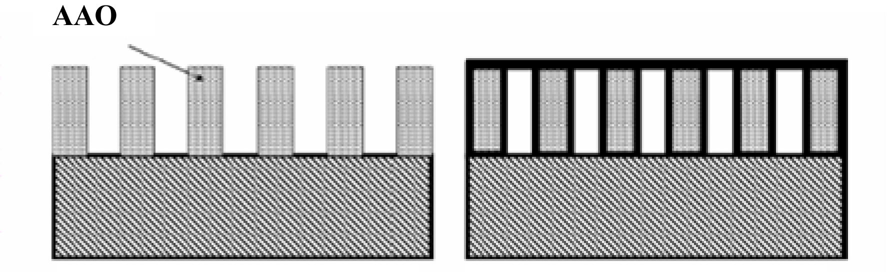
The electronic structure of CNTs can be either metallic or semiconducting depending on their diameter and chirality. As a result of these wide-scale electronic properties, there is the possibility of developing nanoelectronic devices as nanowires or as metal/semiconductor heterojunction by combining metallic and semiconducting carbon nanotubes (Valentini *et.al.*, 2004).

In gas sensing application, the interaction between CNTs and the gas molecule are involved. Electron donating and withdrawing molecules can either transfer electrons or attract electrons from CNTs, giving them more charge carriers or holes which can be changed the conductivities of CNTs (Lu*, el al.,* 2004). The donating and accepting gases such as NO_2, NH_3 or phenol show good electron donor or acceptor properties. This can give large changes of CNT conductivities.

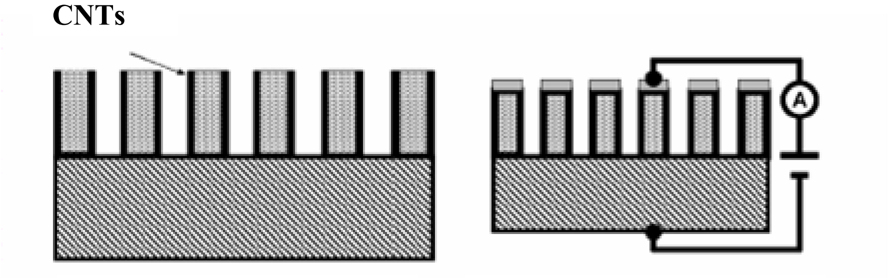
In 2004, Valentivi *et.al* studied the electrical resistance of CNTs thin films to NO_2, CO, NH_3, H_2O and C_2H_5OH for gas sensing applications. The sensor was frabricated by Photolithography. Platinum electrodes were used upon Si_3N_4 and CNTs was grown to Si_3N_4 structure. The electrical response was investigated by exposing the films to the interfering gases at different operating temperature between 25-250^{o}C.

The result showed that the electrical resistance of CNT decrease when it exposed to 10-100 ppb of NO_2. No response has been found by exposing to CO gas. In the contrary, NH_3 leaded to increase the electrical resistance of the films. The experimental result implied that CNTs showed a p-type of semiconductor.

An ammonia gas sensor based carbon nanotubes without metal loading were studied by Hoa *et al.* (2007). In their research, CNTs sensor was fabricated as follows: (i) Anodic aluminum oxide (AAO) was used as the substrate (ii) the CNTs were synthesized on the surface of the nano pore wall. The AAO fabricated on a Si substrate was mechanically stable and formed regular arrays of nanopores of uniformed diameter and length. The CNTs synthesized on the surface of the nanopore wall conformed to the geometry of the nanopores in the AAO, and thus they also formed regular arrays of nanotubes of uniform diameter and length. CNTs were synthesized by a chemical vapor deposition technique as shown in Figure 16.



(a) AAO frabrication (b) Synthesis of CNTs



(c) Open the CNTs (d) Deposit Ag electrode

Figure 16 Schematics of sensor fabrication process. (a) Synthesis of AAO on p-type Si substrate, (b) synthesis of CNTs by thermal CVD, (c) removal of the top carbonlayer by oxygen plasma (for 1200 ◦C synthesis) and (d) Ag electrode deposition.

Source: Hoa *et.al* (2007)

The structure of carbon nanotubes was uniform in diameter and length but they had a lot of defect structure. Then, thin films of silver were sputter-desposited for the electrode preparation. The sputtering process was carried out at a pressure of 5×10^{-3} Torr and a current of 40 mA for 2 min to achieve a silver thickness of 40 nm. The electrical measurement was performed by introducing nitrogen and ammonia gas. The test chamber was first evacuated and then filled with N_2. The initial state of the gas sensing test was established by a steady state resistance of the sensor under a nitrogen flow. The gas sensing properties were measured at atmospheric pressure of the gases at room temperature by measuring the resistance between the top Ag electrode and the bottom semiconductor. Nitrogen and ammonia gases were introduced into the chamber at a rate of 500 sccm using mass flow controllers. The concentrated ammonia was diluted by mixing with high purity N_2 gas. The sensor revealed a fast response and good recovery beheavior. This sensor was high sensitivity toward ammonium gas.

In the contrary, some gas molecules showed no or very small electron donor or acceptor properties such as methane, LPG and carbon monoxide, and therefore no or small changes CNT conductivities were observed (Varghese *el al.,* 2004). The concept of using CNTs decorated with metal cluster for the adsorption of the target molecules has been introduced recently in a theoretical study (Espinosa *et al.*, 2007).

In 2004, Lu *et al.* studied SWNTs loaded with palladium (Pd) nanopartocles by using thermal evaporation. The experimental procedure for Pd-loading was described in thermal evaporation sections. These modified SWNTs can be used for gas detection when loaded appropriately, particularly with transition metals that interact with these molecules. It should be noted that the experimented results of pure SWNTs revealed no sensor response to methane. Pd loaded SWNTs was applied for methane detection at room temperature. Pd attracted electron from SWNTs, when methane molecule was adsorbed in Pd-SWNT matrix to form a weekly bound complex $Pd^{\delta+}(CH_4)^{\delta-}$. As the result, the current through p-typed SWNTs increased with CH_4 concentration.

Metal-decorated multi-walled carbon nanotubes (MWCNTs) for gas sensing applications were studied by Espinosa *et al.,* (2007). Multi-walled carbon nanotubes were deposited with gold or silver nanoclusters by thermal evaporation technique. After that, the decorated MWCNTs were dispersed in an organic medium (glycerol) and dropped the MWCNTs onto silicon micro-machined sensor substrates and dried it at 170°C for 1 h for removing organic medium. Finally, the resulting sensors were to sensitive to NO_2 when operated at room temperature and significantly more selective than sensors based on MWCNT without metal nanoclusters attached to their surface.

3. Catalyst supports

Carbon nanotubes were discovered and extensively studied due to their unique chemical and mechanical properties and for different potential applications (Tessonnier *el al*., 2003). Recently, multiwalled carbon nanotubes have attrached much interest attention. This is form of carbon structurally close to a hollow graphite fiber, except that it has a much higher degree of structural perfection. This multiwalled carbon nanotube possesses a series of unique features, such as high mechanical strength, graphite-like tube-wall structure, sp^2-C-constructed surface, and nanometer-sized channels. They display high thermal and electrical conductivities and excellent performance for adsorption and spillover of hydrogen, all of which give this kind of nanostructures carbon material to be promising as a novel catalyst support or promoter (Min *et al.,* 2007).

MATERIALS AND METHODS

In this section, the synthesis and modification of CNTs were described in detail. Carbon nanotubes were synthesized by chemical vapor deposition (CVD) method using anodic aluminum oxide (AAO) as a template and modified carbon nanotubes by loading reactive metals including platinum (Pt), ruthenium (Ru) and nickel (Ni) into their framework structures using wet impregnation method. Types of metal and the amount of metal loading were the studied variables. The morphology and structure of the obtained multi-walled carbon nanotubes were investigated using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The lone pair electron of carbon nanotubes were characterized by electron spin resonance spectroscopy (ESR). The surface area was characterized by N_2-adsorption technique. The amount of metal loaded on CNTs was characterized by inductively coupled plasma (ICP). The effect of LPG on an electrical property of metal-doped carbon nanotubes-based gas sensor was investigated using electrical resistance measurement technique.

Laboratory Equipments

1. CVD reactor and pipe-line system
2. Alloy tube (Carbolite)
3. Mass flow controllers (Aalborg, GFC171S)
4. Tube furnace (Carbolite, Control-2416)
5. Pressure transmitter (Gefran, TKG-E-1-F-BO2D-M)
6. Digital indicator (PM, CM-004)
7. Digital balance (Metler Toledo, AT 400)
8. Magnetic hotplate and stirrer (SLR Model, Scott)
9. Teflon beaker
10. Quartz wool (Altech)
11. Centrifugal separator
12. Desicator (Schott)

13. Beaker (Schott)
14. Multimeter
15. Glass testing chamber
16. Cover glasses

Equipments for Sample Analysis

1. Scanning Electron Microscopy (SEM) (JEOL, JSM-5600 LV)
2. Transmission Electron Microscopy (TEM) (JEOL, JEM-2010)
3. Electron Spin Resonance Spectrometer (ESR) (ESR model RE-2X)
4. Inductive Coupled Plasma Optical Emission Spectrometer(ICP-OES) (ICP-OES model PLASMA-1000)
5. N_2-Autosorp (Autosorp)(Quantachrome Corporation)

Materials

1. Nitrogen gas (TIG; N_2 99.99 vol.% purity)
2. Acetylene gas (TIG; C_2H_2 99.5 vol.% purity)
3. Hydrofluoric acid, HF (Carlo Erba; 50 wt.% purity)
4. Anodic aluminum oxide template or AAO template (Whatman; Anodise 25: 0.2 µm 25 mm circle)
5. Ruthenium (III) chloride hydrate, $RuCl_3.xH_2O$ (Fluka; 41 wt.% putity)
6. Dihydrogen hexachloroplatinate (IV) hydrate, $H_2PtCl_6.6H_2O$ (Fluka; 38 wt.% putity)
7. Nickel nitrate hexahydrate, $Ni(NO_3)_2{\cdot}6H_2O$ (Unilab; 97 wt.% purity)
8. Sodium borohydride, $NaBH_4$ (Asia Pacific Specialty Chemical Limited; 97 wt.% purity)
9. Ethanol, C_2H_5OH (Merck; 95 wt.% purity)
10. Hydrochloric acid fuming 37%, HCl (Merck; 38 wt% purity)
11. Distilled water

Methods

This part was divided into three steps; carbon nanotubes preparation, activation of carbon nanotubes by loading reactive metals (platinum, ruthenium and nickel) and the performance test of the carbon nanotubes and modified carbon nanotubes for the gas sensor application.

1. Carbon nanotubes preparation

Carbon nanotubes were synthesized using anodic aluminum oxide (AAO) films as the templates via chemical vapor deposition (CVD) method. The detail procedures were as follows:

1.1 AAO templates were placed on the quartz wool packed in a vertical CVD reactor as shown in Figure 17

1.2 Nitrogen gas with a flow rate of 20 ml/min (NTP) was supplied into the CVD reactor under atmospheric pressure.

1.3 The reactor temperature was increased from room temperature to 750^{o}C at the heating rate of 3^{o}C/min and hold there for 30 minutes.

1.4 A gaseous mixture consisted of acetylene and nitrogen was introduced into the CVD reactor at the concentration of 10% acetylene and nitrogen balance. The details of the operating conditions were obtained from the previous study by Sathreanranon *et al.* (2005). The total gas flow rate was fixed at 20 ml/min at 750^{o}C for the reaction time of 150 minutes.

1.5 Carbon nanotubes (CNTs) arrays were formed in the pores of AAO templates as the scheme shown in Figure 17.

1.6 After that the reactor was cooled down to room temperature under nitrogen ambient and CNTs/AAO composites were removed from the CVD reactor. The experiment were repeated and the temperature was changed from 750^{o}C to 1000^{o}C.

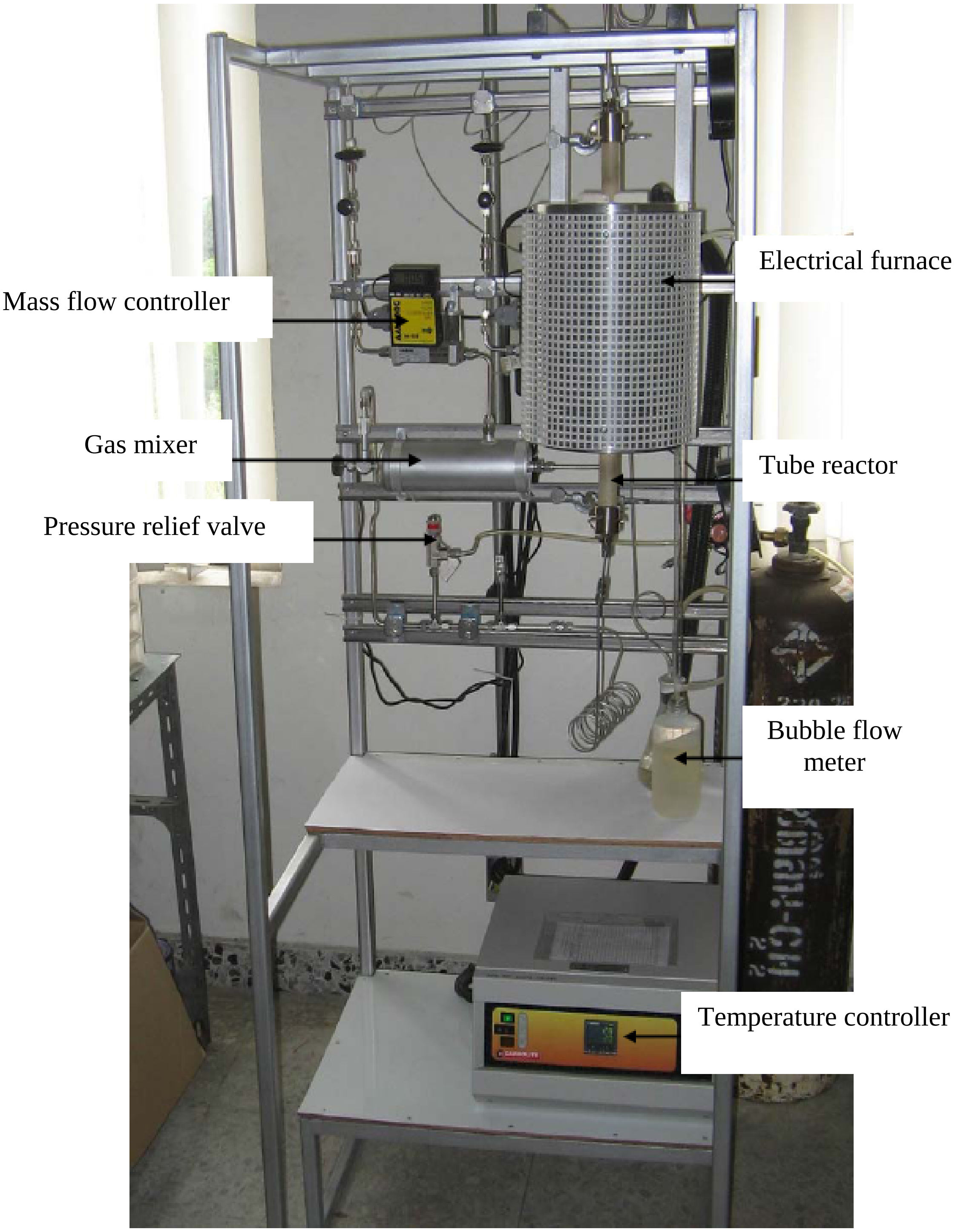


Figure 17 The setup of vertical CVD reactor for synthesis of carbon nanotubes

2. Activation of carbon nanotubes by wetness impregnation

In this section, carbon nanotubes/AAO composites were loaded by using wetness impregnation method. Dihydrogen hexachloroplatinate (IV) hydrate ($H_2PtCl_6.6H_2O$), ruthenium (III) chloride hydrate ($RuCl_3.xH_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) were used as platinum, ruthenium and nickel precursors, respectively. The amounts of metal loaded were fixed at 4 wt%. The experimental detail was described as follows:

2.1 The 20 ml of an aqueous solution of dihydrogen hexachloroplatinate (IV) hydrate salt in ethanol was added into carbon nanotube/AAO composites (CNTs/AAO) in atmosphere of N_2 and soaked at room temperature for 3 hours.

2.2 Carbon nanotubes/AAO composites were then separated from the solution and dried in N_2 ambient at 100^oC for 1 hour.

2.3 After drying process, platinum loaded carbon nanotube/AAO composites were reduced with 200 ml of 0.1 M $NaBH_4$ at room temperature for 2 hours.

2.4 The platinum loaded carbon nanotubes/AAO composites were separated, washed with distilled water at 40^oC, and dried in N_2 atmosphere at 100^oC.

2.5 The experiments were repeated and the metal-precursor was changed to ruthenium (III) chloride hydrate (ruthenium precursor) and nickel nitrate hexahydrate (nickel precursor) with the same condition as mentioned above.

2.6 After that, the carbon nanotubes/AAO composites (CNTs/AAO) and metal-carbon nanotubes/AAO composites (Pt-CNTs/AAO, Ru-CNTs/AAO and Ni-CNTs/AAO) obtained from the preparation stages were characterized by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The specific surface area of carbon nanotubes/AAO composites (CNTs/AAO) and metal-carbon nanotubes/AAO composites were determined by N_2-adsorption technique.

3. Performance test of the carbon nanotubes and modified carbon nanotubes for the gas sensor application

In this performance test, physical properties, adsorption properties, elemental analysis and electrical properties of CNTs/AAO and metal-carbon nanotubes/AAO composites have been examined. The analysis details were described below.

3.1 Physical properties

After the synthesis and loading process, the obtained carbon nanotubes were characterized for their morphology and structure by using scanning electron microscopy and transmission electron microscopy.

3.2 Adsorption properties

The specific surface areas of carbon nanotubes before and after metal loading were determined by N_2-adsorption technique.

3.3 Elemental Analysis

The metal loaded samples were digested with 38% hydrochloric fuming in order to break down the metal loaded carbon nanotubes structure before performing the chemical compositions analysis by Inductive Coupled Plasma Optical-Emission Spectrometer (ICP-OES). The ICP-OES results confirm the existence of active metals (Platinium, Rutinium and Nickel) in the structure of carbon nanotubes. First, the CNTs/AAO, Pt-CNTs/AAO, Ru-CNTs/AAO and Ni- CNTs/AAO) were treated with 50 wt.% hydrofluoric acid for 6 h to dissolve the AAO templates, then the obtained mixture was rinsed with distilled water. The hydrochloric acid was used for acid digestion of CNTs. The 20 ml of hydrochloric acid were added and stirred until the solution turned to black color. The solution of metal-carbon nanotubes was heated to 80^oC and evaporated for 30 minutes. Then, the solid products were separated from the mixture by filtration and washed with the distilled water. The digested solutions were diluted and made up volume to 50 ml and sent for chemical compositions characterization.

3.4 Electrical properties

Electrical resistances of the CNTs/AAO and Pt, Ru and Ni-CNTs/AAO composites were analyzed using an ohmmeter (Model DM879). The CNTs/AAO were placed in a cover glass and connected with copper wires. Then, the analysis cell was transferred to the glass testing chamber with electrical supply. The electrical resistance measurement was measured under a series of LPG and N_2 loading as a cycles which the concentration of LPG at 100 ml/min. All experiments were performed at room temperature and each experiment was replicated for three times.

RESULTS AND DISCUSSION

In this research, carbon nanotubes were synthesized by chemical vapor deposition (CVD) method using anodic aluminum oxide (AAO) as a template and 10% acetylene in nitrogen gas as reactant gases. As the CVD temperature (growth temperature) affecting the wall thickness and the number of layer of carbon nanotubes, the carbon nanotubes on anodic aluminium oxides composites (CNTs/AAO) were synthesized by using the temperatures of 750^{o}C and $1,000^{o}$C. After that, CNTs/AAO were modified by loading reactive metals including platinum (Pt), ruthenium (Ru) and nickel (Ni) into their framework structures using wet impregnation method. The physical properties of the synthesized carbon nanotubes and metal loaded carbon nanotubes were characterized by electron microscopy (SEM), transmission electron microscopy (TEM). The adsorption properties of unloaded carbon nanotubes and metal-loaded carbon nanotubes were analyzed by N_2-sorption technique. The amount of metal loaded on CNTs was characterized by inductively coupled plasma (ICP). Then, the LPG sensing performance was analyzed using electrical resistance measurement technique.

1. Physical properties of unloaded and metal loaded carbon nanotubes

As shown in Figure 18(a), the diameter and thickness of anodic aluminum oxides (AAO) films are 25 mm and 60 µm, respectively. The pore diameter of straight channels is approximately 200 nm. The SEM image in Figure 18 (b) shows that this aluminum oxide film has high pore density, narrow pore size distribution, and straight pore openings.

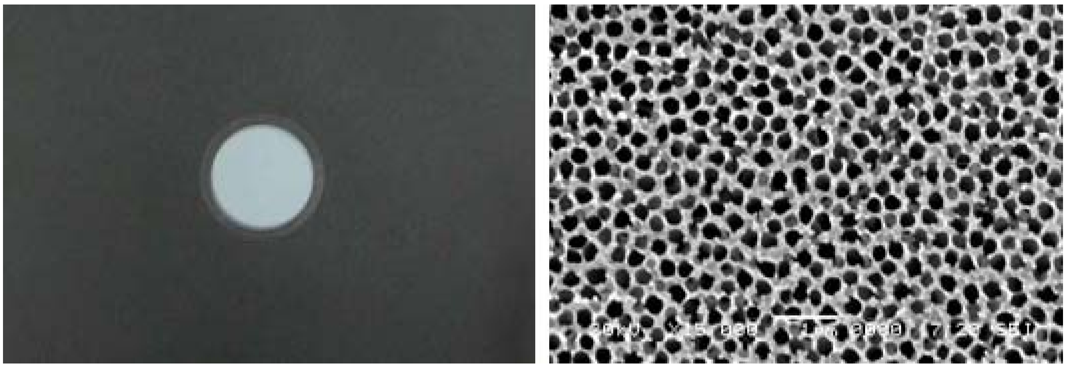


Figure 18 Anodic aluminum oxide (AAO) films (a) photograph (b) SEM image

The anodic aluminum oxide films were used as the templates for carbon nanotubes synthesis via chemical vapor deposition (CVD) method using 10% acetylene in nitrogen and reaction periods at 150 min. The CVD temperature of 750^{o}C and 1,000 ^{o}C were used for synthesis of CNTs. The synthesized carbon nanotubes/AAO composites are defined as CNTs/AAO-750 and CNTs/AAO-1000. The carbon nanotubes/AAO composites obtained from both of the CVD temperatures found to be a little twisted and bent as shown in Figure 19. It was caused by the different expansion rates between two sides of the AAO film during the exposure with reactant gases under high temperature. The black color and glitter of CNTs/AAO composites were observed after the deposition of carbon nanotubes into the template. After that, the CNTs/AAO composites were soaked with 50 wt% hydrofluoric acid for 6 h to remove the AAO templates as shown in Figure 20 for investigating morphology and the wall thickness of carbon nanotubes using transmission electron microscopy (TEM).

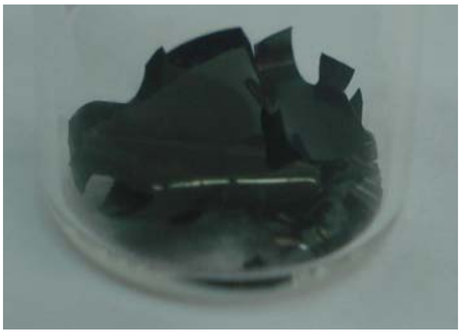


Figure 19 Photograph of carbon nanotubes/AAO composites

Figure 20 Photograph of carbon nanotubes without AAO template

Figure 21 show the schematic of formation in the pores of AAO templates. The result revealed a uniform carbon tubes with accurately control of the tube diameter and thickness.

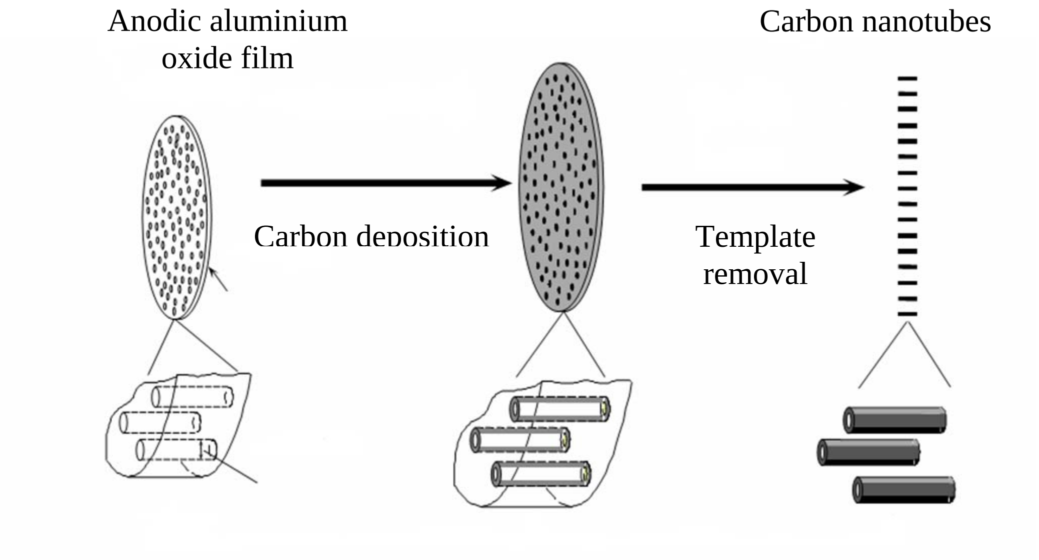


Figure 21 Preparation procedure of carbon nanotubes synthesis in anodic aluminum oxide (AAO) template via chemical vapor deposition (CVD) method

(a) Scheme of the pores of AAO template

(b) Scheme of carbon nanotubes formation in the pores of AAO template

(c) Scheme of carbon nanotubes after dissolution of the AAO template

After the AAO template was removed, the morphology and the wall thickness of carbon nanotubes were obtained by TEM image as shown in Figure 22. The result revealed the high purify, smooth walls and complete tubes of carbon nanotubes at the growth temperature of 750^{o}C (CNTs-750). These carbon nanotubes were opening straight tubes with uniform diameter, length and wall thickness. There were no other formed of carbon nanotubes from in the products. Similar results were observed for carbon nanotubes at growth temperature of 1,000^{o}C (CNTs-1000). Figure 23(a) shows the outer diameter of the tubes which is approximately 300 nm.

.

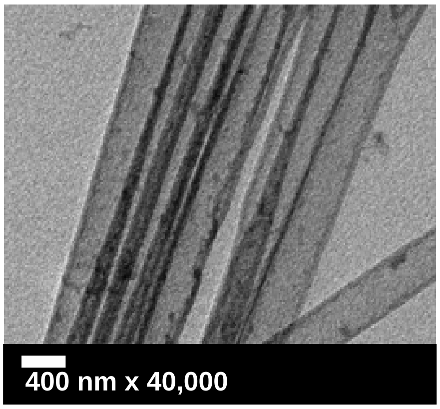


Figure 22 TEM images of carbon nanotubes at growth temperature of 750^{o}C

The wall thickness and layer numbers of carbon nanotubes were determined from the TEM image by comparing the wall thickness of carbon nanotubes with the scale bar length. The obtained size of wall thickness was divided by the constant spacing length between the graphitic layers (0.34 nm). Then, the calculated result was added by the value of 1 and the layer numbers of carbon nanotubes were calculated. For example, Figure 23(b) shows the wall thickness of carbon nanotubes at growth temperature of 750^{o}C. The length of the wall thickness and the scale bar were 19 and 17 mm, respectively. The ratio between these two values is was 19/17 = 1.12 which was equal to 1.12 x 20 or 22.4 which was the wall thickness of carbon nanotubes. The wall thickness was then divided by spacing between the graphitic layer (0.34). Therefore, the layer numbers of carbon nanotubes is 66+1 = 67.

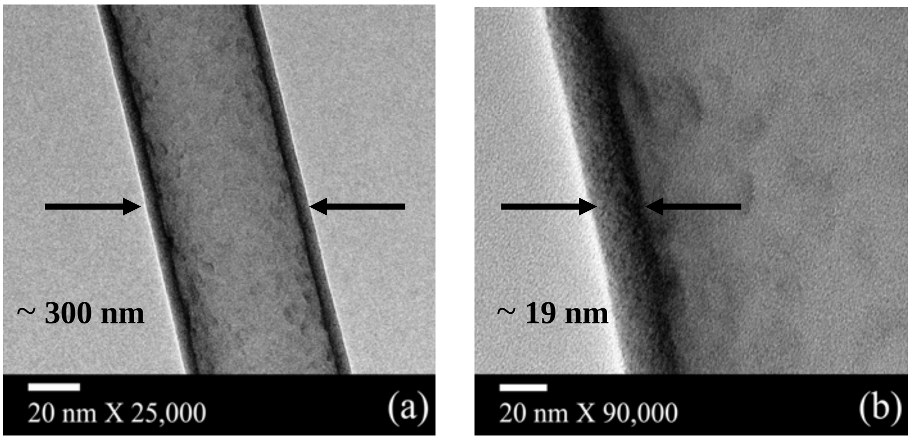


Figure 23 (a) The outer diameter of synthesized carbon nanotubes at the growth temperature 750 ^{o}C (b) The wall thickness of carbon

From Figure 24, the outer diameter is 300 nm and the wall thickness of carbon nanotubes is 35 mm. The wall of thickness and layer numbers of carbon nanotubes can be determined by using the same method as mentioned above. The lengths of the wall thickness were the scale bars are 35 and 18 mm, respectively Therefore, the layer numbers of carbon nanotubes is 114+1 = 115. As the result, the wall thickness and the number of layers were increased with increasing the growth temperature. This result was corresponded to Sathreanranon *et al*. (2005) where the layer of carbon nanotubes was increased from 35 to 50 layers with the growth temperatures of 150 and 180 ^{o}C, respectively.

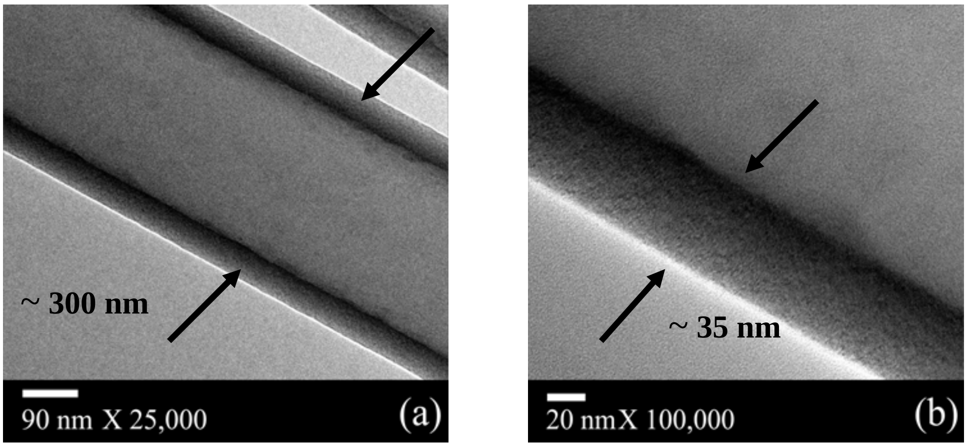


Figure 24 (a) The outer diameter of synthesized carbon nanotubes at the growth temperature of 1000°C (b) the wall thickness of carbon

From SEM and TEM analysis, the results confirmed that multi-walled carbon nanotubes (MWNTs)/AAO composite product were synthesized. This result corresponds to the work reported by Sathreanranon *et al.* (2005) who synthesized carbon nanotubes CVD method using AAO as templates and 1b0% acetylene in nitrogen gas as the reactant gas 750°C for 150 min (Figure 25). The wall thickness and layers were approximately 12 nm and 35 layers, respectively.

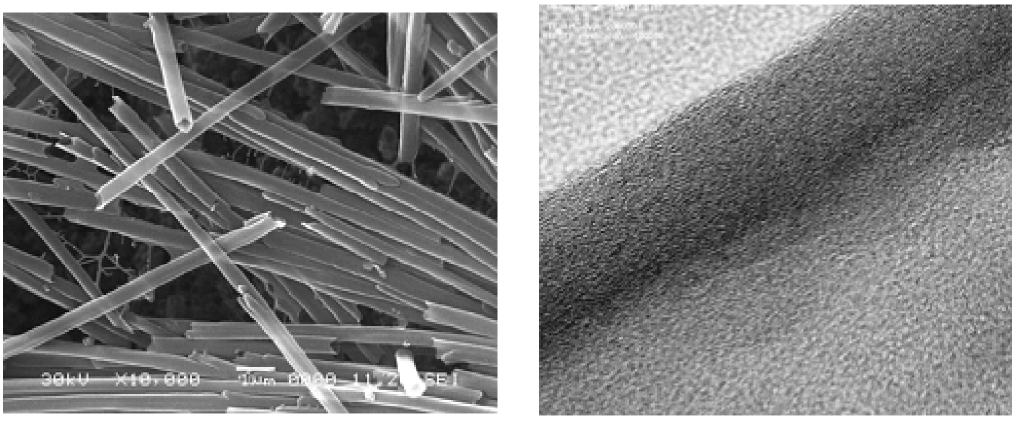


Figure 25 Carbon nanotubes synthesized using 10% acetylene in nitrogen as the reactant gas at the CVD temperature of 750°C for 150 min (a) SEM image (b) TEM image

Source: Sathreanranon *et al*. (2005)

After the synthesis of multi-walled carbon nanotubes via the CVD reaction, the carbon nanotubes/AAO composites were modified by loading reactive metals such as platinum (Pt), ruthenium (Ru) and nickel (Ni) into their framework structures using wet impregnation method. Chloroplatinic acid hexahydrate, ruthenium (III) chloride hydrate and nickel nitrate hexahydrate are used as a platinium, ruthenium and nickel precursors, respectively. To investigate the framework structure of the metal loaded carbon nanotubes obtained after the loading process, the TEM technique was applied.

Since, chloroplatinic acid hexahydrate was used as platinum precursors, chloroplatinic acid hexahydrate was dissolved in ethanol and CNTs/AAO composites were soaked in the obtain solution. Pt loaded CNTs/AAO was reduced with 0.1M $NaBH_4$ at room temperature. From TEM image of the obtained product was shown in Figure 25 (a) the dark spots were thoroughly distributing in structure of CNTs/AAO-750. Figure 25 (b) shows the enlargement of the circled section in Figure 25 (a). This revealed the dark spots were also inserted between the layers of multi-walled carbon nanotubes as can be seen in the dark circle areas. The particle size of particle was about 3-4 nm. To confirm the existence of platinum in the CNTs/AAO-750, Energy Dispersive X-ray Spectrometer (EDX) technique was applied as the result shown in Figure 26. There are small peaks at the energy dispersion of 2.13 keV and 9.85 keV of which corresponded to the platinum particles.

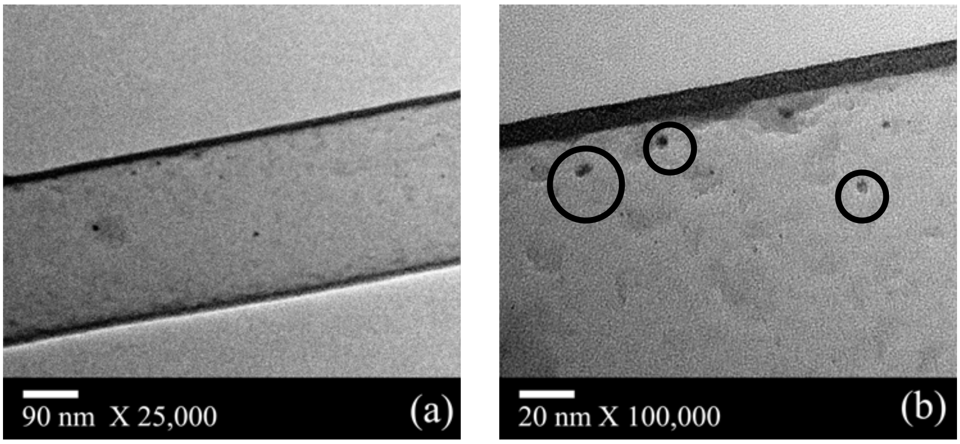


Figure 26 Platinum loaded CNTs/AAO-750 (a) TEM image (b) the enlargement of the circled section (a)

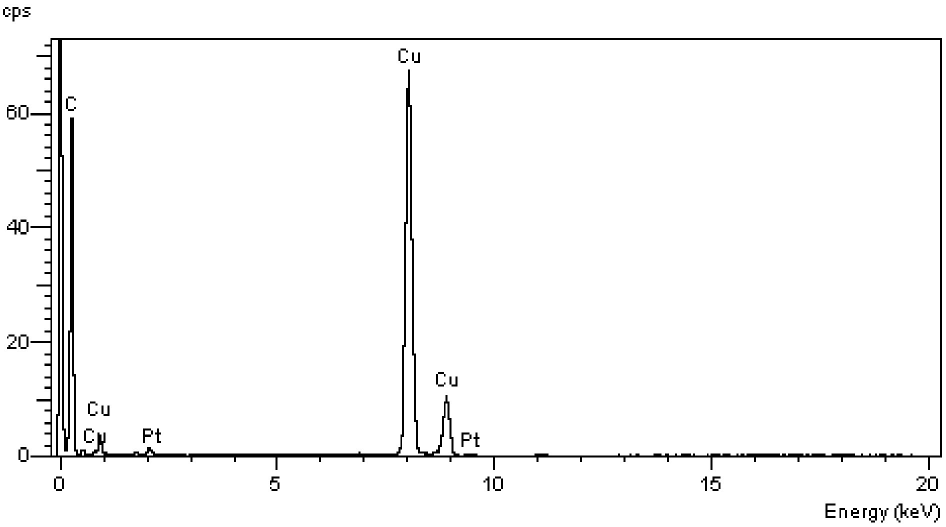


Figure 27 EDX spectrum of Pt-CNTs/AAO-750

The Pt-CNTs/AAO-1000 was prepared by using the same method as mentioned above. The support was changed from CNTs/AAO-750 to CNTs/AAO-1000. TEM technique was also applied to investigate the framework structure of the metal loaded carbon nanotubes. Figure 27(a) show the dark spots thoroughly distributing in whole structure of CNTs/AAO-1000. The same pattern of EDX spectra is observed in Pt-CNTs/AAO-1000.

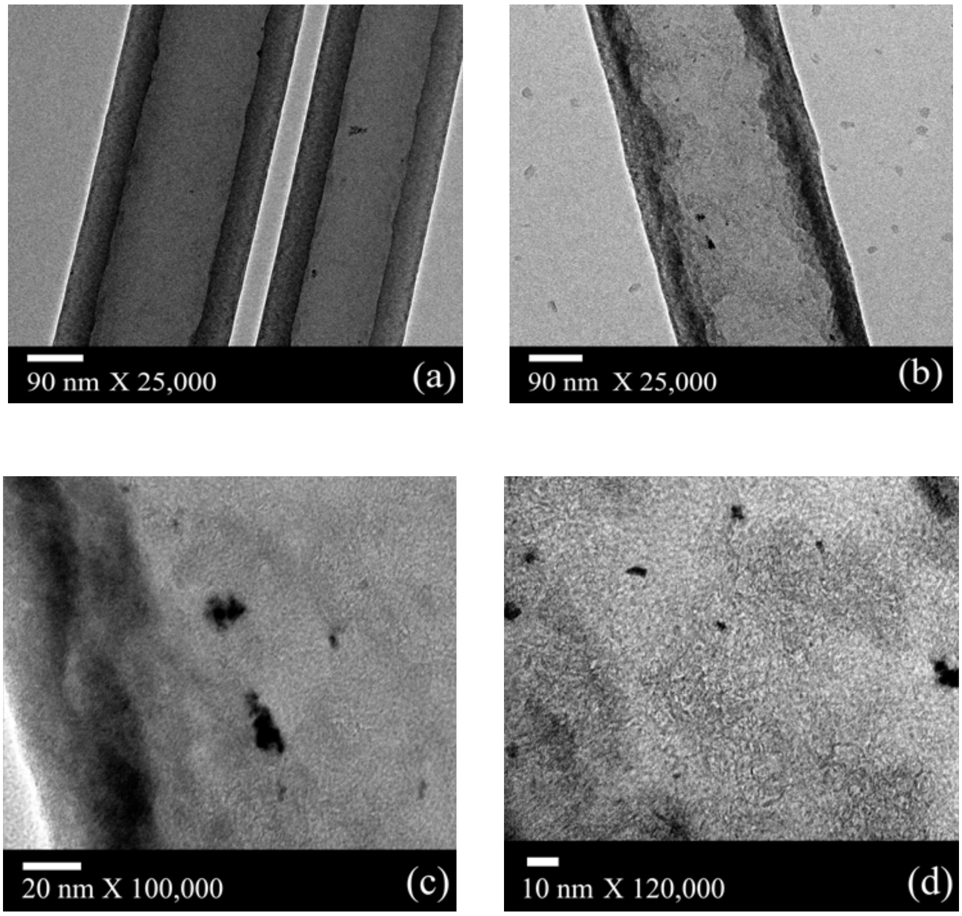


Figure 28 (a), (b) TEM images of Pt CNTs/AAO-1000 (c), (d) the enlargement of Pt-CNTs/AAO-1000

Ruthenium chloride hydrated was used as ruthenium precursors. Ruthenium could be loaded using same method as that of platinum. Ruthenium is widely used for many reactions such as ammonium decomposition, aniline waste water treatment and catalytic decomposition of hydrocarbons. Ruthenium chloride hydrated was dissolved with ethanol solution and then the obtained specimen was reduced with 0.1M $NaBH_4$ at room temperature. To investigate the framework structure of the ruthenium loaded carbon nanotubes/AAO composites (Ru-CNTs/AAO-750), the TEM technique was applied as shown in Figure 29. The small particles were located inside the structure of CNTs/AAO-750. The similar result was obtained for CNTs/AAO-1000 as shown 30. To confirm the existence of ruthenium in the CNTs/AAO-750, Energy Dispersive X-ray Spectrometer (EDX) technique was applied as shown in Figure 28.

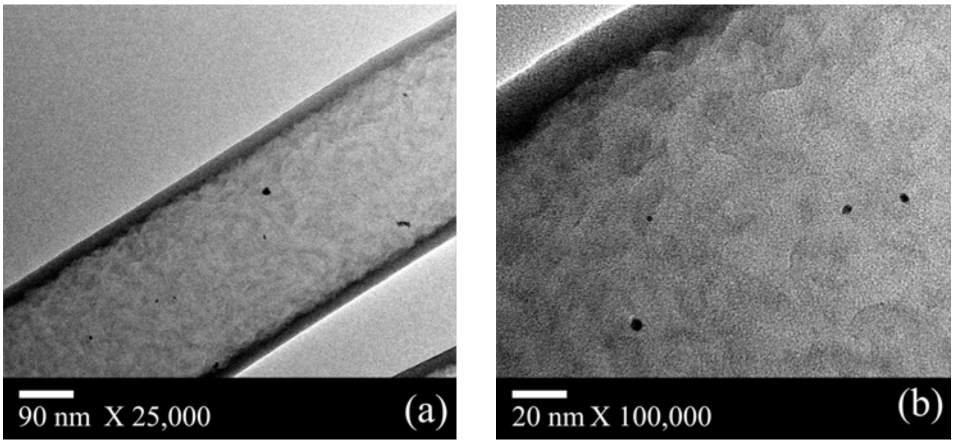


Figure 29 Ruthenium loaded CNTs/AAO-750 (a) TEM images of Ru-CNTs/AAO-750 (b) the enlargement of Ru-CNTs/AAO-750

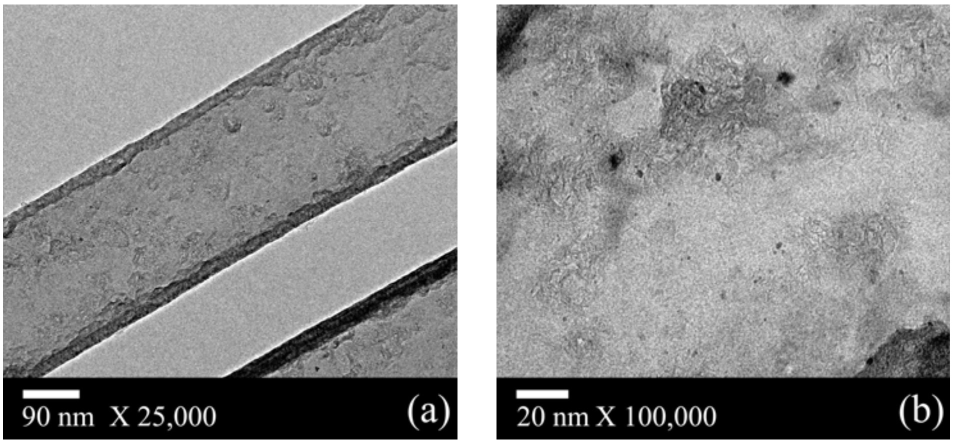


Figure 30 Ruthenium loaded CNTs/AAO-1000 (a) TEM images of Ru-CNTs/AAO-1000 (b) the enlargement of Ru-CNTs/AAO-1000

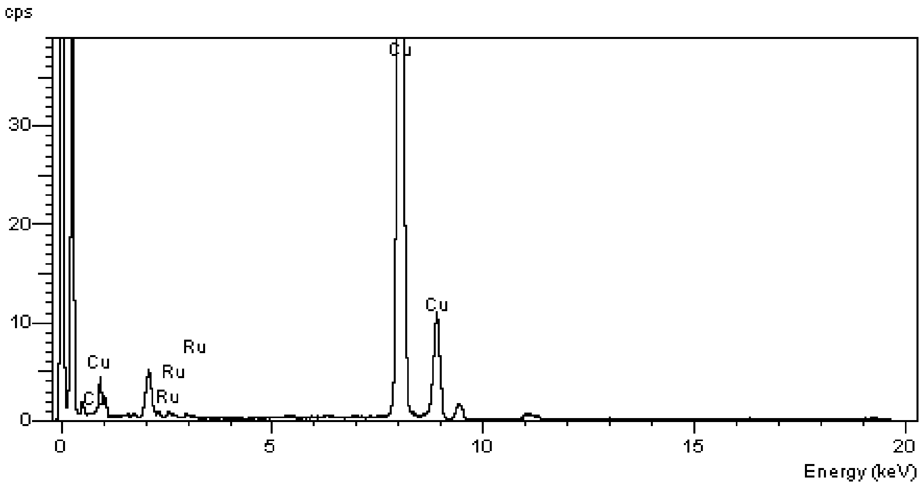


Figure 31 EDX spectrum of Ru-CNTs/AAO-750

For the loading of nickel metal, nickel nitrate was loaded onto carbon nanotubes/AAO composites (Ni-CNTs/AAO) in ethanol solution. After that Ni-CNTs/AAO was reduced by using 0.1 M $NaBH_4$. Figure 29 shows the TEM images of Ni-CNTs/AAO-750, there were no metal particle depositing inside the CNTs/AAO-750 structure. However, when the support was changed from CNTs/AAO-750 to CNTs/AAO-1000, is small nickel particles were observed inside the structure of CNTs/AAO-1000 as shown in Figure 30. Energy Dispersive X-ray Spectrometer could not be confirm the existence of nickel due to the small amount of Ni particles inside the CNTs/AAO structure. The Inductive Couple Plasma-Optical Emission Spectroscopy (ICP-OES) technique was then used to analyzed the amount of metal loaded presented in the structure of metal-loaded carbon nanotubes/AAO composites.

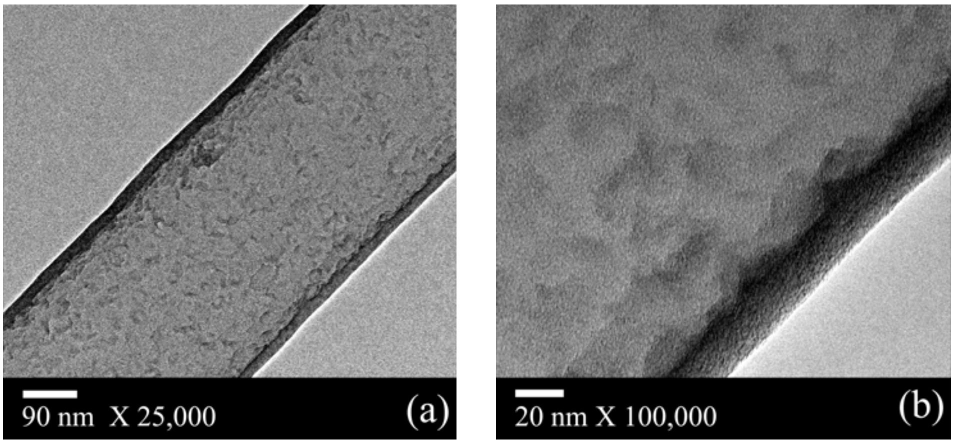


Figure 32 Nickel loaded CNTs/AAO-750 (a) TEM images of Ni-CNTs/AAO-750(b) the enlargement of Ni-CNTs/AAO-750

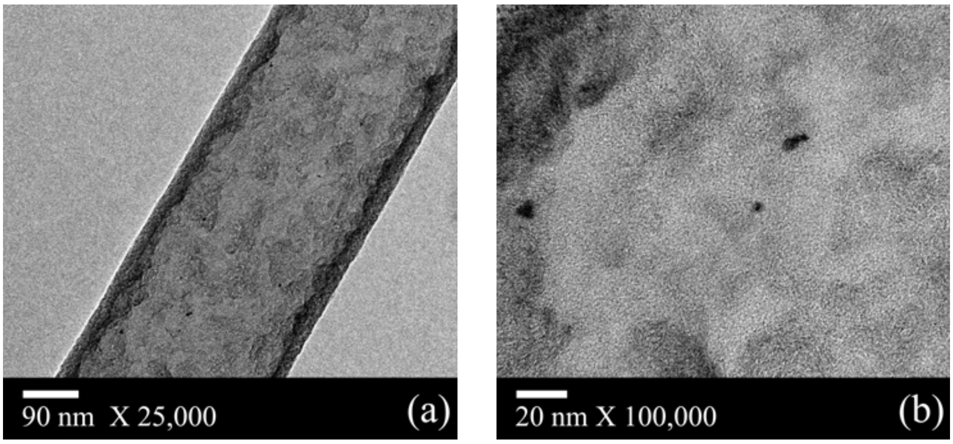


Figure 33 Nickel loaded CNTs/AAO-1000 (a) TEM images of Ni-CNTs/AAO-1000(b) the enlargement of Ni-CNTs/AAO-1000

Table 1 The Chemical composition of metal-loaded CNTs/AAO-750 and CNTs/AAO-1000 analyzed by ICP technique.

Catalysts	Composition (μg/g)
Ni-CNTs/AAO-750	24.48
Pt-CNTs/AAO-750	52.63
Ru-CNTs/AAO-750	230.76
Ni-CNTs/AAO-1000	106.66
Pt-CNTs/AAO-1000	151.61
Ru-CNTs/AAO-1000	441.76

Table 1 shows the amount of metal presented in the metal-loaded CNTs/AAO-750 and CNTs/AAO-1000. The order of the amount of metal loaded onto CNTs/AAO can be arranged from the maximum to minimum order as follows: Ruthenium > Platinum > Nickel. The existence of ruthenium give the highest value of metal-loaded both of CNTs/AAO-750 and CNTs/AAO-1000. According to the result, the amount of three kinds of metals were increased with the number of the layer of carbon nanotubes. The result can be explained that the amount of CNTs/AAO-1000 has more layer of graphite sheet than CNTs/AAO-750 which can be increased the site of CNTs/AAO and can also be increased the amount of metal adsorbed on CNTs/AAO surface. The metals are also inserted between the layers of multi-walled carbon nanotubes which correspond to the results reported by Tsai *et al.* (1996). Figure 31 show TEM images of Pt-CNTs/AAO composites which were synthesized by Tsai *et al.* (1996).

In the case of nickel, there was the smallest amount of metal particle inside the CNTs/AAO structure. The reason can be explained that nickel nitrate needed the higher temperature to dissociate the nickel nitrate to nickel oxide. The forms of nickel nitrate can be reduced with high temperature. Sodium borohydride was used as a reducing agent for this research, which could be convert metal ion to metal particles in room temperature.

With platinum and ruthenium, the higher amounts of the metal particles than that of nickel were loaded. The order of the amount of metal loaded onto CNTs/AAO can be arranged from the maximum to minimum order as follows: Ruthenium > Platinum > Nickel. Comparing between Pt and Ru metals, it can be explained that platinum size was relatively larger than ruthenium and then it was hardly loaded into the CNTs/AAO.

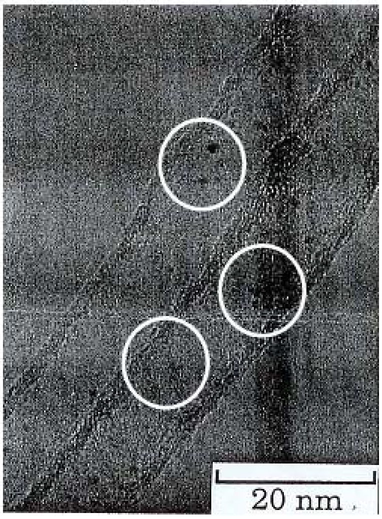


Figure 34 Platinum loaded onto the inter layer of multi-walled carbon nanotubes

Source: Tsai *et al*. (1996)

Table 2 shows that metal loading onto CNTs/AAO led to decrease of both BET surface area and the total pore volume. The result was corresponding to the ICP result as mentioned in Table 1 that that ruthenium can be greatly loaded onto the CNTs/AAO when compare with those of platinum and nickel. The surface areas of the composites after metal loading have found to be decreased. This can be explained that the metal nanoparticles were dispersed inside the structure of carbon nanotubes.

Table 2 BET surface area and total pore volume of unloaded CNTs/AAO and metal-loaded CNTs/AAO

Catalysts	BET surface area (m^2/g)	Total pore volume (cc/g)
CNTs/AAO-750	9.6	5.0
Ni-CNTs/AAO-750	7.4	4.2
Pt-CNTs/AAO-750	7.3	4.6
Ru-CNTs/AAO-750	3.6	2.7
CNTs/AAO-1000	7.3	4.8
Ni-CNTs/AAO-1000	5.7	4.3
Pt-CNTs/AAO-1000	5.3	3.9
Ru-CNTs/AAO-1000	2.6	2.2

2. Electrical properties of the CNTs/AAO and metal-CNTs/AAO based LPG sensor

The electrical resistance measurements of CNTs/AAO-750, CNTs/AAO-1000, metal-CNTs/AAO-750 and metal-CNTs/AAO-1000 were performed in a gas testing chamber at the room temperature. The CNTs/AAO were placed in a cover glass and connected with copper wires. Then, the analysis cell was transferred to the glass testing chamber with electrical supply. The electrical resistance measurement was measured under a series of LPG and N_2 loading as a cycle which the gas flow rate of 100 ml/min. All experiments were replicated for three times. Without metal loading, the result shows that the resistance of CNTs/AAO-750 did not change toward LPG supply. Similar result was observed for CNTs/AAO-1000 as shown in Figure 36. It can be concluded that carbon nanotubes without metal loading could not adsorb the LPG molecules.

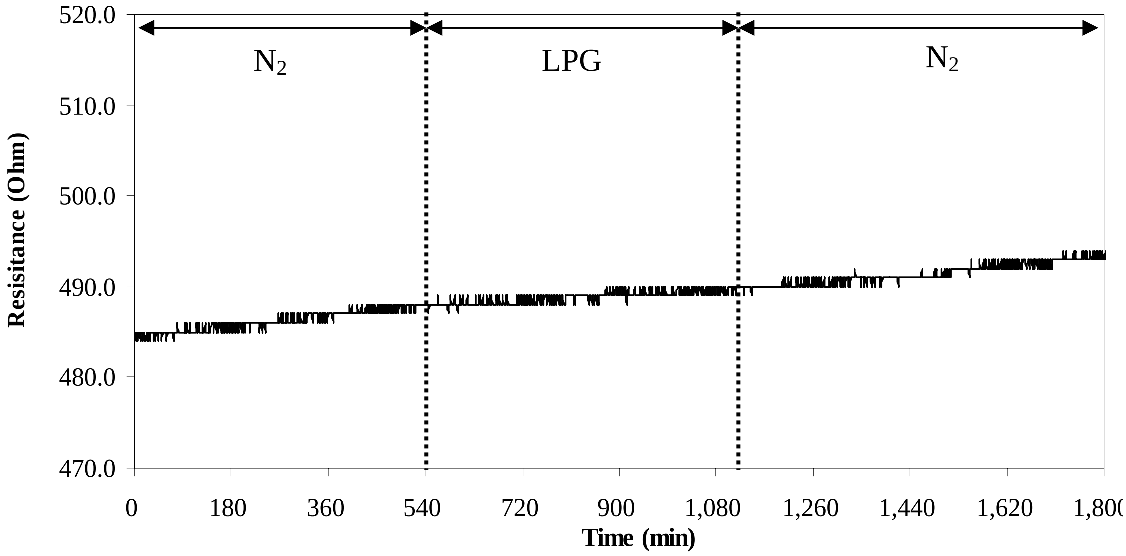


Figure 35 The electrical resistance of CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycle

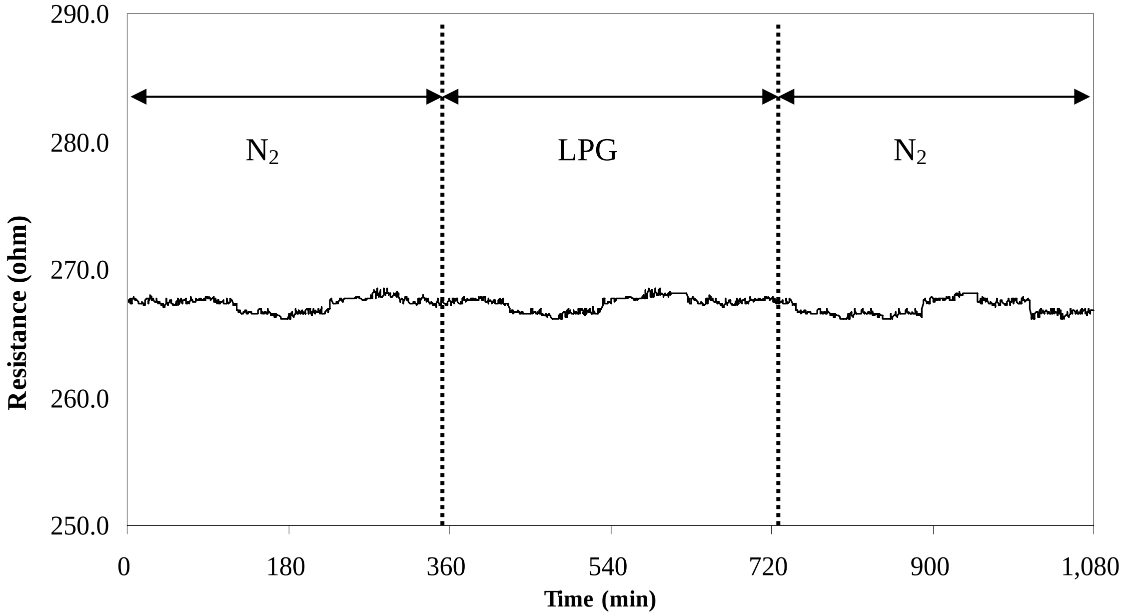


Figure 36 The electrical resistance of CNTs/AAO-1000obtained from a series of LPG and N_2 loading as a cycles

The result as shown in Figure 35 and 36 was in good agreement with that of Valentini *et al.* (2004) who studied the electrical response of carbon nanotubes thin films to various gas including NO_2, CO, NH_3, H_2O and C_2H_5OH. The electrical response was investigated by exposing the films to these interfering gases at the operating temperatures between 25-250^oC. They found that the electrical resistance of CNT decreased when it exposed to 10-100 ppb of NO_2 and no response was found by exposing to CO gas, resulting from very small electron donor or acceptor properties of CNTs.

The concept of electrical response of CNTs toward small electron donor and acceptor gases was studied by several researchers. Penza *et al.* (2007) prepared the metal modified MWNTs and tested gas as gas sensor. The test gas was likely dissociated by a spillover effect on the catalyst surface and the dissociated fragment was then dissolved into the catalyst bulk. This dissociation of fragmented molecule caused an increase in the electron transfer. Considering metal-loaded CNTs/AAO-750 which the amount of metal loaded was less than that of CNTs/AAO-1000, the resistance is lower than unloaded CNTs/AAO-750. The result revealed that Pt could promote the interaction between CNTs and LPG. Figure 37 shows the electrical resistance of Pt-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycle at the flow rate of LPG and N_2 of 100 ml/min. A slightly changed in the resistance was found, according to the reason that very few platinum amount was loaded onto CNTs/AAO. Moreover, the adsorption capacity of platinum was quite low at room temperature.

The electrical resistance of Pt-CNTs/AAO-1000 obtained from a series of LPG and N_2 loading as a cycle is shown in Figure 38. There was a significant change of the resistance in the a series of LPG and N_2 loading. It suggested that platinum formed strong attractive force to interact the LPG molecule onto the surface. However, the response period of Pt-CNTs/AAO was relatively slow as 180 min for observing the change of response after the LPG exposure. It can be suggested that the interaction between LPG and Pt was strongly depended on the platinum loading amount.

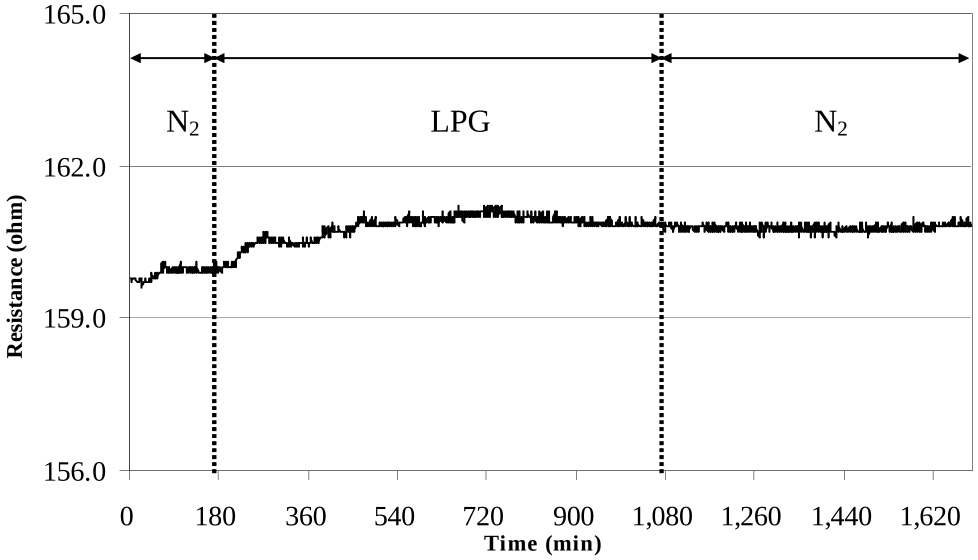


Figure 37 The electrical resistance of Pt-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycle

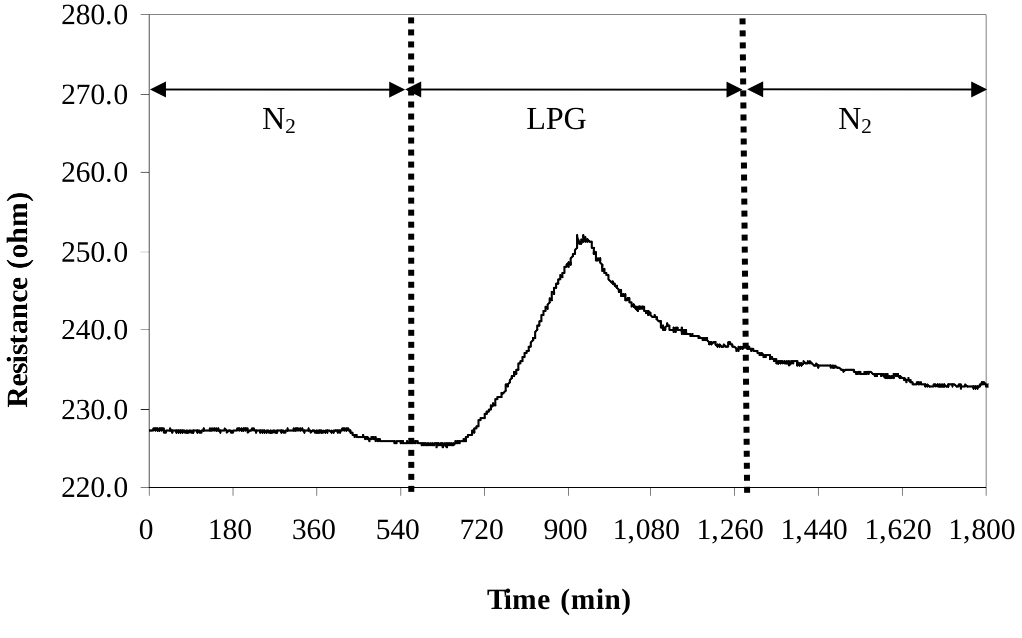


Figure 38 The electrical resistance of Pt-CNTs/AAO-1000 obtained from a series of LPG and N_2 loading as a cycle

Figure 39 shows the electrical resistance of Ru-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycle at the flow rate of LPG of 100 ml/min. The response period of Ru-CNTs/AAO was 280 min for observing the change of response after LPG exposure. It can be concluded that Ru-CNTs/AAO can detect the LPG gas even there was a small amount of ruthenium loaded inside the CNTs/AAO, showing the high adsorption capacity of ruthenium at room temperature. LPG are adsorbed on the Ru sites and donated the electron to LPG gas which Ru species can be increased the electron transfer

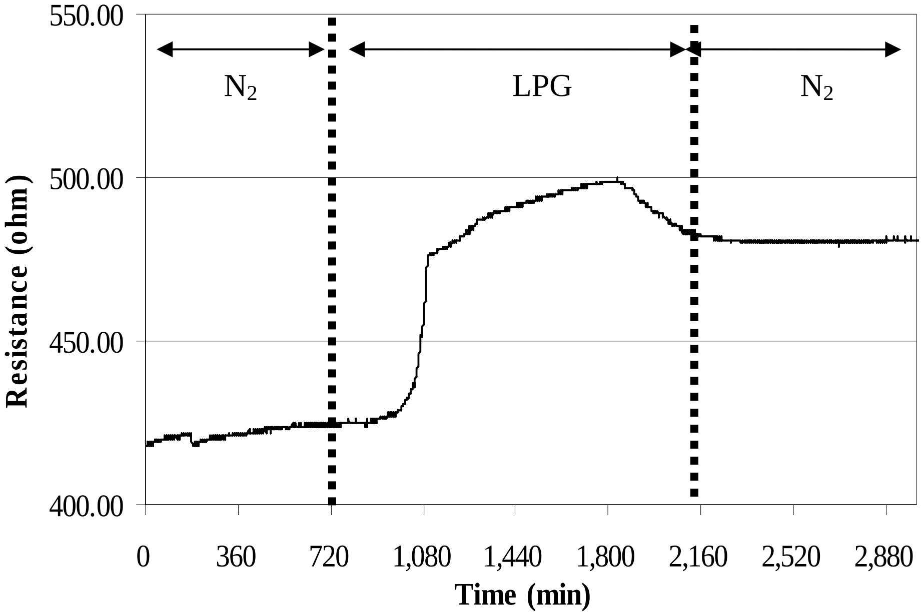


Figure 39 The electrical resistance of Ru-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycles

The electrical resistance of Ru-CNTs/AAO-1000 obtained from a series of LPG and N_2 loading as a cycle is shown in Figure 40. After the LPG was introduced into the system, the resistance slightly increased from 165 to 168.8 ohm after the period of exposure 100 min.

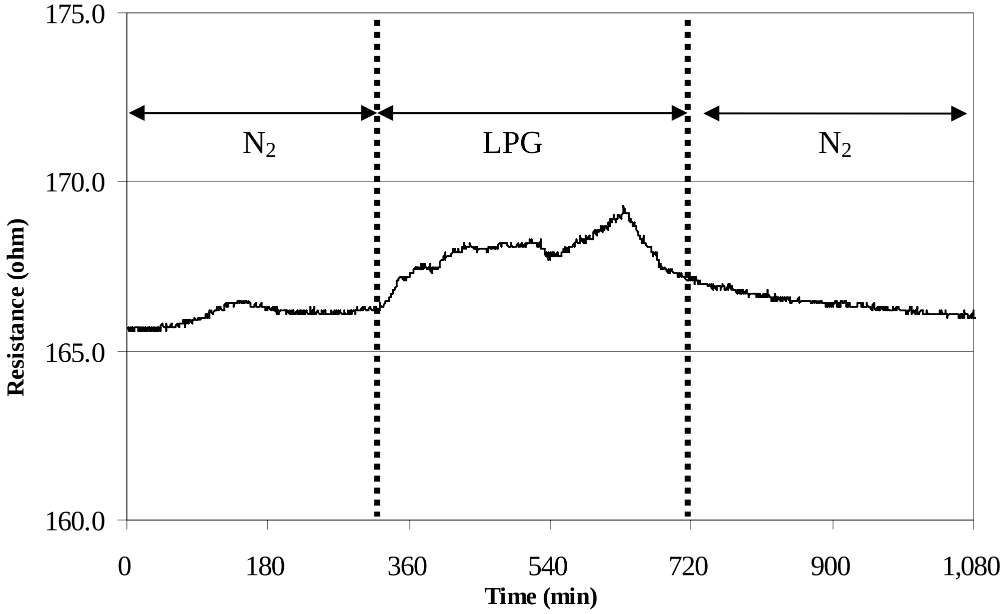


Figure 40 The electrical resistance of Ru-CNTs/AAO-1000 obtained from a series of LPG and N_2 loading as cycles

Figure 41 shows the electrical resistance of Ni-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycle at LPG flow rate of the flow rate at 100 ml/min. No resistance change in Ni-CNTs/AAO because the amount of nickel loaded inside the carbon nanotubes was relatively low when compared with those of platinium and ruthenium. However, Ni-CNTs/AAO-1000 revealed a significant change of resistance even small amount of nickel was loaded inside the structure of Ni-CNTs/AAO. Nickel particles are generally use as a catalyst for cracking of hepthane (Zhang *et al.*, 2002). Nickel particle is small that can be used for cracking the liner hydrocarbon. As a result, LPG gas of which mostly composed of propane and buthane or linear hydrocarbons, the strong interaction between nickel surface and LPG molecule then could be formed at even low amount of nickel metals loaded onto CNTs/AAO.

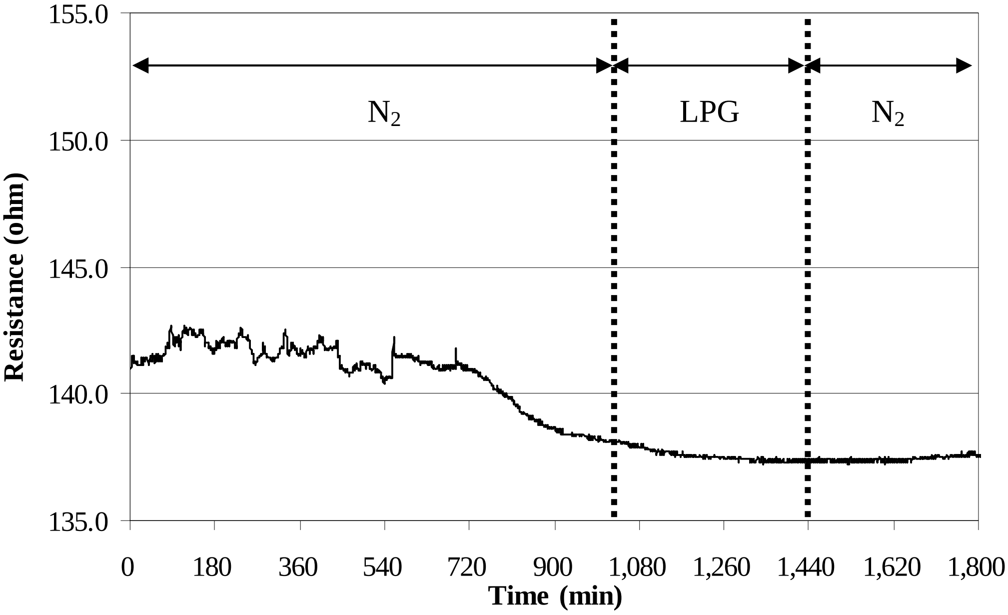


Figure 41 The electrical resistance of Ni-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycles

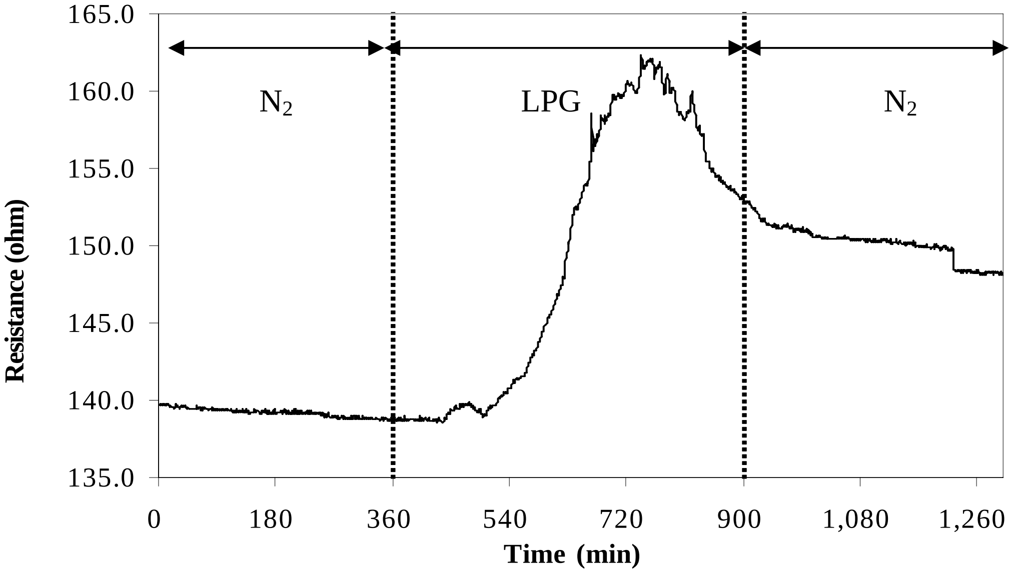


Figure 42 The electrical resistance of Ni-CNTs/AAO-750 obtained from a series of LPG and N_2 loading as a cycles

CONCLUSION AND RECOMMENDATIONS

Conclusion

This research studied the synthesis of carbon nanotubes over anodic aluminum oxide films at 750 and 1000°C by CVD technique. The obtained carbon nanotubes were modified by loading reactive metals including platinum (Pt), ruthenium (Ru) and nickel (Ni) on their framework structures using wet impregnation method. Types of metal and the amount of metal loading were the studied variables. The properties and morphology of carbon nanotubes product were characterized. It can be concluede that:

1. The CVD temperature affected the wall thickness and the number of CNTs layers. The wall thickness and the number of layers were increased with increasing the growth temperature. From this research, the layer of carbon nanotubes was approximately 67 and 117 when the growth temperatures were 750 and 1000, respectively.

2. The obtained CNTs/AAO products were modified by loading reactive metals including platinum, ruthenium and nickel into their framework structures using wet impregnation method. The order of the amount of metal loaded onto CNTs/AAO could be arranged as follows:

Ruthenium > Platinum > Nickel

3. The amount of metals was increased with increasing the number of the carbon nanotube layers.

4. The Ni-CNTs/AAO-1000 product revealed the highest performance for LPG detection as it had a large significant change of resistance even small amount of nickel was loaded inside the structure of CNTs/AAO. However, the response time of Ni-CNTs/AAO-1000 of 180 min. This was quite long response time and was not practical at this moment.

Recommendations

1. The CNTs/AAO composites should be removed the air inside the structure of the composites before metal loaded. This is because some part of air could be adsorbed into the site of carbon nanotubes that caused the small amount of metal loaded inside the structure.

2. During the impregnated CNTs/AAO composites, the sample solution should be sonicated to increase the dispersive between metal and CNTs/AAO. CNTs are hydrophobic that the solvent are hardly filled inside their structure.

3. The flow rate of LPG gas should be lower that 100 ml/min that the adsorption of LPG is rapidly changed. The interaction between metal and carbon nanotubes is van der Waals force which are not strong and can be remove with a high flow rate.

LITERATURE CITED

Ajayan, P. M. and Zhou, O. Z. 2001. Applications of Carbon Nanotubes. **Department of Materials Science and Engineering Rensselaer Polytechnic Institute** 80: 391 – 425.

Cantalini, C., Valentini, L., Armentano, I., Kenny, J. M., Lozzi, L. and Santucci, S. 2004. Carbon nanotubes as new materials for gas sensing applications. **Journal of the European Ceramic Society** 24: 1405 – 1408.

Daenen, M., de Fouw, R. D., Hamers, B., Janssen, P. G. A., Schoutedon, K. and Veld, M. A. J. 2003. The Wondrous World of Carbon Nanotubes. Academic Press. Eindhoven University of Technology. Available source: http://students.chem.tue.nl/ifp03/default.html

Ding, D., Chen, Z., Rajaputra and S., Sing, V. 2006. Hydrogen Sensor based on alighed carbon nanotubes in an anodic aluminium oxide template with palladium as a top electrode. **Sensors Actuators B** 124: 12-17

Ebbesen, T., Bisher, M., Treacy, J., Shreeve, L. and Keyer, R.1996. Decoration of carbon nanotubes. **Advance Materials** 8: 155

Espinsa, E., Ionescu, R., Bittencourt, C., Felten, A., Erni R., Tendeloo, G., Pireaux, J. and Llobet, E. 2007. Metal-decorated multi-wall carbon nanotubes for low temperature gas sensing. **Thin Solid Films** 515: 8322–8327

Feng, S., Xu, B., Ching-Fai Ng, and Chak-Tong Au. 2003. Nano Ru/CNTs: a highly active and stable catalyst for the generation of CO_x-Free hydrogenation in ammonia decomposition. **Applied Catalyst** 48: 237-241

Huang, J. R., Li, M. Q., Huang, Z. Y. and Liu, J. H. 2006. A novel conductiveb humidity sensor based on field ionization from carbon nanotubes. **Sensors and Actuators A**, Article in press.

Hoa, N., Quy, N., Cho, Y., and Kim, D. 2007. An ammonia gas sensor based on non-catalytically synthesized carbon nanotubes on an anodic aluminium oxide template. **Sensors Actuators B** 127: 441-454

Iijima, S. 1991. Helical microtubules of graphitic carbon. Nature 354: 56 – 58.

Li, X.and I.-Ming Hising 2006. The effect of the Pt deposition method and the support on Pt dispersion on carbon nanotubes. **Electrochimica Acta** 51: 5259-5258

Lu, Y., Li, J., Han, J. ,Binder, C., Partridge C., Meyyappan, M. 2004. Room temperature methane detection using palladium loaded single-walled carbon nanotubes sensors. **Chemical Physical Letters** 391: 344-348

L. Valentini, C. Cantalimi, I. Armentano, J.M. Kenny, L. Lozzi and S. Santucci 2004. Highly sensitive and selective sensors based on carbon nanotubes thin films for molecular detection. **Diamond and Related Materials** 13: 1301-1305.

M. Daenen, R.D.de Fouw, B. Hamers, P.G.A Janssen and K.Schouteden. **The Wondrous World of Carbon nanotubes a review of current carbon nanotubes technologies.** Eindhoven University of Technology.

M. Penza, R. Rossi, M. Alvisi, G.Cassana, M.A. Singnore, E. Serra and R.Giorgi. 2008. Pd- and Pt-nanoclusters functionalized carbon nanotubes networked films for sub-ppm gas sensors. **Sensors and Actuators B** xx: xxx

P. Ayala, F.L. Freire Jr, L. Gu, David J. Smith, I.G. Solorzano, D.W. Macedo, J.B. Vander Sande, H. Terrones and J. Rodriguez-ManZo, M. Terrones 2006. Decoration carbon nanotubes with nanostrutured nickel particles via chemical methods**. Chemical Physical Letters** 431: 104-109

R.Ionescu, E.H.Espinosa, E. Sotter, E. Llobet, X. Vilanova, X. Correig, A. Felten, C. Bittencourt, G. Van Lier and J.-C. Charlier 2006. Oxygen functionalisation of MWNT and their use as gas sensitive thick-films layers. **Sensor and actuators B** 113:36-46

Sathreanranon, K. 2005. Synthesis and control of layer numbers of carbon nanotubes. Master Thesis, Kasetsart University, Bangkok, Thailand.

Serp, P., Corrias, M and Kalck, P. 2003. Carbon nanotubes and nano fibers in catalysis. **Applied Catalysis A** 253: 337-358

Tsai, L., 1996. **The study of carbon nanotubes synthesis using anodic aluminum oxide films as the templates**. Master Thesis, Tohoku University, Sendai, Japan.

Xu, Z., Chen, X., Qu, X., Jia, J. and Shaojun Dong. 2004. Single-wall carbon nanotube-based voltammetric sensor and biosensor. **Biosensors and Bioelectronics** 20: 579–584**.**

Zhang, X., Jiang , W., Song, D., Liu, J. and Li, F. 2008. Preparation and catalytic activity of Ni/CNTs nanocompositions using microwave irradiation heating method. **Materials Letters** xx: xxx

Zhang, Y., Nathan, W., Robert, F., Chen, Dai.2000 Metal coating on suspended carbon nanotubes and its implication to metal-tube interaction. **Chemical Physical Letters** 331: 35-41