การประยุกต์ใช้คาร์บอนนาโนฮอร์นแบบผนังเดี่ยวที่ปรับปรุงพื้นผิว ด้วยพลาสมาเพื่อการปลดปล่อยพีวีพีไออย่างช้า

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APPLICATION OF PLASMA-MODIFIED SINGLE-WALLED CARBON NANOHORNS FOR PVPI SLOW RELEASE

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ปิยะพงษ์ ฤกษ์ประเสริฐกุล : การประยุกต์ใช้คาร์บอนนาโนฮอร์นแบบผนังเดี่ยวที่ปรับปรุงพื้นผิวด้วยพลาสมาเพื่อการปลดปล่อยพีวีพีไออย่างช้า (APPLICATION OF PLASMA-MODIFIED SINGLE-WALLED CARBON NANOHORNS FOR PVPI SLOW RELEASE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. ธวัชชัย ชรินพาณิชกุล, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ดร. ขจรศักดิ์ เฟื่องนวกิจ, 80 หน้า.

งานวิจัยนี้ สังเคราะห์คาร์บอนนาโนฮอร์นแบบผนังชั้นเดี่ยวด้วยวิธีการอาร์คในน้ำที่มีการพ่นก๊าซ คาร์บอนนาโนฮอร์นที่สังเคราะห์ได้จะถูกนำไปปรับปรุงพื้นผิวด้วยออกซิเจนพลาสมาเพื่อเพิ่มคุณสมบัติความชอบน้ำแก่คาร์บอนนาโนฮอร์น ในการปรับปรุงพื้นผิวได้ศึกษาผลกระทบของระยะเวลาในการปรับปรุงพื้นผิว ผลกระทบของความดันในระบบและกระแสไฟฟ้าในการสร้างพลาสมาที่มีผลต่อการปรับปรุงพื้นผิวของคาร์บอนนาโนฮอร์น จากผลการทดลองพบว่าคาร์บอนนาโนฮอร์นแบบผนังชั้นเดี่ยวที่ถูกปรับปรุงพื้นผิวด้วยออกซิเจนพลาสมาสามารถกระจายตัวในน้ำได้นานขึ้นเปรียบเทียบกับคาร์บอนนาโนฮอร์นแบบผนังชั้นเดี่ยวที่ไม่ได้ปรับปรุงด้วยออกซิเจนพลาสมา สาเหตุที่ทำให้คาร์บอนนาโนฮอร์นสามารถกระจายตัวในน้ำได้ดีขึ้นเป็นเพราะมีหมู่ฟังก์ชั่นของคาร์บอกซิลิค (C=O) บนผิวเนื่องมาจากการปรับปรุงพื้นด้วยออกซิเจนพลาสมา นอกจากนี้ผลของศักย์ซีต้ายืนยันถึงความสามารถของการกระจายตัวในน้ำของคาร์บอนนาโนฮอร์นแบบผนังเดี่ยว คาร์บอนนาโนฮอร์นที่ไม่ได้ปรับปรุงพื้นผิวและที่ปรับปรุงพื้นผิวถูกทำให้ชุ่มด้วยพีวีพีไอ จากผลการทดลองพบว่าคาร์บอนนาโนฮอร์นที่ถูกปรับปรุงพื้นผิวด้วยออกซิเจนพลาสมาสามารถช่วยลดอัตราการคายซับของพีวีพีไอซึ่งนำไปสู่การปลอดปล่อยพีวีพีไออย่างช้า เป็นผลมาจากการมีอนุมูลอิสระและหมู่ฟังชั่นออกซิเจนอยู่ การศึกษาจลนพลศาสตร์ของการคายซับเป็นไปตามแบบจำลองทางคณิตศาสตร์จลนพลศาสตร์การคายซับอันดับสองเสมือน

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PIYAPONG LERKPRASERTKUN: APPLICATION OF PLASMA-MODIFIED SINGLE-WALLED CARBON NANOHORNS FOR PVPI SLOW RELEASE. ADVISOR: ASSOC. PROF. TAWATCHAI CHARINPANITKUL, D.Eng., CO-ADVISOR : KAJORNSAK FAUNGNAVAKIJ, D.Eng., 80 pp.

In this work, SWCNHs synthesized by gas-injected arc-in-water (GI-AIW) method have been modified by oxygen plasma for increasing their surface hydrophilicity. The effects of treatment parameters, which are irradiating time, pressure and electricity current on characteristics of plasma-treated SWCNHs was investigated and reported. It was found that oxygen plasma treatment enhanced hydrophilic property of SWCNHs. SWCNHs treated by oxygen plasma can be dispersed in deionized water for a long time period when compared with pristine SWCNHs. It is also reasonable to imply the presence of C=O, carboxylic group, on the surface of SWCNHs treated by oxygen plasma treatment would lead to a higher level of their dispersion. In addition, zeta potential analysis could confirm the stability of the plasma-treated SWCNHs. For examining slow releases behavior polyvinylpyrrolidone-iodine (PVPI) was impregnated onto the pristine and plasma-treated SWCNHs. It was found that plasma-treated SWCNHs can help reduce the desorption rate of PVPI, leading to its slow release because of functional groups. The pseudo 2nd order kinetic model could be fitted for estimating PVPI release.

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Field of Study : Chemical Engineering Advisor's Signature ....
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CONTENTS

Page

CHAPTER

CHAPTER **Page**

CHAPTER **Page**

CHAPTER **Page**

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

INTRODUCTION

1.1 Background and Motivation

Various methods toward effective drug delivery exhibit specific problems that scientists are attempting to address. Many drugs healing and therapeutic effects are limited due to degradation of drug before they reach the target site in patient body. Slow release of drugs is therefore a critical issue concerning drug therapy, making the development of controlled-release drug delivery system (DDS) very attractive. Development of DDS has become increasingly important in the pharmaceutics because of the DDS are patent protected formulation that modify drug release profile, absorption and distribution for the benefit of improving product efficacy , as well as patient convenience.

Recently, nanometer-sized materials have been highlighted as a new class of slow release drug delivery devices. Among various nanomaterials, single-walled carbon nanohorns (SWCNHs) are interested by many researchers because of their nanostructure similar to single-walled carbon nanotubes (SWCNTs) with one end closed in a cone-shaped cap (horn). Typically, SWCNH exhibit a diameter between 2 and 5 nm and a length between 40 and 50 nm. Around thousands of SWCNH would assemble to form a spherical aggregate with a narrow diameter distribution range between 80 and 100 nm. SWCNH aggregates have been regarded as potentially good drug carriers, possessing some advantages over other carriers [1, 2]. SWCNHs can be synthesized in an easy way on a large scale with a high production yield and can be used without any additional purification. Based on our previous works, SWCNHs can be synthesized by an easy way using the gas-injected arc in water method (GI-AIW) [3-5].

Incorporating SWCNHs in biomedical application as a slow release is one of major challenge of Carbon nanoparticles (CNPs) research to date for therapeutic molecules in DDS. Meanwhile, for typical DDS, hydrophilicity is usually a required property as an aqueous solution of drug is frequently used in the preparation of DDS [6].

Unfortunately, SWCNHs are rather hydrophobic makes their use in aqueous systems impossible. Surface modification of SWCNHs is therefore required to increase their hydrophilicity. To improve their solubility, CNTs are functionalized by different methods. The easiest way to covalently attach chemical groups (e.g., carboxylic, carbonyl groups) is by oxidation process, such as acid treatment (nitric and/or sulfuric acid) and plasma treatment[7], resulting in the introduce oxygen-containing group on the surface of the nanotubes. These groups can be CNT a high dispersion in water. Addition, CNTs can be dispered in water by surfactant such as poly(ethylene glycol, PEG). Plasma treatment is an efficient technique for modification of various material surfaces. The excited species, radicals, electrons, ions, and UV light within plasma strongly interact with the surfaces of CNTs breaking the C=C bonds and creating active sites for binding of functional groups, and, as a result, chemical and physical modifications occur on the surfaces. Compared to other treatment methods, the plasma treatment method has the advantages of shorter irradiation time, environmental friendly[8, 9] and providing a several of different functional groups depending on plasma parameters such as power, used gases, irradiation time, and pressure.

Poly-vinylpyrrolidone-iodine (PVP-I) was introduced to the pharmaceutical as an antiseptic agent in 1950 [10] and is as effective as iodine itself against a broad spectrum of disease-causing microorganisms. PVP-I is used in both human and veterinary medicine to an antiseptic with antimicrobial activity such as fungi, protozoans and several viruses. The slowly release of PVP-I can be prevent infection for bacterial resistance.

The object of this research is to study effect of plasma treatment on the hydrophilic properties of SWCNHs was investigated. Release characteristics of PVP-I from the surface of pristine SWCNHs and modified SWCNHs were also experimentally examined with an expectation that the surface-modified SWCNHs could help reduce the release of PVPI.

1.2 Objectives of the Research

The objective of this research is to synthesize SWCNTs by a gas-injected arc-in-water (GI-AIW) method. Then study effect of plasma surface modification on stable suspension characteristics of SWCNHs will be conducted. Slow-release characteristics of poly-vinylpyrrolidone-iodine (PVP-I) from surface-modified SWCNHs would also experimentally be examined with an expectation that the surface-modified SWCNHs could help reduce the release of PVPI.

1.3 Scope of the Research

1.3.1 Synthesis of Single-walled Carbon Nanohorns (SWCNHs) ; The Method to Synthesize Single-walled Carbon Nanohorns (SWCNHs) by Gas-injected Arc in Water (GI-AIW) Method

- Arc current is 80 A
- N_2 flow rate is 5 l/min
- Anode will be a graphite rod (purity 99.9995%) of 3 mm diameter and cathode will be a graphite rod (purity 99.9995%) of 12 mm diameter with a hole of 8 mm diameter and 25 mm depth on its bottom.
- The anode-ascending speed will be controlled at 1.5 mm/s

1.3.2 Surface Modification of Single-walled Carbon Nanohorns by Plasma Treatment

- Effect of modification time, in a range of 0.5 – 60 min
- Effect of pressure, in a range of 1 – 100 mbar
- Effect of current, in a range of 1.5 – 5.5 A

1.3.3 Single-walled Carbon Nanohorns Are Impregnated with Polyvinyl-pyrrolidone-iodine (PVPI)

- Effect of mass ratio of PVPI to SWCNHs , 1 – 3 %wt
- Comparison between of free PVPI, pristine SWCNHs and plasma-treated SWCNHs
- Study of PVPI released from SWCNHs

1.3.4 Characteristics of the Synthesized Particles

- Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) was used to characterize the morphology of SWCNHs
- Raman spectroscopy was used to evaluate the crystallinity of SWCNHs
- Fourier Transform Infrared (FT-IR) spectrometer was used to characterize functional group (C-O, C=O and COOH) on SWCNHs
- Zetasizer was used to measure the zeta potential and size of SWCNHs
- Conductivity meter was used to measure the conductivity of aqueous solution
- Thermogravimetric Analysis (TGA) was used to measure quantity of PVPI

1.4 Procedure of the Research

- Execution of literature survey and review
- Preparation of experimental materials and setup
- Synthesis of Single-walled Carbon nanohorns (SWCNHs) by gas-injected arc in water (GI-AIW) method
- Characterization of SWCNHs properties by SEM, TEM, Raman spectroscopy and BET
- Preparation of modify SWCNHs by discharge plasma
- Discussion on effect of modification parameter and determination of optimum conditions
- Characterization of surface-modified SWCNHs properties by SEM, TEM, Raman spectroscopy, FT-IR and Zetasizer
- Preparation PVPI impregnated into SWCNHs
- Execution of test and analyze the release of PVPI from SWCNHs
- Making discussion and conclusion of experimental results
- Writing thesis and preparation of draft manuscript for journal publication

1.5 Expected Benefit

- Obtain knowledge of synthesis of SWCNHs by GI-AIW and surface modification by plasma treatment
- Obtain optimum condition for impregnating PVPI onto SWCNHs

CHAPTER II

THEORY AND LITERATURE REVIEW

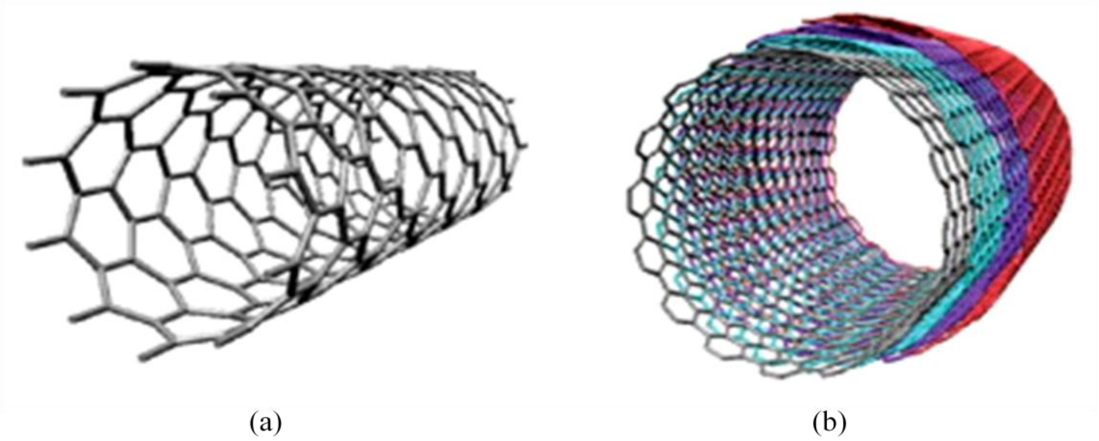
2.1 Carbon Nanoparticles (CNPs)

Carbon is known to be the most versatile element that exists on the earth. It has many different properties. Carbon in the form of graphite was discovered in 1779, and 10 years later in the form of a diamond. In 1985 Kroto and Smalley discovered fullerenes[11]. Carbon nanoparticles (CNP) such as carbon nanotubes (CNTs), carbon nanohorns (CNHs) and carbon nanocapsules (CNCs). Among these structures, CNTs have attracted the attention and interest of researchs in mamy fields because of their potentially useful in extremely small scale electronic and mechanical applications.

2.1.1 Carbon Nanotubes (CNTs)

Carbon nanotubes (CNTs) were discovered in 1991. The CNTs are allotropes of carbon with a cylindrical nanostructure. The bonding in carbon nanotubes is sp^2, with each atom joined to three neighbours, as in graphite. The tubes can therefore be considered as rolled-up graphene sheets (graphene is an individual graphite layer).

There are two main types of CNTs that can have high structural perfection. Single-walled carbon nanotubes (SWCNTs) consist of a single rolled graphite sheet seamlessly wrapped into a cylindrical tube. Multi-walled carbon nanotubes (MWCNTs) consist of multiple layers of graphite rolled in on themselves to form a tube Shape. Typically SWCNTs have a diameter of close to 1 nm while the diameter of MWCNTs are in the range of 5 nm to 50 nm and distance between sheets about 0.34 nm as shown in Figure 2.1 (a) and (b), respectively.

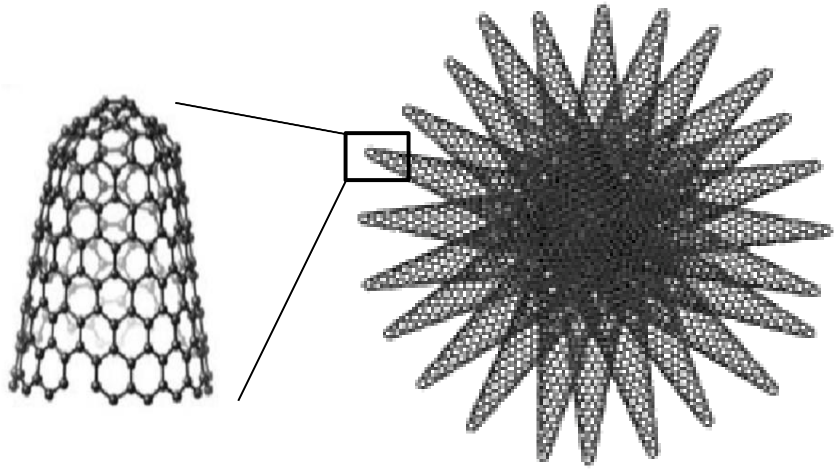


(a) (b)

Figure 2.1 Structures of (a) SWCNTs and (b) MWCNTs[12].

2.1.2 Single-walled Carbon Nanohorns (SWCNHs)

Single-walled carbon nanohorns (SWCNHs) [13] are a new material that are similar to single-walled carbon nanotubes (SWCNTs) Their physico-chemical characteristics and some applications have been reviewed. In this feature article, we review the chemistry of SWCNHs in a wide range with possible future applications. Three different types of single-walled carbon nanohorns (SWCNHs), ‘dahlia-like’, ‘bud-like’, and ‘seed-like’. SWCNHs have horn-shaped tips, the diameter of 2–5 nm, tubule length of 40–50 nm and cone angle of approximately 20° is shown in Figure 2.1 (a). About 1000 of SWCNHs assemble to form a spherical aggregate (diameters: 80–100 nm) as shown in Figure 2.2 (b). SWCNHs are composed of single-graphene which are similar to SWCNTs [2].



(a) (b)

Figure 2.2 Structures of (a) SWCNHs and (b) aggregate SWCNHs. (http://en.wikipedia.org/wiki/Single_walled_carbon_nanohorns)

Both SWCNHs and SWCNTs are tubes made of single graphene sheets with hollow spaces inside. The diameter of a SWCNT is small, and therefore molecules confined in SWCNTs are arranged in a one-dimensional-like ordering, allowing detailed studies of their physics and chemistry in a highly constrained geometry. On the other hand, the diameter of an SWCNH is large, so molecular movements, cluster formation and chemical reactions inside SWNHs are three-dimensional-like, which is useful for many applications in materials engineering. The irregular tube structure of SWCNHs has the advantage of opening holes not only at the tips but also on the sidewalls, and the large diameters of the tubules allow the hole sizes to be enlarged to 2nm or larger. Due to the large diameters of holes and tubules, the incorporation and release of molecules are easy, which suggests that SWCNHox can function as a carrier and supplier of materials. Unlike the bundle aggregates of SWCNTs, the rough surface of the SWNH spherical aggregates seems to be useful for holding catalysts or other materials and keeping their particle sizes small. The absence of metal catalyst particles in SWNHs may be an additional advantage of SWCNHs over SWCNTs in practical use[1].

The toxicity of SWNHs has been studied intensively because it will be critical for fundamental studies and applications. No cytotoxicity has been found, and animal tests have shown no measurable toxicity. Thus, no short-term toxicity has been found to date. The nature and amount of toxicity from long-term exposure is still unclear[14].

2.2 Arc Discharge Technique

The arc discharge used technique to produce nanoparticles, carbon nanotube. An arc discharge is a device in which an electric current (a flow of electrons) is caused to flow between two points separated by a gas. The two points are called electrodes, cathode and anode. The cathode and anode are connected to the power supply, one to the positive charge and one to the negative charge as shown in Figure 2.3 . The anode is moved towards the cathode until the distance between them is less 1 mm then a high current passes through the electrodes and plasma is generated between them. The average temperature of plasma between the electrode at about 4000 K. There are several advantages of choosing this method over the other techniques such as laser ablation and chemical vapor deposition such as low cost, easy way and high production rates (several hundred mg in ten minutes)

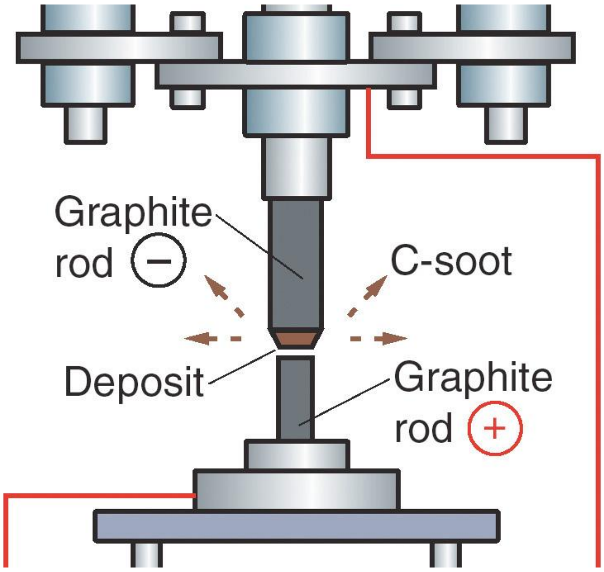


Figure 2.3 Arc discharge apparatus.

(http://mrsec.wisc.edu/Edetc/SlideShow/images/nanotubes/arc.jpg)

2.3 Plasma

Plasmas can be defined as the state of ionized gas consisting of positively and negatively charged ions, free electrons and activated neutral species (excited and radical), and are generally classified into two types, thermal (or equilibrium) plasma and cold (or nonequilibrium) plasma, based on the difference in characteristics.

The thermal plasma is the state of fully ionized gas characterized by a high gas temperature and an approximate equality between the gas and electron temperature ($Tg \approx Te$) and can be generated under atmospheric pressure. The energetic of this plasma is very high enough to break any chemical bond, so that this type of plasma can be excluded from most of organic chemistry, let alone from the field of pahramceutical science. In contrast, the cold plasma is most characterized by a low gas temperature and a high electron temperature ($Tg << Te$), and easily generated by electric discharges under reduced pressure. The field of plasma chemistry deals with occurrence of chemical reactions in the cold plasma including atmosphere pressure glow discharge plasma. One of the characteristics of surface treatment by cold plasma irradiation is the fact that it is surface limited so that only the surface properties can be changed without affecting the bulk properties[15]. The effect of plasma on a given material is determined by the chemistry of the reactions between the surface and the reactive species present in the plasma. Different plasma treatment in the various other gases the changes of related chemical functional group were list in Table 2.1. Each gas produces a unique plasma composition and results in different surface properties. In addition, plasma contains very high-energy UV radiation. This UV energy creates additional similar free radicals on the surface. Free radicals, which are thermodynamically unstable, quickly react with the polymer backbone itself or with other free-radical species present at the surface to form stable covalently bonded atoms or more complex groups, see Figure 2.4.

Table 2.1 The related chemical functional groups change at different plasma treatment[16].

Plasma gaseous	Increased functional group	Decreased functional group
O_2	C-OOH, C=O, C-O	C-OH, C-O-C
N_2	C-OH, C-O-C–, O=C-O, pyridine and quaternary nitrogen	– C=O (aromatic ring)
NH_3	N-H	-

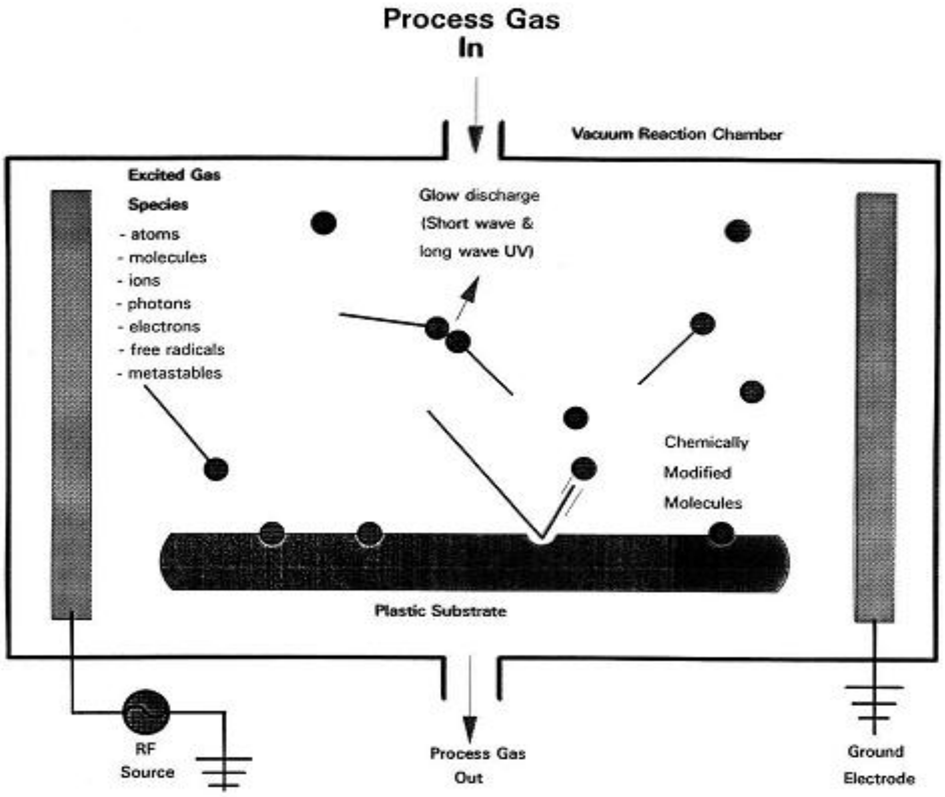


Figure 2.4 Schematic of plasma surface modification within the plasma reactor. (http://www.astp.com/plasma-equipment/applications)

2.3.1 Oxygen Plasma Treatment

Oxygen gas is a cheap, non-polluting and non toxic. Oxygen plasma treatment had already shown to be an important technique for cleaning surfaces [17, 18]. Plasma cleaning removes organic contamination from surfaces primary via chemical reactions with physical ablation being secondary. The UV light from plasma is effective in breaking the organic bonds (i.e., C-H, C-C and C=C) of surface contaminants. This helps to break apart high molecular weight contaminants. A second cleaning action is carried out by the oxygen species created in the plasma (O_2^+, O_2^-, O_3, O, O^+, O^-, ionized ozone, metastably-excited oxygen, and free electrons). These species react with organic contaminants to form H_2O, CO, CO_2, and lower molecular weight hydrocarbons. The ionization of oxygen into the various species found in an oxygen plasma can be represented by the possible reaction as following[19]:

$$O_2 + e^- \rightarrow O_2^- \rightarrow O + O^- \tag{1}$$

$$O + e^- \rightarrow O^+ + 2e^- \tag{2}$$

$$O_2 + e^- \rightarrow O_2^+ + 2e^- \tag{3}$$

$$2O_2 + e^- \rightarrow O_2^- + O_2 \tag{4}$$

$$O_2^- + O \rightarrow O_3 + e^- \tag{5}$$

$$O_2 + e^- \rightarrow O^* + O + 2e^- \tag{6}$$

$$O_2 + e^- \rightarrow O^- + O \tag{7}$$

The oxygen plasma treatment is an efficient of modification in surface of various materials such as carbon nanotubes[16]. The negative charge on surface of carbon nanotube was bought after the oxygen plasma treatment was due to dissociation of newly formed acidic groups as a result chemical and physical modification occur on the surfaces.

2.4 Literature Reviews

2.4.1 Synthesis of Single-Walled Carbon Nanohorns (SWCNHs)

Sano[4] synthesized SWCNHs using the arc in water method with the support of N_2 gas injection, which is the lowest cost process ever know. It is elucidated that rapid quenching of the carbon vapor in an inert gas at atmospheric pressure is necessary for SWCNHs formation. The SWCNHs were found as fine floating powder of the water surface. It was remarkable that the concentration of SWCNHs seemed more than 80% and the so-called bud-like structure, CNT do not found in these floating powders. The particle size distribution of the SWCNHs was determined by dynamic light scattering (DLS), results in an approximately 70 nm in diameter. The production rate of the SWCNHs is depend on the arc discharge current, which ranges from 30 to 80 A by increasing the production rate from 0.2 to 3.4 g/h.

Sano et al.[5] synthesized SWCNHs by a gas-injected arc-in-water (GI-AIW) method with varied N_2 flow rate, arc current and gas component with He, Ne, Ar, CO_2 and Kr. It was found that there were optimized values of N_2 flow rate and arc current at 5 L/min and 80 A to maximize the production rate, the yield and specific surface area of the as-grown SWCNHs. The effect of gas component on the production rate and yield was found maximized when N_2 was used. When CO_2 was used, the production rate found very low. Interestingly, it was discovered that the structure of SWCNHs formed under the condition of gas component. The dahlia-like SWCNHs can be produced by use of CO_2 as the bud-like SWCNHs were formed when either He, Ne, Ar, CO_2 and Kr was used.

Poonjarernsilp et al.[3] synthesized SWCNHs by gas-injected arc-in-water (GI-AIW) method. GI-AIW is known as one of the cost-effective methods to obtain SWCNHs. It was revealed that the yield of SWCNHs significantly decreases with the increase in water temperature, which range from 2 – 79 °C, although the purity of as-grown SWCNHs is not dependent on the temperature change. It is proposed model of relevant reactions in the GI-AIW system by a accounting the emission of carbon vapor and diffusion of water vapor in the cathode hole. It is proposed model of the reaction field in GI-AIW system that have three zones [(1) arc plasma zone, (2) quenching zone and (3) downstream zone] which would reasonably exist in the cathode. The arc plasma zone plays a role to generate carbon vapor. The quenching zone leads to conversion of carbon vapor to SWCNHs. In the downstream zone, water vapor is generated at the liquid-gas interface, resulting in the diffusion of the water vapor toward the quenching zone. The side reaction between H_2O and C produces H_2 and CO gas and consumes a certain amount of carbon vapor, resulting in the hindered SWCNH formation.

Sano et al.[20] studied the arc discharge duration time on the yield of SWCNHs in the synthesis using gas-injected arc-in-water (GI-AIW) method. The yield increase with duration time of arc discharge, while an increase in arc plasma temperature with time simultaneously. The arc plasma temperature exhibited a rapid increase from approximately 29 sec since the arc discharge was generated. The rapid increase of arc plasma temperature should lead to a disturbance in the steady state of the reaction field, temperature around 5100 K. The high temperature of reaction field affects the plasma density containing carbon radicals, should be to achieve a high yield.

2.4.2 Surface Modification of Carbon Nanomaterials

2.4.2.1 Surface modification by other techniques

Zhang et al.[21] investigated effect of chemical oxidation on the structure of single wall carbon nanotube (SWCNTs) by using different oxidants. The SWCNTs oxidized with three kinds of oxidants: (1) nitric acid (2.6M), (2) mixture of sulfuric (98%) and nitric acid (16M) (v/v = 3/1) and (3) $KMnO_4$. The results found that the different functional groups can be introduced when the SWCNTs are treated with different oxidants. The dilute nitric can be introducing the carboxylic acid groups only at those initial defect that already exist. The H_2SO_4/HNO_3 generated the incidence of carboxylic acid groups at newly created defect sites along the surface of

SWCNTs. In case of $KMnO_4$ can be introduced some quinine groups to the ends or side wall of SWCNTs. However, such a situation could not be observed in either treatment by HNO_3 or H_2SO_4/HNO_3, even for a very short time treatment. The oxidation processes begin mainly with the oxidize defect of SWCNTs. The processes can be divided into two step: (1) the defect-generating step and (2) the defect-consuming step. The defect-generating step, the oxidants attack the grapheme structure and generate active site. And the defect-consuming step, the grapheme structure was destroyed by oxidation in step 1. The defect-generating step is much faster than the defect-consuming step.

Li and Zhang[22] used H_2SO_4/HNO_3 (5:3) controlling oxidation time for cut into different lengths of Multi wall carbon nanotubes (MWCNTs). The resulting shorted MWCNTs (s-MWCNTs) formed stable dispersion state in the polar solvent without the help of surfactants. As a result of the introduced hydrophilic group, i.e., the carboxyl group. From FT-IR spectra of s-MWCNTs, there is additional peak at 1719 $^{-1}$cm which corresponds to the C=O stretching of carboxylic acids. Further, Solution of NaOH was used to determine the percentage of acidic sites on surface of s-MWCNTs, calculated about 0.2 – 1%.

Shieh et al.[23] treated carbon nanotubes (CNTs) by acid treatment. The acid treatment produce carboxylic acid group (COOH) and/or hydroxyl group (OH) on surface of CNTs via oxidations of C=C in the grapheme wall. From FT-IR spectra of the CNT treated at 1640 cm^{-1} corresponding to the H-bonded carbonyl group (C=O) that conjugate with C=C in the grapheme wall, indicating the presence of carboxyl group. The concentrations of the COOH groups increase with increasing temperature or time of the acid treatment. Solubility of CNTs, the untreated CNTs can be seen to precipitate from deionized water at 30 min and exhibit more precipitate one week later. The CNTs treated dissolve or well disperse in the deionized water for at least one week. However, the acid treatment can damage the tube structure depend on condition of acid treatment.

Xu et al.[24] used different polyethylene glycol (PEG) for modification surface of Single wall carbon nanohorns (SWCNHs). Ceramideconjugated PEG (CPEG) and phospholipid-conjugated PEG (DPEG) are surfactant assisted dispersion of SWCNHs in water. The zeta potential of SWCNHs was change to be more negative by CPEG and DPEG wrapping.

2.4.2.2 Surface modification by plasma treatment

Takada et al.[25] modified surface of carbon black by microwave oxygen plasma treatment. From result, the O/C atomic ratio increases with the treatment time and saturates at 120 minutes. The introduction rate of oxygen-containing groups onto surface of carbon black increased by increasing the input power for generate plasma. The oxygen plasma was indicated to cause changes in surface on surface, such as C=O, O-C-O and O-C=O functional groups.

Xu et al.[26] reported surface modification of multi-walled carbon nanotubes (MWCNTs) by O_2 plasma. The Oxygen plasma treatment is an effective way for modifying the MWCNTs can graft polar functional groups (carbonyl groups (C=O) and carboxyl groups (COOH)), more quickly but also an easy damage of MWCNTs after longer time. It was found that the surface of MWCNTs powder might be changed in three steps-expansion (loosed structure formed), peel off and oxidization with increasing of treatment time during the irradiation. The plasma treatment method could be a simple, nonpolluting and shorter treatment time for purification of MWCNTs.

A´vila-Orta et al.[27] modified multi-walled carbon nanotubes using plasma polymerization with ethylene glycol (EG). It is reported that plasma polymerization could give multi-walled carbon nanotubes (MWCNTs) a high dispersion in several solvents, water methanol and ethylene glycol. The untreated MWCNTs are highly hydrophobic. The modified MWCNTs showed very stable dispersion with water, methanol and ethylene glycol, confirming a hydrophilic behavior of the treated MWCNTs. After modification, a new functional group is much larger than untreated. This functional group is carboxyl group (C=O).

Chen et al.[28] treated multi-walled carbon nanotubes (MWCNTs) by microwave-excited Ar/O_2 surface-wave plasma (SWP) treatment. Oxygen-containing groups were introduced onto surface of MWCNTs. This research studied effect of gas flow rate, treatment time and plasma power on changes of the atomic contents and structure properties of MWCNTs. After plasma treatment, oxygen-containing groups, such as C-O, C=O and O-C=O were generated on the surfaces of MWCNTs. The effect of gas flow rate, the C-O and C=O fraction first increase and then decrease with increasing flow rate and the O-C=O fraction increases with flow rate. When plasma treatment was 15 min compared with 10 min, there are almost no change in the fraction of C-O, C=O and O-C=O group which the C=C fraction was slightly decrease. And effect of plasma power, oxygen-containing on surface of MWCNTs increase with plasma power.

Liu et al.[29] treated multi-walled carbon nanotubes (MWCNTs) by oxygen plasma for surface modification with varied process duration of 30 – 120 s. The results show that when MWCNTs were treated for 30 s the fragile amorphous carbon on the surface are apparently remove. After 60 s treatment, the MWCNTs are melt-like and the appearances of MWCNTs not easily distinguished. When treated for 120 s, most of the MWCNTs are almost destroyed. Based on Raman spectra, the I_D/I_G ratio of MWCNTs treated by oxygen plasma for 0, 30, 60, 90 and 120 s are 0.59, 0.21, 1.15, 1.31 and 1.52 respectively. After surface modification, it was generated functional groups (hydroxyl groups (C–O), carbonyl groups (C=O) and carboxyl groups (COO)).

2.4.3 Application of SWCNHs for Drug Delivery System

Ajima et al.[30] demonstrated that oxidized single-wall carbon nanohorns (SWCNHs) entrap cisplatin, an anticancer agent. They found that the cisplatin structure was maintained inside the nanometer-size hollow space of SWCNHs and that the cisplatin was slowly released from the SWCNHs in phosphate-buffered saline for 72 h. The released cisplatin was effective in terminating the growth of human lung-cancer cells, while the SWCNHs themselves had no such effect. Cisplatin-incorporated oxidized SWNHs are thus a potential drug delivery system.

Ajima et al.[31] investigated the reason for CDDP (cisplatin) release rates and quantities of CDDP@NHh differing from those of CDDP@NHox, examined the effect of in PBS adsorption on NHox and NHh. The NHox is carbon nanohorns (NHs) treated by oxygen gas at 570 – 580 °C for 10 min. The NHh was obtained by removing the oxygen-containing functional group by treating NHox in hydrogen gas 1200 °C for 3 h. The quantity of CDDP release from CDDP@NHox in PBS was only 15%, while that from CDDP@NHh was 70%. The CDDP release stopping from NHox was due to –COOH and –OH group at the hole edges changed mainly to –COONa and –ONa groups. These groups hindered the CDDP release from NHox. These results indicate that the release quantity and rate of the drug or material from inside NHox would be controlled release by chemically modifying the functional groups at the hole edges of NHox.

Xu et al.[6] succeeded in using oxidized single wall carbon nanohorns (SWCNHox) to incorporate vancomycin hydrochloride (VCM), often called the antibiotic of last resort, for its controlled release by taking advantage of the interactions between VCM and SWCNHox. DSPE-PEG (1,2-distearoylsn-glycero-3-phosphoethanolamine–N-[amino(polyethy-lene glycol)2000] was used to modify the hydrophobic surface of SWCNHox to improve its dispersion in aqueous systems. The phospholipid chains of DSPE–PEG can attach on the nanohorn surface due to the hydrophobic interaction, as used in a similar manner for carbon nanotubes. After attachment of DSPE–PEG on VCM–SWCNHox for one week did not observe any obvious precipitation in the VCM–SWCNHox-PEG Solution. As results of release VCM from VCM-SWCNHox-PEG are fast release within the first few hours. After one day, the system started to give a slow release and stable release up to 10 days.

Though there are some previous works related to application of SWCNHs for drug delivery system as potentially controlled release of drug. Unfortunately, SWCNHs are rather hydrophobicity so that their surface modification would be required before being dispersed in drug solution. A promising method for material surface modification is plasma treatment because of environmental friendly, easy, short time and low cost advantages. From previous work related to surface modification by plasma treatment show that could give increase hydrophilicity on surface of CNTs. As the aim of this research, In this research, effect of plasma modification on the slow-release characteristics of PVPI impregnated onto the modified SWCNHs will be investigated. It is expected that the SWCNHs could help reduce the release of PVPI for longer period of time.

CHAPTER III

EXPERIMENT

Procedures of experiment and characterization are described in this chapter. Based on our literature survey, the following experimental procedures are designed as a tentative guideline. Experimental works would be separated into 3 parts; which are (i) Synthesis of Single-walled Carbon nanohorns (SWCNHs) by gas-injected arc in water (GI-AIW) method, (ii) surface modification of SWCNHs by plasma treatment and (iii) Impregnation of PVPI into SWCNHs.

3.1 Synthesis of Single-walled Carbon Nanohorns (SWCNHs) by Gas-injected Arc in Water (GI-AIW) Method

Two carbon electrodes (Graphite rod purity 99.9995%, Alfa Aesar) are immersed vertically in 2000 ml of de-ionized water to form an arc discharge system. The arc discharge operation is carried out at 80 A and 220 V. The anode is a graphite rod of 3 mm in diameter and with 10 mm length. The cathode is a graphite rod of 12 mm in diameter with a hole of 8-mm diameter and 25-mm depth at its bottom. The arc discharge could be initiated at a 1-mm gap between the two electrodes. The anode is moved vertically upward into the hole at the cathode bottom at a controlled speed of 1.5 mm/s. During the operation, nitrogen (N_2) gas is injected downward into the two narrow channels at the top of the cathode at a flow rate of 5 l/min [3]. After the arc discharge is finished, samples of particulate products will be collected from the water surface then dried at 100 °C overnight then to characterization. The schematic diagram of experimental apparatus has shown in Figure 4.1

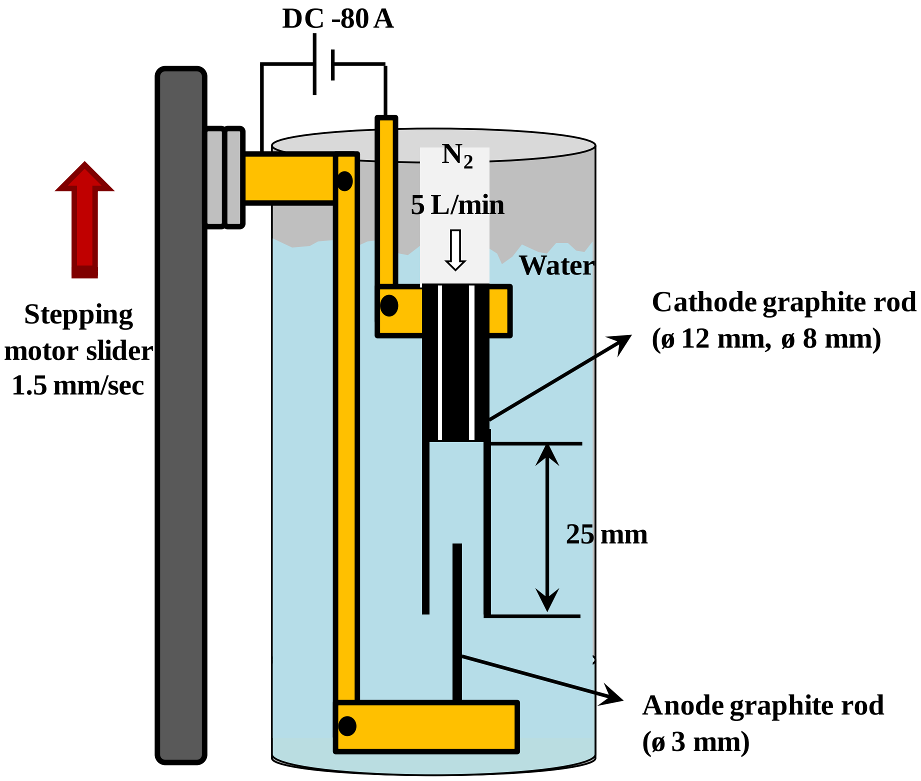


Figure 3.1 Schematic diagrams of experimental apparatus for GI-AIW method.

3.2 Surface Modification of SWCNHs by Oxygen Plasma Treatment

Oxygen plasma treatment was used for surface modification of SWCNHs. Figure 3.2 shows a schematic diagram of the oxygen plasma treatment system used in this work. The system mainly consists of a glass tube (40 mm in diameter) with two stainless steel electrodes placed at both ends opposite to each other[32]. The SWCNHs (about 10 mg) was loaded on a boat that was placed in the glass tube. The distance between the two electrodes is set to 60 mm. A DC high-voltage generator is used to generate the glow-discharge plasma. The applied voltage supplied to the electrodes is set to 5 - 20 kV. Oxygen gas was used as the plasma-forming gas at a flow rate of 50 cc/min. Initially the system was evacuated to a low pressure using a vacuum pump (Vacuum-pump system: Vacuum pump unit, PC510, Vacuubrand). A series of plasma treatment experiment was conducted to modify surface of the synthesized SWCNHs. The detailed experimental parameters are represented in Table 3.1.

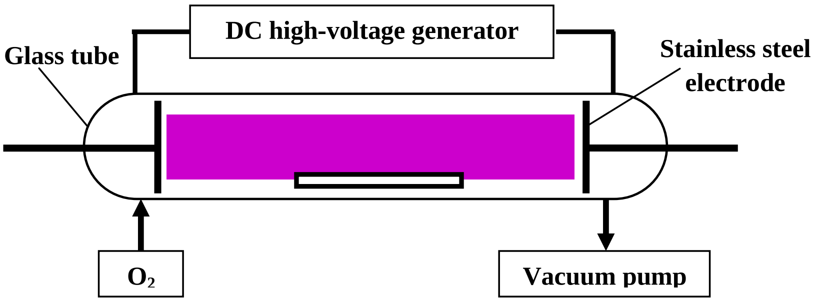


Figure 3.2 Schematics diagram of experimental setup for surface modification of SWCNHs by oxygen plasma treatment.

Table 3.1 The condition for surface treatment work studied.

Parameter	Range
Irradiation time (min)	0.5 – 60
Pressure (mbar)	1 – 100
Electric Current (mA)	1.5 – 5.5

3.3 Impregnation of PVPI into SWCNHs and Its Release

Polyvinylpyrrolidone-iodine (PVP-I), chemical structure shown in figure 3.3, was impregnated onto pristine-SWCNHs and treat-SWCNHs using a typical impregnation. 10 mg of SWCNHs was impregnated by 0.1 ml of PVPI solution with concentration of 100 mg/ml in methy alcohol. The PVPI-impregnated SWCNHs (PVPI@SWCNHs) were dried in an oven 40 °C and kept for further investigation on the release characteristics of the PVPI-impregnated SWCNHs. The parameter is various mass ratio of PVPI-to-SWCNHs between 1 and 100 (%wt).

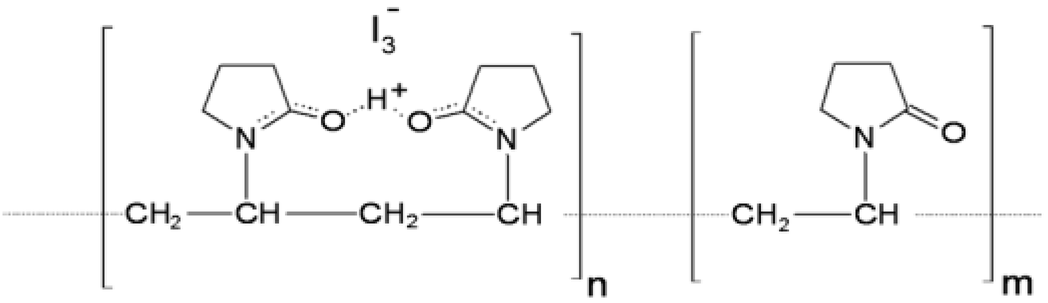


Figure 3.3 Chemical structure of PVPI.

3.4 Characterization

3.4.1 *Weight loss (%) of SWCNHs after Surface Modification*

The Weight loss is defined as the ratio of the sample weight change to the initial weight of the SWCNHs as follow equation 3.2

$$Weight\ loss\ (\%) \ = \ \frac{initial\ \ weight \ \ - \ \ final\ \ weight}{initial\ \ weight} \times 100 \tag{3.2}$$

3.4.2 *PVPI released (%) from SWCNHs*

The PVPI released is defined as the ratio of the concentration change to initial concentration of PVPI as follow equation 3.3

$$PVPI\ \ released\,(\%) = \frac{initial\,concentraton - any\,time\ concentraton}{initial\,concentraton} \times 100 \tag{3.3}$$

3.4.3 Quantitative Evaluation of the COOH Groups

The modified SWCNHs material was quantitatively analyzed by titration to determine the COOH concentrations on the surface of the treated SWCNHs. In a typical experiment, the carboxylated SWCNHs were added in to a 50 ml 0.01 N NaOH solution and stirred for 48 h to allow the solid SWCNHs material to equilibrate with the NaOH solution. The solution is then deposited onto a Milipore Nylon membrane with 0.2 μm pores via vacuum filtration. The residual solution was titratec with a 0.01 N HCl solution to determine the excess NaOH in solution and the concentration of the carboxylates on SWCNHs.

3.4.4 Dispersion of Plasma-Treated SWCNHs

A 1 mg of pristine SWCNHs or plasma-treated SWCNHs was added to 1 ml of deionized water then sonication for 10 min. The solution was left still for 1 month to investigate the solubility or dispersion of SWCNHs in the deionized water and recorded by a digital camera.

3.4.5 Scanning Electron Microscopy (SEM)

Morphology of the synthesized SWCNHs was studied using scanning electron microscope (SEM, JSM-6400) equipped with energy dispersive X-ray spectroscopy (EDS) at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. A photo of the Scanning Electron Microscopy (SEM) is shown in Figure. 3.4.

Figure 3.4 Scanning Electron Microscope (SEM)

The energy dispersive X-ray spectroscopy (EDS) analysis was also performed for analyzing elemental composition in each synthesized product as shown in Figure 3.5. It was found each typical product was composed mainly of carbon (88.66 wt %) with some small amount of oxygen.

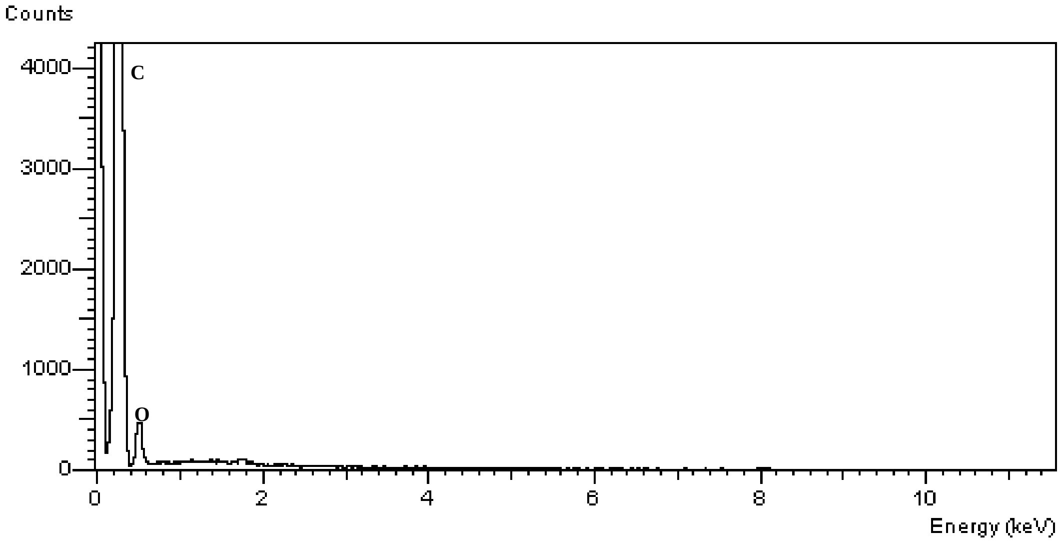


Figure 3.5 EDS spectrum of SWCNHs.

3.4.6 Transmission Electron Microscope (TEM)

The structure of the synthesized SWCNHs was investigated by Transmission Electron Microscope (TEM, JEOL JEM-2100) , operated at 80-200 KV at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. A photo of the Transmission Electron Microscope (TEM) is shown in Figure. 3.6.

Figure 3.6 Transmission Electron Microscope (TEM)

3.4.7 Raman Spectroscopy

Purity and crystallinity of the synthesized carbon nanoparticles were characterized by Raman Spectroscope (DXR SmartRaman, Thermo Scientific) at Excellence in Particle and Technology Engineering laboratory, Chulalongkorn University. A photo of the Raman Spectroscopy is shown in Figure. 3.7.

Figure 3.7 Raman Spectroscopy

Raman spectroscopy was used to evaluate the crystallinity of each synthesized product. Typical Raman spectrum of carbonaceous materials consists of a G-band peak at a Raman shift of 1580 cm^{-1} and a D-band peak at 1330 cm^{-1}as shown in Figure 3.8. The G-band peak represents an axial vibration of the sp2 carbons comprising graphitic hexagons while the D-band peak refers to the sp3 carbons as well as disorder and defective carbons with non-six-membered[33]. The ratio of D-band intensity (I_D) to G-band intensity (I_G) represents the level of the disorder carbon to the sp2 carbon in each carbonaceous material. A lower I_D/I_G ratio represents a smaller portion of defective carbons within the sample.

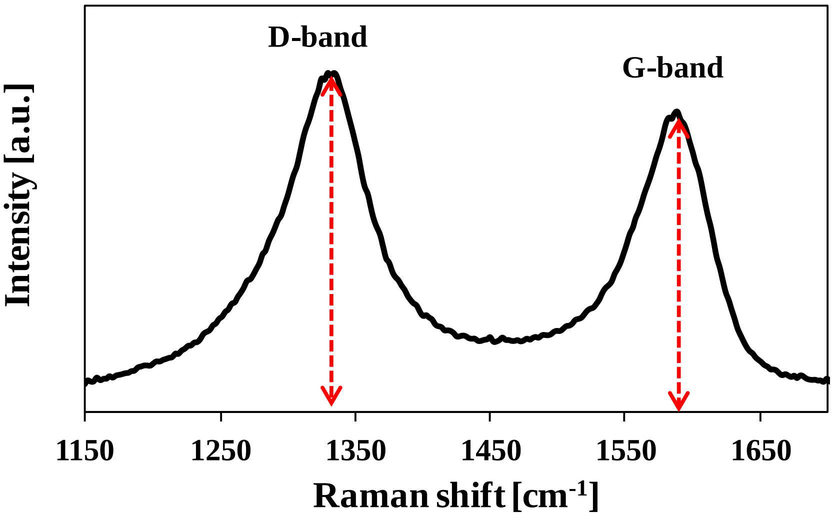


Figure 3.8 Raman spectrum of carbonaceous materials.

3.5.8 Fourier Transform Infrared Spectroscopy (FT-IR)

The functional groups in the samples were determined by using a Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Scientific) at Center of Excellence in Particle and Technology Engineering laboratory, Chulalongkorn University. The spectra were recorded at wavenumber between 400 and 4000 cm^{-1} with resolution of 2 cm^{-1}. The number of scan for the measurement was 100. A photo of the Fourier Transform Infrared Spectroscopy is shown in Figure. 3.9.

Figure 3.9 Fourier Transform Infrared Spectroscopy (FT-IR).

3.5.9 Zetasizer

The zeta potential of samples was measured by using zetasizer (Malvern Nano – ZS), concentration 1 mg of SWCNHs dissolved 10 ml in de-ionized water at National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency. A photo of zetasizer is shown in Fig. 3.10.

Figure 3.10 Zetasizer

3.5.10 Conductivity Meter

Amount of impregnated PVPI was indirectly analyzed by examining the electro conductivity meter (FR30, Mettler Toledo) to measure conductivity of aqueous solution prepared by immersing the PVPI@SWCNH in de-ionized water at Excellence in Particle and Technology Engineering laboratory, Chulalongkorn University. A photo of conductivity meter is shown in Fig. 3.11.

Figure 3.11 Conductivity meter

3.5.11 Auto Titration

The quantity of NaOH in the solution was determined by auto titration (T50 Titrator) at National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency. A photo of auto titration is shown in Fig. 3.12.

Figure 3.12 Auto Titration

3.6.12 Thermogravimetric (TGA)

The quantities of PVPI in PVPI-impregnated SWCNHs were estimated by using thermogravimetric analysis on a Mettler-Toledo TGA/DSC1 STARe System at Center of Excellence in Particle and Technology Engineering laboratory, Chulalongkorn University. The analysis was performed from temperature of 25 to 1,000 °C under a heating rate of 10 °C/min in oxygen flow of 40 ml/min. A photo of Thermogravimetric is shown in Fig. 3.13.

Figure 3.13 Thermogravimetric

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Synthesis of Single-walled Carbon Nanohorns (SWCNHs) by Gas-injected Arc in Water (GI-AIW) Method

Gas-injected arc in water (GI-AIW) method is an operation of arc discharge in water with nitrogen gas injection into the arc plasma. Graphitic carbon anode is consumed during the arc discharge, resulting in formation of carbon vapor which would undergo self-assembling process to form carbon nanoparticles (CNPs). The product synthesized by GI-AIW can be separated into three types of bulk products; the first is the floating on the water surface, the second is the cathode deposit and the rest is sedimentary at the bottom as shown in Figure 4.1. We have found that the products floating on surface mainly consist of aggregates consisting of single-walled carbon nanohorns (SWCNHs). The cathode deposit and sedimentary at the bottom consist of multi-walled carbon nanotubes (MWCNTs), carbon nanoparticles (CNPs) and SWCNHs.

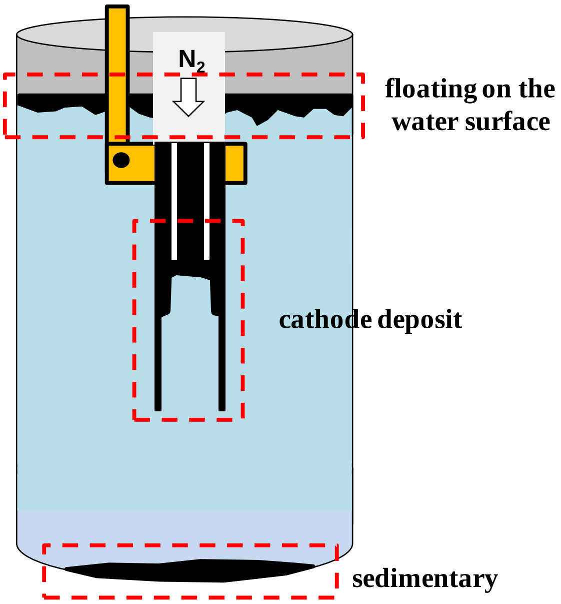


Figure 4.1 Schematic product synthesized by GI-AIW.

Morphology of all synthesized products were observed by scanning electron microscopy (SEM) and transmission electron microscope (TEM). SEM images of the floating product are shown in Figure 4.2. The floating product mainly consist of uniform spherical aggregates with diameters in the range of 60 to 100 nm. Detailed SEM examination reveals that these is no polyhedral graphitic fragments of nanohorn particles existing in the bulk product.

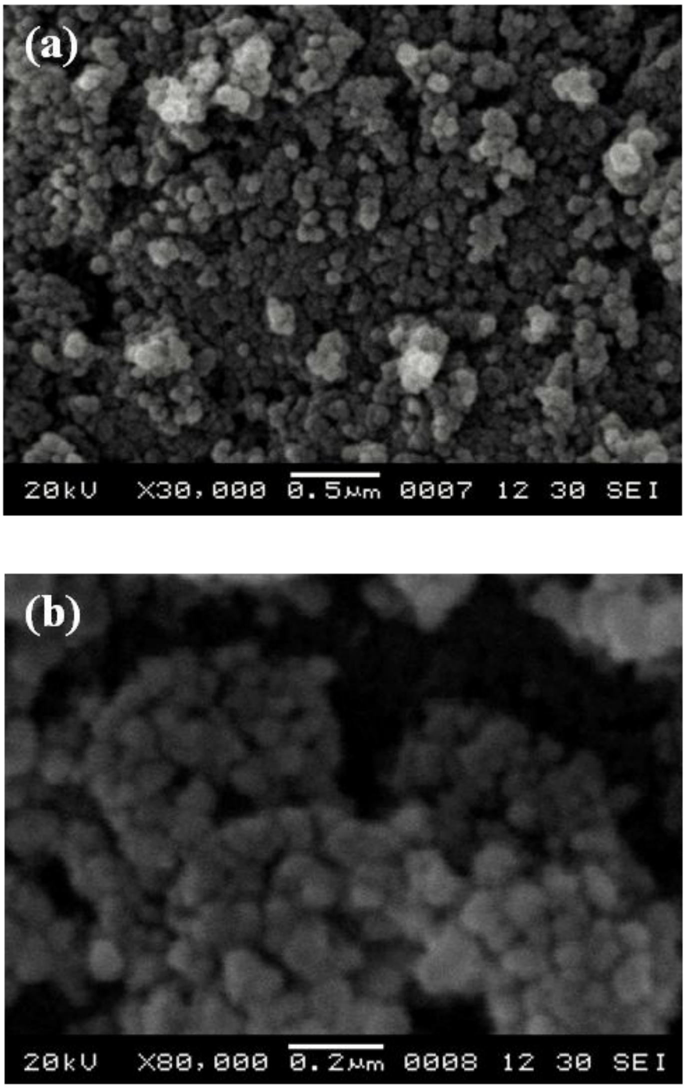


Figure 4.2 Typical SEM images of agglomerated SWCNHs, which floating on water surface (a) low magnification and (b) high magnification image.

Typical TEM images of the floating product are shown in Figure 4.3. It is clearly seen that the SWCNHs exhibit an aggregate structure with a diameter in the range of 60 to 100 nm. Purity of SWCNHs is very high (about 90-95%). MWCNTs and CNPs were not found in these floating products.

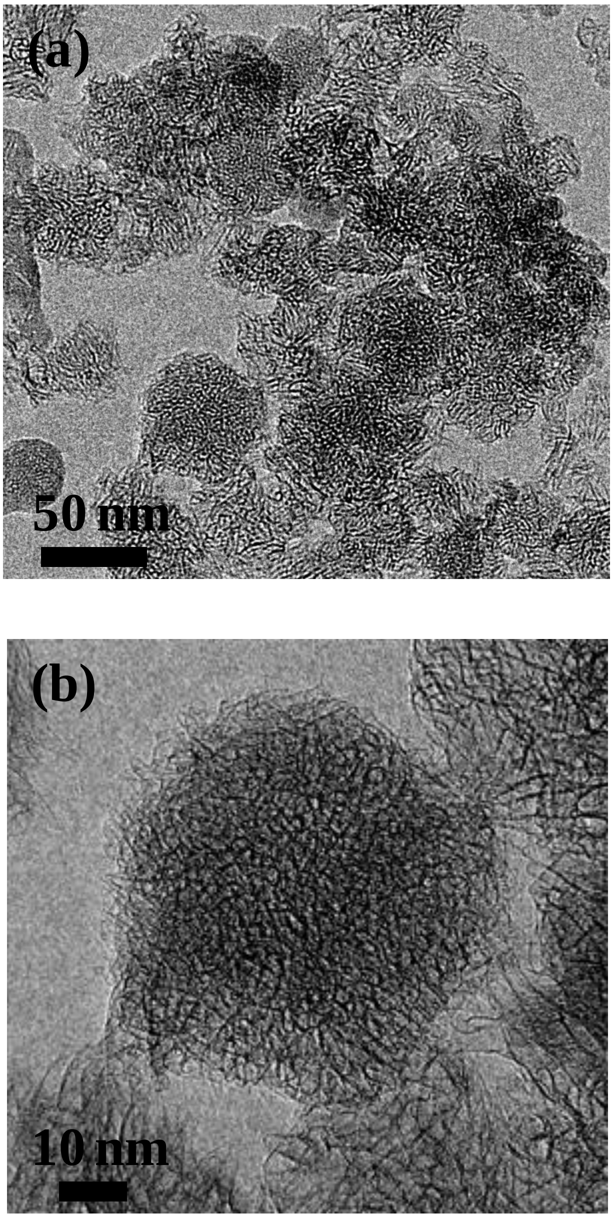


Figure 4.3 Typical TEM images of agglomerated SWCNHs, which floating on water surface (a) show low magnification image and (b) show high magnification image.

The cathode deposit products are consisted of MWCNTs with a diameter in the range of 15 – 30 nm and length of 250 – 300 nm, CNPs with nominal diameter of 100 – 300 nm and some SWCNHs with a diameter in the range of 60 – 100 nm as shown in Figure 4.4 (a). Meanwhile, Figure 4.4 (b) shows that nanostructures obtained from sedimentary at the bottom are mainly consisted of CNTs with nominal diameter of 60-100 nm. Some MWCNTs with a diameter in the range of 10 – 20 nm and length of 100 – 150 nm and SWCNHs with nominal diameter of 60 – 80 nm. Some MWCNTs attached with aggregate of CNPs and SWCNHs were also found. This result is in good agreement with those of previous works reported by Sano[4]. After the experiment was completed, it can be separated by weight percent of three types of bulk products. The weight percent of cathode deposit, sedimentary and floating product were 55.30, 14.95 and 5.64 %, respectively. Nevertheless, the cathode deposit and sedimentary products are consisted of the mixture of MWCNTs, CNP and SWCNHs, can’t be separate. For floating product is mainly consist SWCNHs very high purity. It was not found of MWCNTs and CNPs in these floating products.

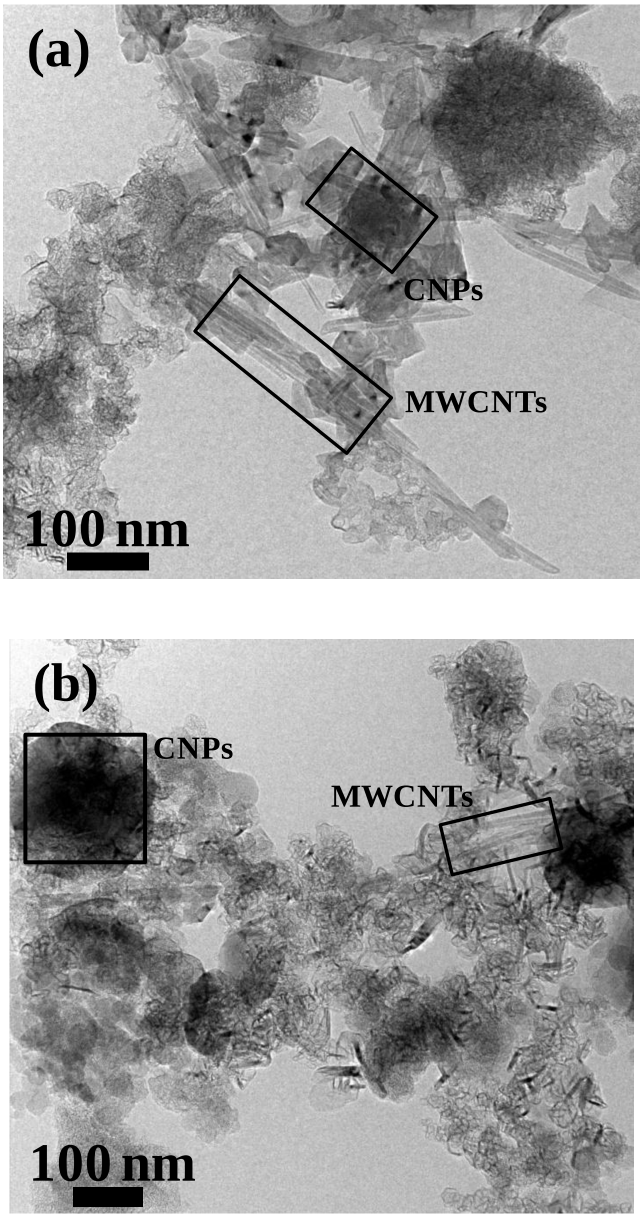


Figure 4.4 Typical TEM images of product at (a) cathode deposit and (b) sedimentary at the bottom.

4.2 Surface Modification of SWCNHs by Oxygen Plasma Treatment

Effects of oxygen plasma treatment parameters which were electric current, irradiation time and pressure were experimentally investigated and discussed. First, effect of electric current for determining on appropriate condition to surface modification of SWCNHs with a stable. Effect of electric current on generates the oxygen plasma.

4.2.1 Effect of Electric Current

Effect of the electric current at the current of 1.5, 3.0 and 5,5 mA on weight loss (%), functional groups on surface of SWCNHs after oxygen plasma treatment was studied under the same condition of irradiation time of 10 and 30 min and pressure of 1 mbar.

The weight loss (%) of SWCNHs after oxygen plasma treatment with different electric current of 1.5, 3.0 and 5.5 mA as shown in Figure 4.5. Effects of electric current on generate the oxygen plasma. At electric current of 1.5 mA initial generate the oxygen plasma. Plasma was generated discontinuously because low numbers of electron affect to form generated plasma. Plasma was generated at low current have form spark. At electric current of 5.5 mA, plasma was generated continuously. From Figure 4.5, at electric current of 1.5 mA would lead to a lower electron but leading to a higher weight loss. It could be noted that electric current of 5.5 mA would also contribute to the higher content of electron which would continuously with the generate plasma, leading to a lower weight loss. Addition, longer irradiation time would lead to a higher weight loss, leading to the higher of oxidation reaction of carbonaceous content. The amounts of emerging gaseous were produced from carbon gasification are CO_2 and CO. The carbon gasification is oxygen atoms and radical molecules formed in the plasma react with graphene structure proposed in Eq. (1)[25].

$$2C + \frac{3}{2}O_2 \rightarrow CO + CO_2 \qquad (1)$$

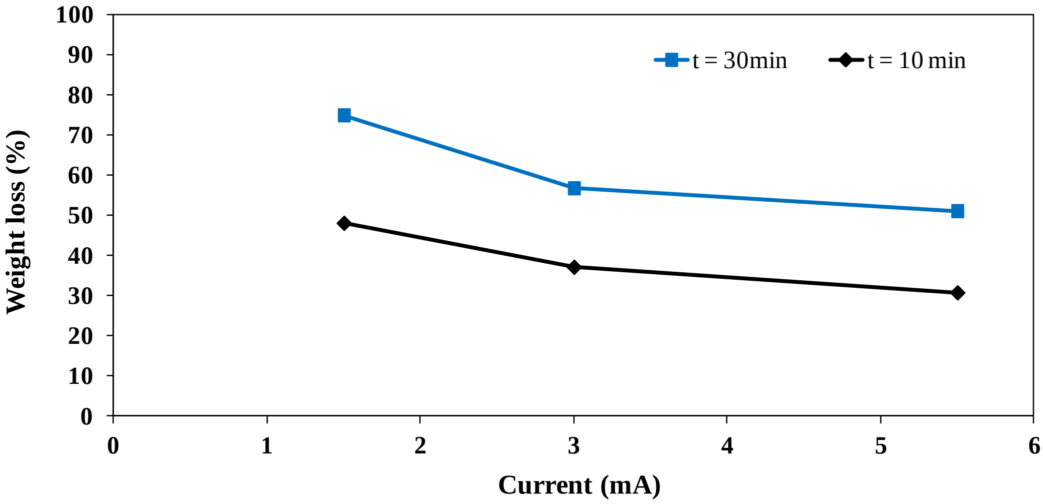


Figure 4.5 Weight loss (%) of SWCNHs after oxygen plasma treatment at different electric current of 1.5, 3 and 5.5 mA at irradiation time of 10 and 30 min.

Figure 4.6 shows the transmission signal of FT-IR spectra of SWCNHs which are subject to oxygen plasma stimulated by different electric current with a constant irradiation time of 10 min and pressure of 1 mbar. For pristine SWCNHs, typical peaks at 2921 and 2851 cm^{-1} could be assigned to asymmetric and symmetric stretching of $–CH_2$. Another peak at 1585 cm^{-1} represents an aromatic stretching vibration of C=C while a peak at 3430 cm^{-1} could be assigned to vibrational mode of the –OH group from carboxyl groups (O=C−OH and C−OH) [16, 34]. The last peak at 1210 cm^{-1} represents stretching vibrations of C-O group, indicating the presence of ether group. Meanwhile, in the case of plasma treated SWCNHs, there is an additional peak at around 1721 cm^{-1} which corresponds to the C=O stretching, indicating the presence of carboxyl group [16, 34, 35]. Addition, hydrogen atoms of COOH are formed moisture. It could be noted that electric current of 5.5 mA especially provides the transmission signal at 1721 cm^{-1}. In the later past of the study, the stimulating electric current of 5.5 mA would be employed as a reference conditions for investigation other treatment parameters.

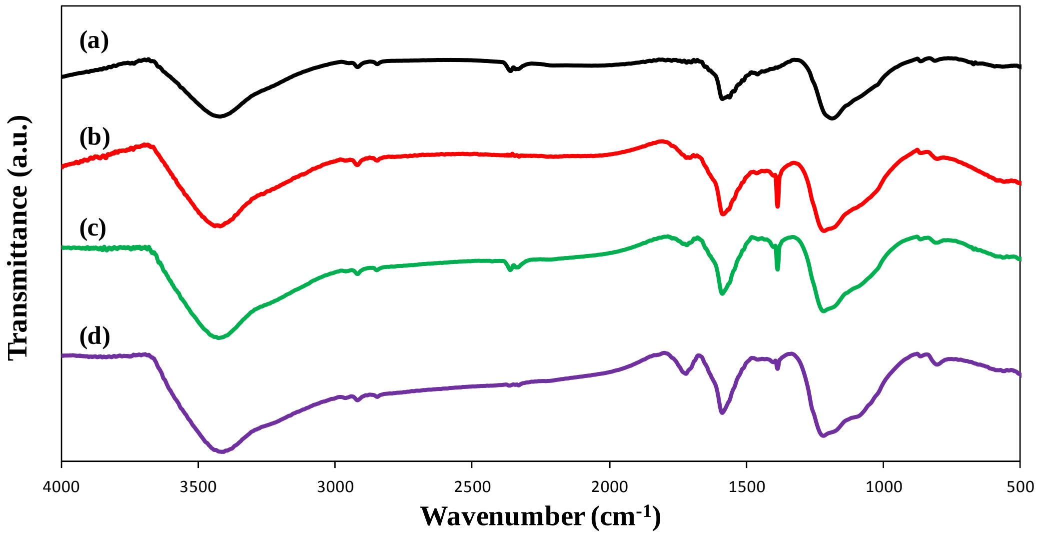


Figure 4.6 FT-IR spectro of (a) pristine SWCNHs and plasma treated SWCNHs under electric current of (b) 1.5 mA, (c) 3 mA and (d) 5.5 mA.

4.2.2 Effect of Irradiation Time and Pressure

Effect of irradiation time and pressure on weight loss (%), functional groups on surface, morphology, crystallinity and purity, dispersion, zeta potential, size and the presence of COOH groups of SWCNHs after oxygen plasma treatment with a stimulating electric current of 5.5 mA was studied. The irradiation time was varied in a range of 0.5, 1, 10, 30 and 60 min while the treatment pressure was in a range of 1, 10, 20, 50 and 100 mbar

The weight loss (%) of SWCNHs after oxygen plasma treatment with different irradiation time and pressure is shown in Figure 4.7. An increase in the weight loss of SWCNHs treated by oxygen plasma treatment was clearly observed with a longer irradiation time and a higher treatment pressure. The longer treatment time would lead to enhanced gasification of carbonaceous content so that only crystalline carbon structure would remain in the treated samples. Similarly, the higher pressure would also contribute to the higher content of oxygen which would react with the carbonaceous content, leading to a higher weight loss and higher amount of emerging gaseous products, such as CO_2 and CO generated from carbon gasification.

Such CO_2 and CO could be produced from oxidation of defective amorphous carbonaceous content which is more reactive than sp^2 carbon [28, 36].

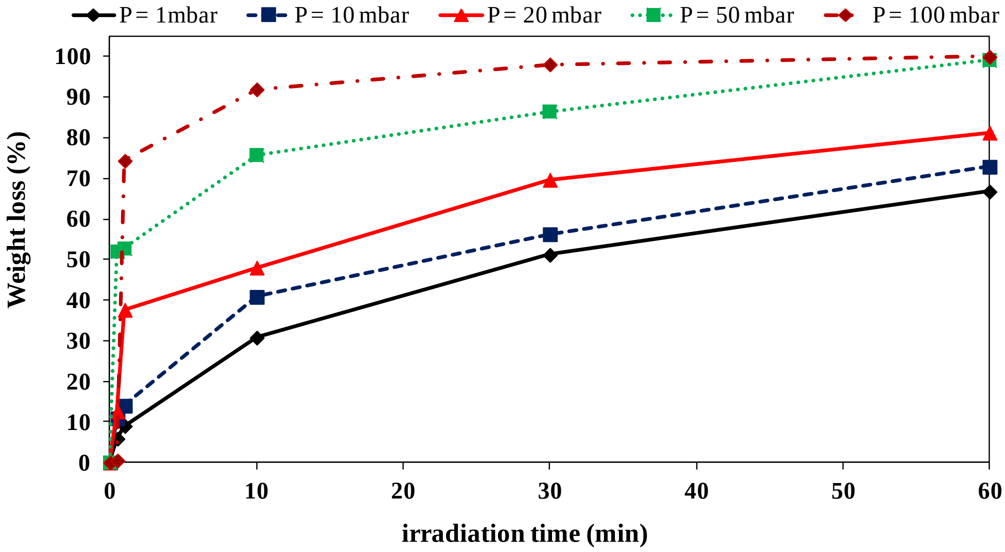


Figure 4.7 Weight loss (%) of SWCNHs after oxygen plasma treatment at different irradiation time and pressure.

Figure 4.8 shows the transmission signal of FT-IR spectra of SWCNHs which were subject to oxygen plasma treatment with different irradiation time at a constant stimulating current of 5.5 mA and pressure of 1 mbar. Similarly, FT-IR spectra of all treated samples exhibit the same characteristic peaks as these in Figure 4.6. It should be noted that the C=O strength vibration peak at 1721 cm^{-1} become stronger with a longer irradiation time. This result would suggest that with a longer irradiation time a higher content of oxygen treatment will introduce more C=O groups to the end or the side of the SWCNHs. However, with the irradiation time of 60 min the 1721 cm^{-1} peak shifted to 1635 cm^{-1}, suggesting an increase in COOH groups along with the longer treatment time[21]. It is noteworthy that with the higher amount of COOH groups existing on the surface of SWCNHs, the interaction of hydrogen bonds between the COOH groups would be stronger as shown in Figure 4.9.

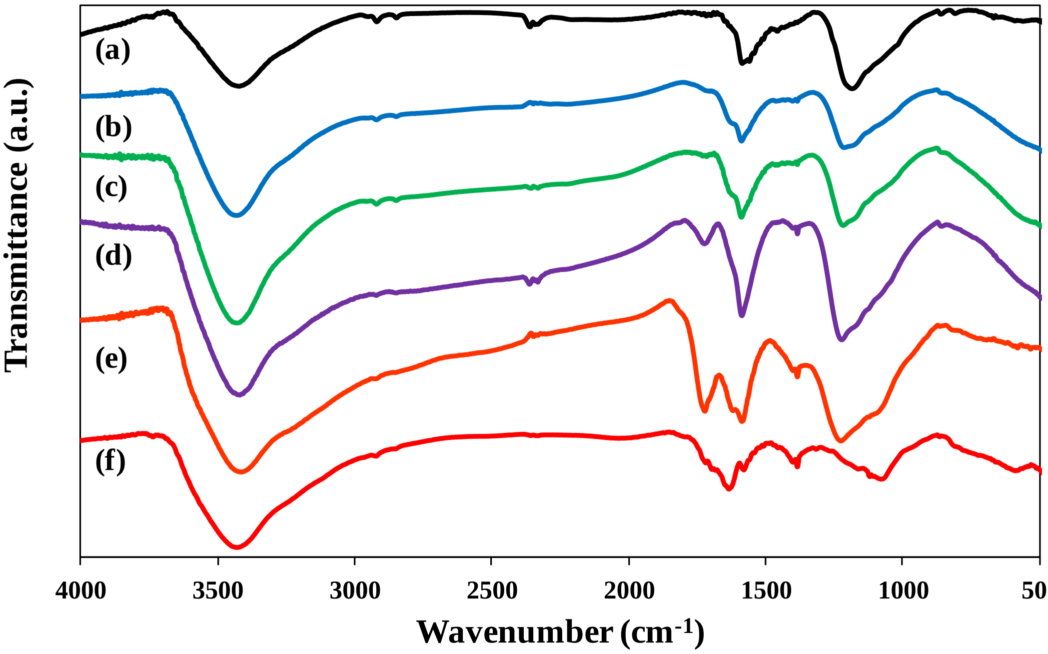


Figure 4.8 FT-IR spectra of (a) pristine SWCNHs and plasma treated SWCNHs under irradiation time of (b) 0.5 min, (c) 1 min, (d) 10 min, (e) 30 min and (f) 60 min.

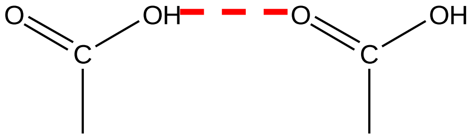


Figure 4.9 Schematic representation of hydrogen bond between COOH.

Figure 4.10 shows the transmission signal of FT-IR spectra of SWCNHs which are subject to oxygen plasma treatment with different treatment pressure at a constant electric current of 5.5 mA and irradiation time of 10 min. Likewise, FT-IR spectra of all treated SWCNHs show the agree with characteristic peaks as these in Figure 4.6. It could be noted that addition peak at 1721 cm^{-1} which corresponds to the C=O stretching compare with pristine SWCNHs. Meanwhile, a higher treatment pressure would also enhance the oxidation reaction will introduce more C=O groups on surface of the SWCNHs.

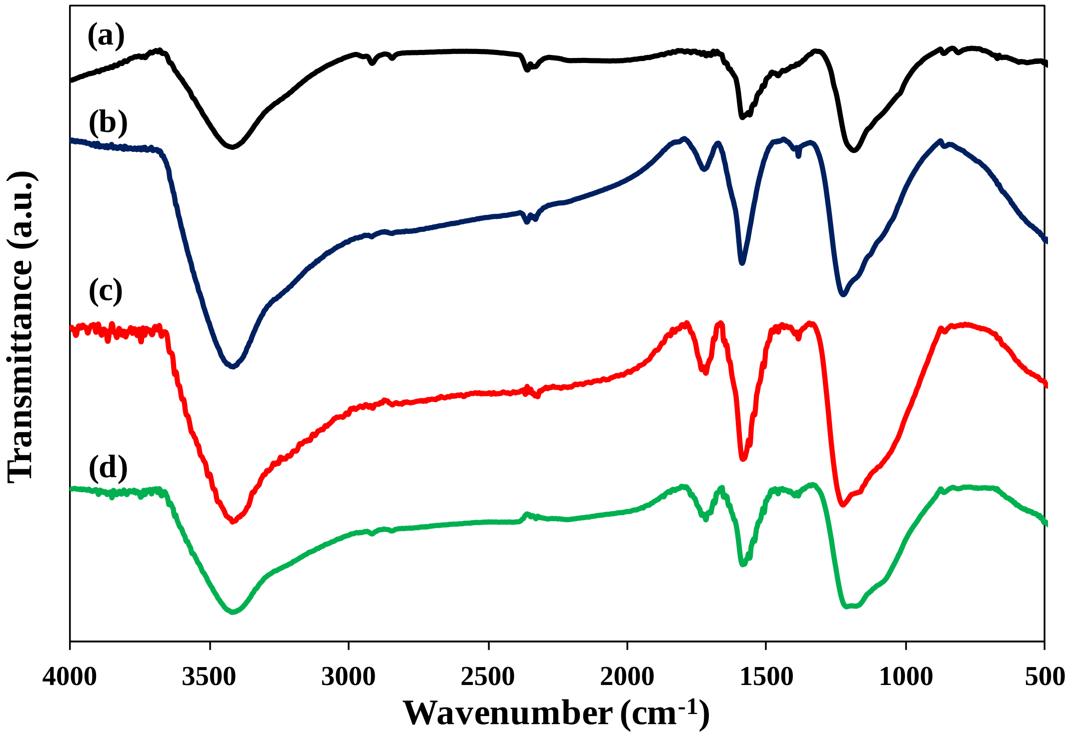


Figure 4.10 FT-IR spectra of (a) pristine SWCNHs and plasma treated SWCNHs under pressure of (b) 1 mbar, (c) 10 mbar and (d) 20 mbar.

It is known that oxygen plasma would stimulate different reactions which are related to the presence of excited species generated by the plasma. Mechanisms of functionalization of SWCNHs in oxygen plasma treatment would reasonably be similar to those of carbon nanotubes because of the similar structure of graphene. Generally, carbon gasification is involved with oxygen atoms and radical molecules that are formed in the plasma. The radicals would be generated on the surface of graphene structure, which then further react with other active oxygen atoms. This process may produce C-O bonds then the C-OH bonds are later formed by reacting with hydrogen atom. The hydrogen atoms would be introduced during synthesis phase of carbon nanotube or impurity of oxygen gas. Similarly, some oxygen atoms would react with radicals on the surface carbon nanotubes at defect structure and some radicals would further react with species from the plasma to form oxygen functional groups[28]. In oxygen plasma, chemical etching is predominant and excited species are able to react with surface to produce gases such as CO and CO_2.

Besides these spectroscopic analyses, microscopic observation of treated SWCNHs would also be necessary for investigating the effect of oxygen plasma treatment. Typical morphology of SWCNHs was observed by SEM and TEM images. Figure 4.11 shows the surface morphology of pristine SWCNHs and treated SWCNHs with different irradiation time at pressure of 1 mbar by SEM images. In Figure 4.11(a), pristine SWCNHs exhibit spherical agglomerate with an average diameter in a rage of 60 – 100 nm. For SWCNHs treated by oxygen plasma for 0.5, 1 and 10 min, as shown in Figure 4.11(b) – (d), the morphology of SWCNHs was insignificantly changed. However, the SWCNHs treated for 30 and 60 min exhibit an enhanced behavior of aggregation as shown in Figure 4.11(e) – (f).

Figure 4.12 shows the surface morphology of pristine SWCNHs and treated SWCNHs with different irradiation time at a constant pressure of 1 mbar observed by TEM. In Figure 4.12(a), the SWCNHs exhibit an aggregate structure with an average diameter in the range of 60 – 100 nm. However, the morphology of SWCNHs treated by oxygen plasma for 0.5, 1 and 10 min was insignificantly changed as shown in Figure 4.12(b) – (d). With a treatment time of 30 min, intimately connecting aggregates of SWCNHs could be observed as shown in Figure 4.12 (e) and (f) respectively. However, the SWCNHs which were treated for 60 min contain a higher content of rugged sheet-like aggregates, as illustrated in Figure 4.12 (g) and (h).

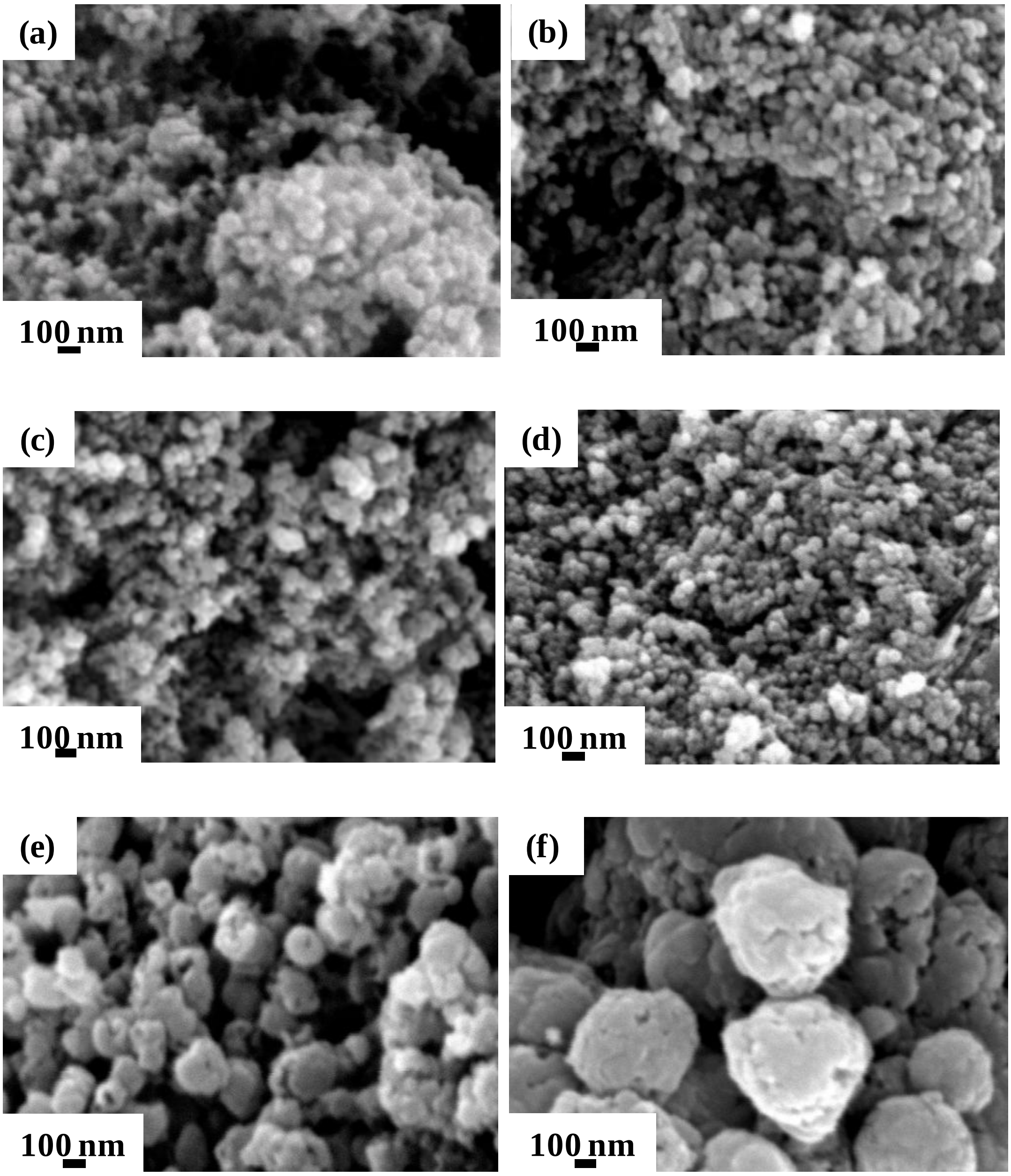


Figure 4.11 Typical SEM images of the SWCNHs, (a) pristine SWCNHs, SWCNHs treated by oxygen plasma for (b) 0.5, (c) 1, (d) 10, (e) 30 and (f) 60 min.

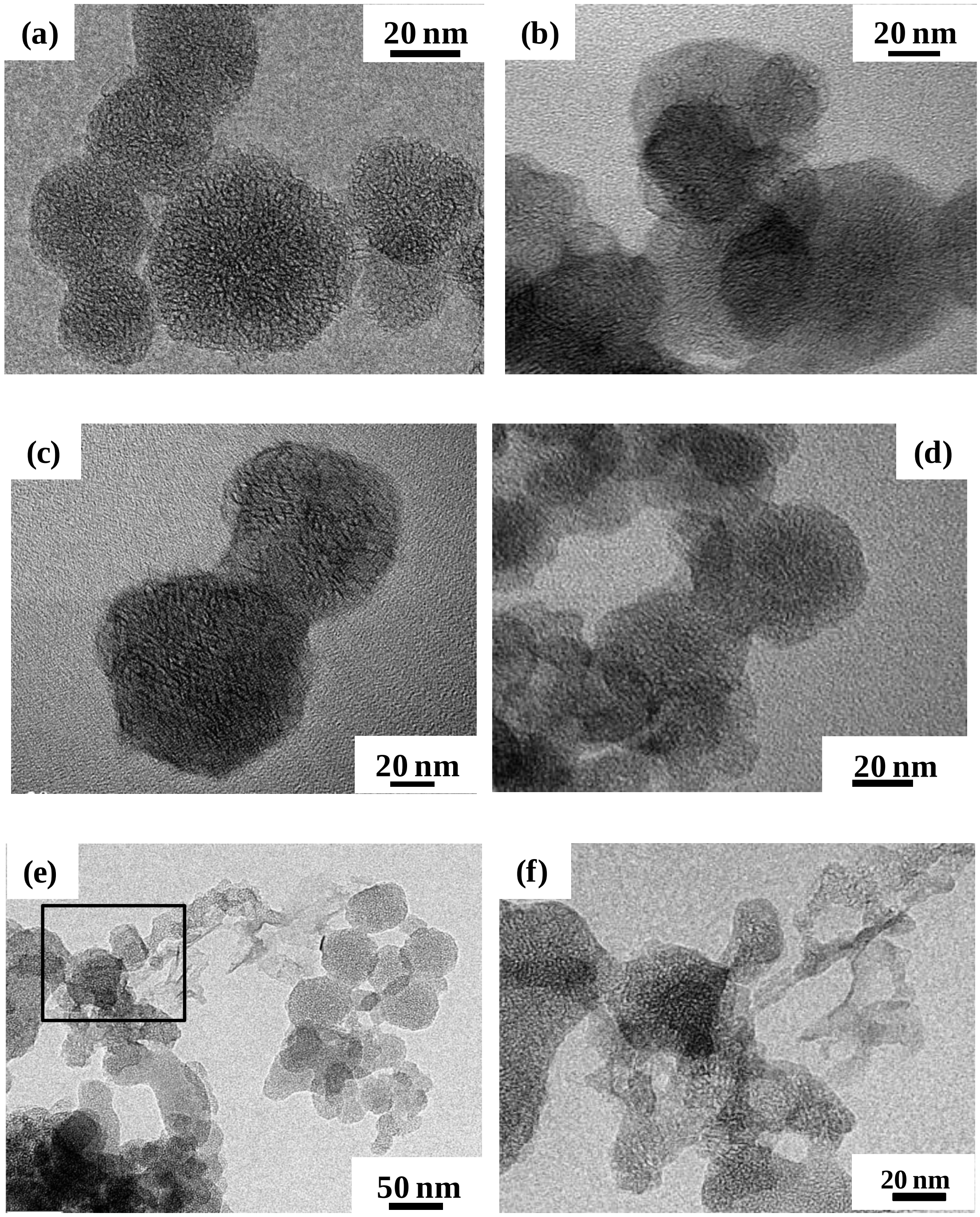


Figure 4.12 Typical TEM images of the SWCNHs, (a) pristine SWCNHs, SWCNHs treated by oxygen plasma for (b) 0.5, (c) 1, (d) 10, (e) 30 and (g) 60 min: (f) and (h) high magnification image of the square marked in (e) and (g) respectively.

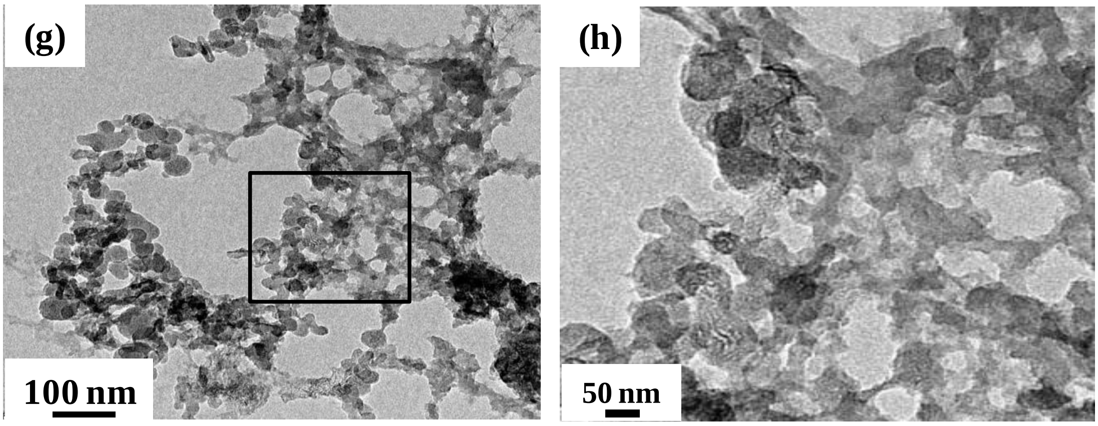


Figure 4.12 (continued)

Figure 4.13 illustrates typical Raman spectra of pristine SWCNHs and SWCNHs treated by oxygen plasma with different irradiation time at pressure of 1 mbar. The Raman spectra of SWCNHs treated with the irradiation time of 0.5 and 1 min are similar to that of pristine SWCNHs. In general, Raman spectrum of SWCNH consists of a G-band peak at a Raman shift of 1580 cm^{-1} and a D-band peak at 1330 cm^{-1}. The ratio of D-band intensity (I_D) to G-band intensity (I_G) represents the level of the disorder carbon to the sp^2 carbon in each carbonaceous material. Figure 4.13 shows the I_D/I_G ratio of SWCNHs treated by oxygen plasma with different irradiation time and pressure at electric current 5.5 mA. The Table 4.1 are summarizes the I_D/I_G ratios of SWCNHs treated by oxygen plasma with different irradiation time and pressure at 5.5 mA.

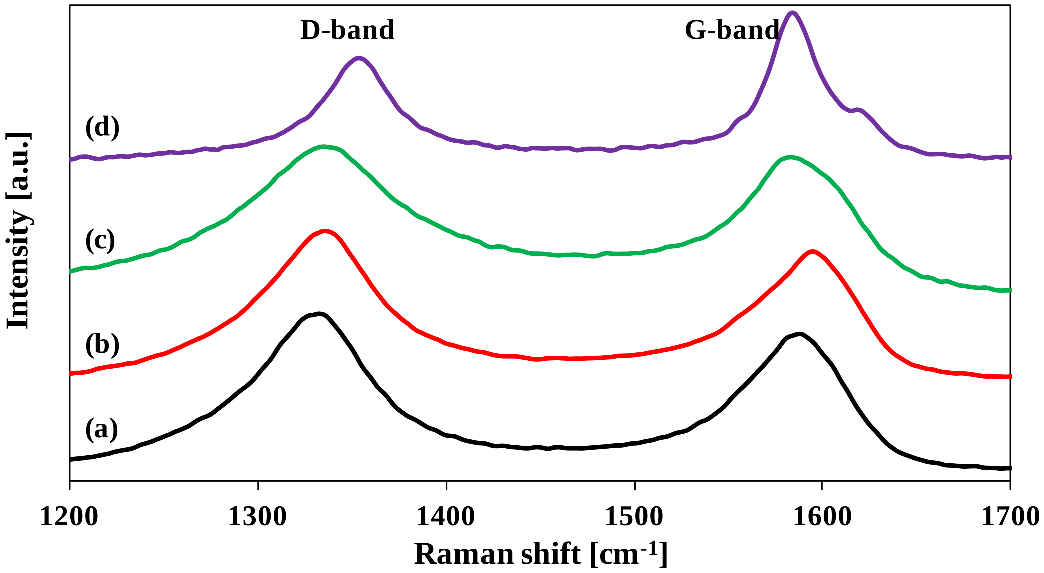


Figure 4.13 Raman spectra of the (a) pristine SWCNHs and SWCNHs treated by oxygen plasma with different irradiation time: (a) 10, (b) 30 and (c) 60 min.

Table 4.1 I_D/I_G ratios of for the treated SWCNHs.

Pressure / **Time (min)**	**P = 1mbar**	**P = 10 mbar**	**P = 20 mbar**
Pristine	1.14	1.14	1.14
0.5	1.14	1.14	1.12
1	1.13	1.13	1.12
10	1.13	1.10	1.08
30	1.04	1.02	0.91
60	0.70	0.72	0.79

I_D/I_G ratios shown in Figure 4.14 revealed that the oxygen plasma treatment affected the crystallinity and purity of treated SWCNHs. The value of I_D/I_G ratios of SWCNHs treated by oxygen plasma becomes lower with longer treatment time. The gradual decrease in I_D/I_G with respect to the longer treatment time would be attributed to the continual removal of reactive carbonaceous parts which would be consumed by oxidation reaction. Meanwhile, an increase in the treating pressure from 1 to 20 mbar would also enhance the carbon gasification, which is ascribed to a higher content of oxygen gas. As a result, the higher treating pressure would also lead to a lower I_D/I_G. However, for 60 min of treatment increase in I_D/I_G with respect to the higher pressure. At higher pressure, interaction of oxygen plasma with the surface of the SWCNHs will break C-C bonds and create defect or amorphous sites in the SWCNHs structure. With treatment by oxygen plasma irradiation, ion bombardment continues to react with the amorphous and defect carbon until they are peeled totally from the carbon nanohorns[26]. The amorphous and defect carbon would be oxidized under oxygen plasma irradiation due to the sp^3 bonding energy is quite low to sp^2 structure [28, 36]. Excited species of oxygen is able to react with the amorphous carbon to produce CO_2 and CO. The functional groups along with the amorphous and defect carbon are eliminated due to oxygen plasma will react with those more easily than sp^2 carbon. Therefore, significant change of I_D/I_G ratio of the treated SWCNHs could be observed. These results would suggest that the oxygen plasma treatment could contribute to the surface and structure modification of SWCNHs.

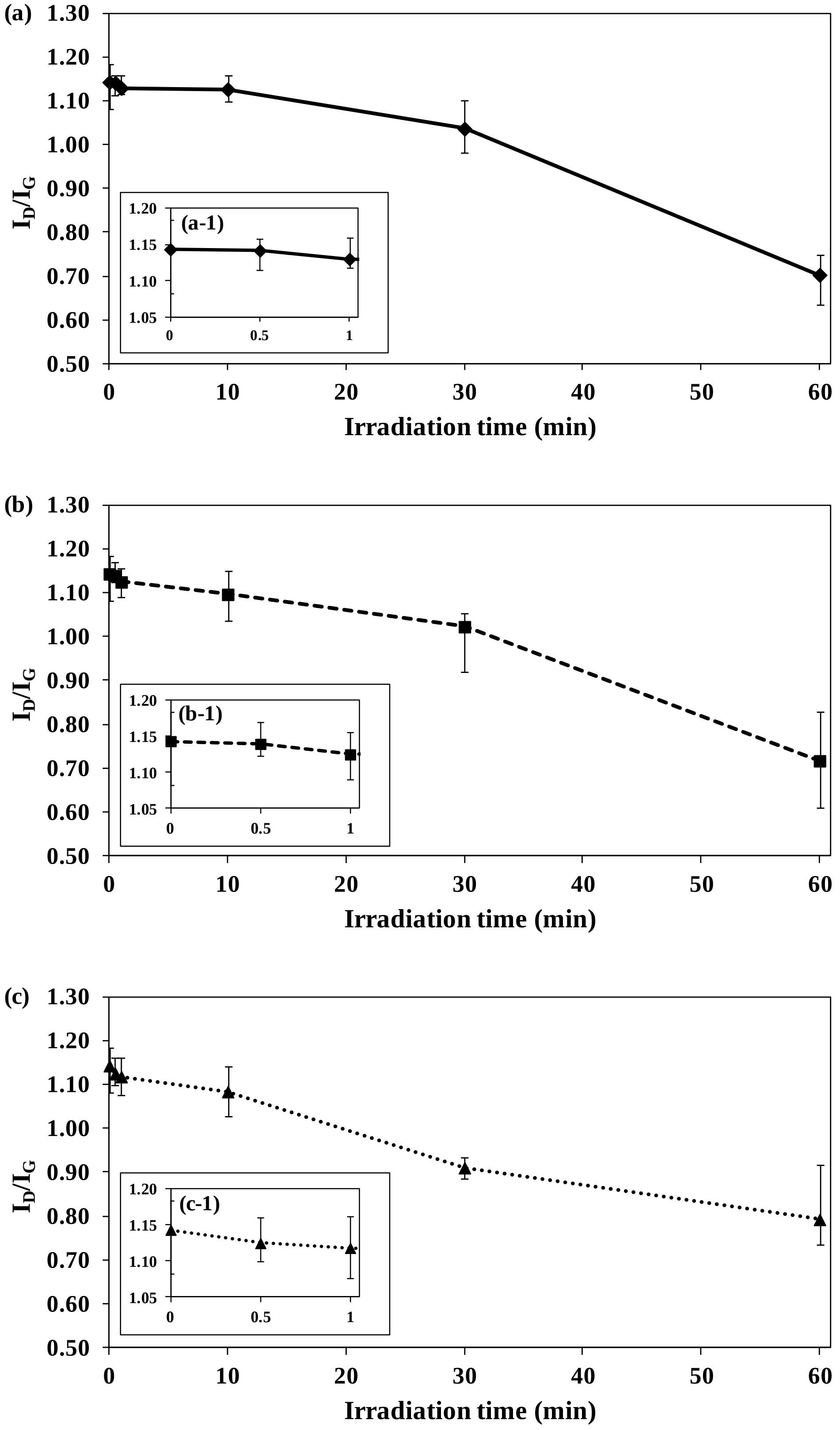


Figure 4.14 I_D/I_G ratios of the SWCNHs treated by oxygen plasma with different irradiation time and pressure of (a) 1, (b) 10 and (c) 20 mbar.

In Figure 4.15 presents photographic images of pristine SWCNHs and SWCNHs treated by oxygen plasma with different irradiation time and pressure of dispersion in deionized water (DI) after 1 month. The concentration of SWCNHs in the water was 0.1 mg/ml. The pristine SWCNHs are highly hydrophobic. The results clearly show that the pristine SWCNHs are sedimentary and floating on surface almost immediately. SWCNHs after oxygen plasma treatment disperse well in deionized water and do not form aggregation after a long settling time, 1 month. However, longer irradiation time and higher pressure form aggregation after a long settling time. Chen et.al. reported MWCNTs could exhibit a very good dispersion in aqueous solution after carboxyl groups were added onto their improved hydrophilicity[28]. It is also reasonable to imply that the presence of C=O on the surface of SWCNHs treated by oxygen plasma treatment would lead to a higher level of their dispersion in water. For pristine SWCNHs, it floated on the water surface due to their lower density (compare with water). Water molecules can diffuse into SWCNHs hollow structure would lead to the changing of their density when prolong the immersing time. Moreover, SWCNHs could aggregate and settle down to the bottom of vial as shown Figure 4.15 (i).

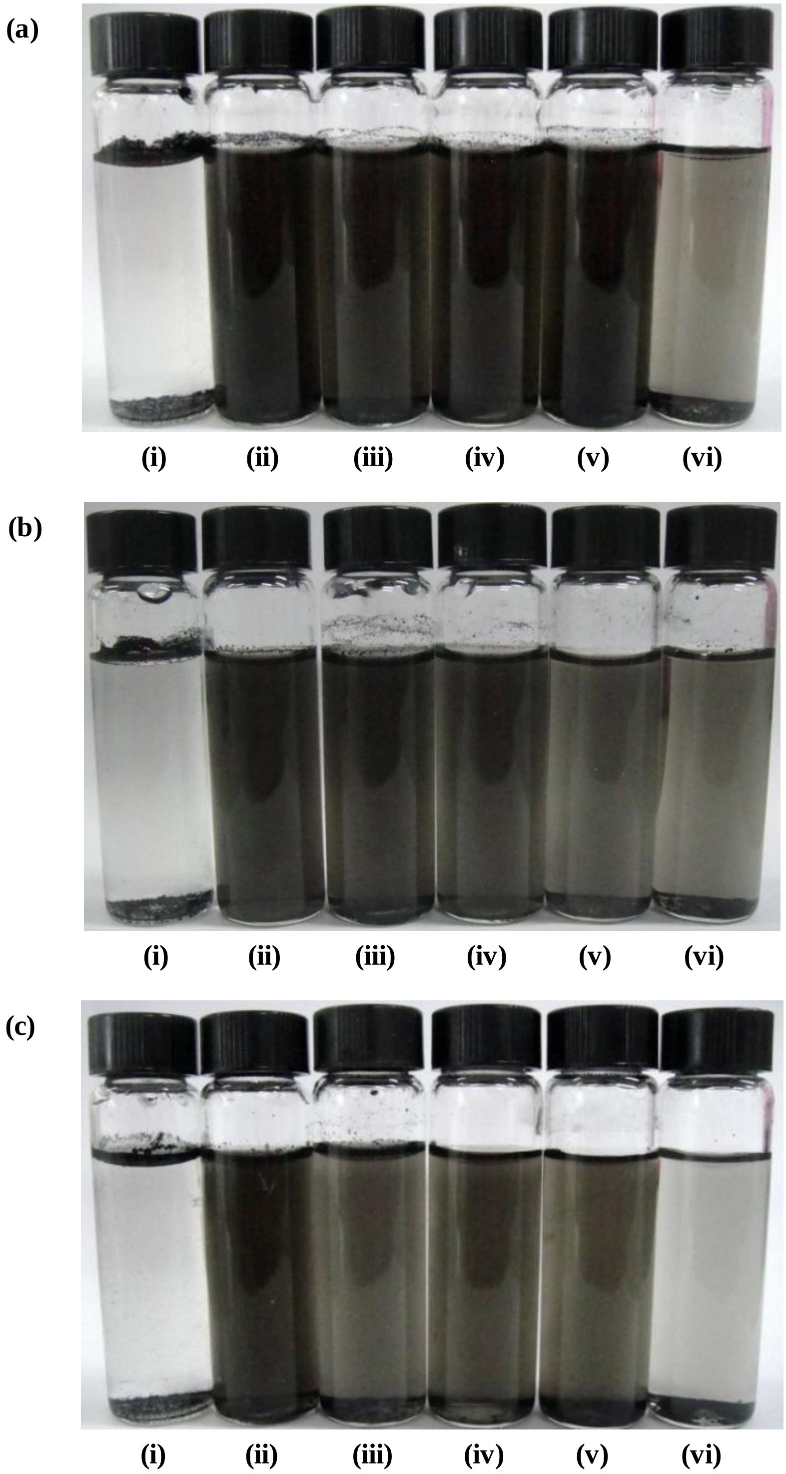


Figure 4.15 Dispersion of pristine SWCNHs and treated SWCNHs in deionized water after 1 month with different irradiation time and pressure of (a) 1, (b) 10 and (c) 20 mbar: (i) pristine, (ii) 0.5, (iii) 1, (iv) 10, (v) 30 and (vi) 60 min.

The ionization or dissociation of acidic groups (COOH) on the surface of SWCNHs gives rise to a negatively charged surface. To quantitatively predict long-term stability of the SWCNHs particle in dispersion, zeta potential is measured in this study. Zeta (ζ) potential is a parameter characterizing electric properties of interfacial layers in dispersions. The magnitude of the zeta potential can be used as an indication of the potential stability of the dispersion system. If the particles have low zeta potential values then there is no force to prevent the particles coming together and coagulating. The general dividing line between stable and unstable dispersions is generally taken at zeta potentials more positive and negative than +30 and -30 mV, respectively as described in ASTM Standard D 4187-82.

Figure 4.16 shows the zeta potential of pristine SWCNHs and treated SWCNHs in water of different irradiation time and pressure. The zeta potential of pristine SWCNHs is -23 mV, an indication that the pristine SWCNHs cannot form stable dispersion in deionized water agree with photographic images of pristine SWCNHs in Figure 4.15: (i). The zeta potential of pristine SWCNHs and treated SWCNHs becomes higher and decreased gradually with longer treatment time. This result would suggest that the addition oxygen-containing group on surface of SWCNHs would be generated under the initial condition. The gradual decrease of zeta potential with aspect to the longer treatment time wound be caused by the continual addition oxygen-containing group would lead to higher concentrations of COOH group. The finding that higher concentrations of COOH group on the treated SWCNHs result in denser aggregates can thus be attributed to the intermolecular hydrogen bonding of COOH groups [23, 37]. Meanwhile, an increase in the pressure affects higher content of oxygen gas would lead to enhanced oxidation reaction.

This high value of the zeta potential improves the dispersion of material in the matrix and prevents the agglomeration of the CNHs. This finding agrees with previous result of dispersion that the zeta potentials more positive and negative than +30 and -30 mV can be stable in solution.

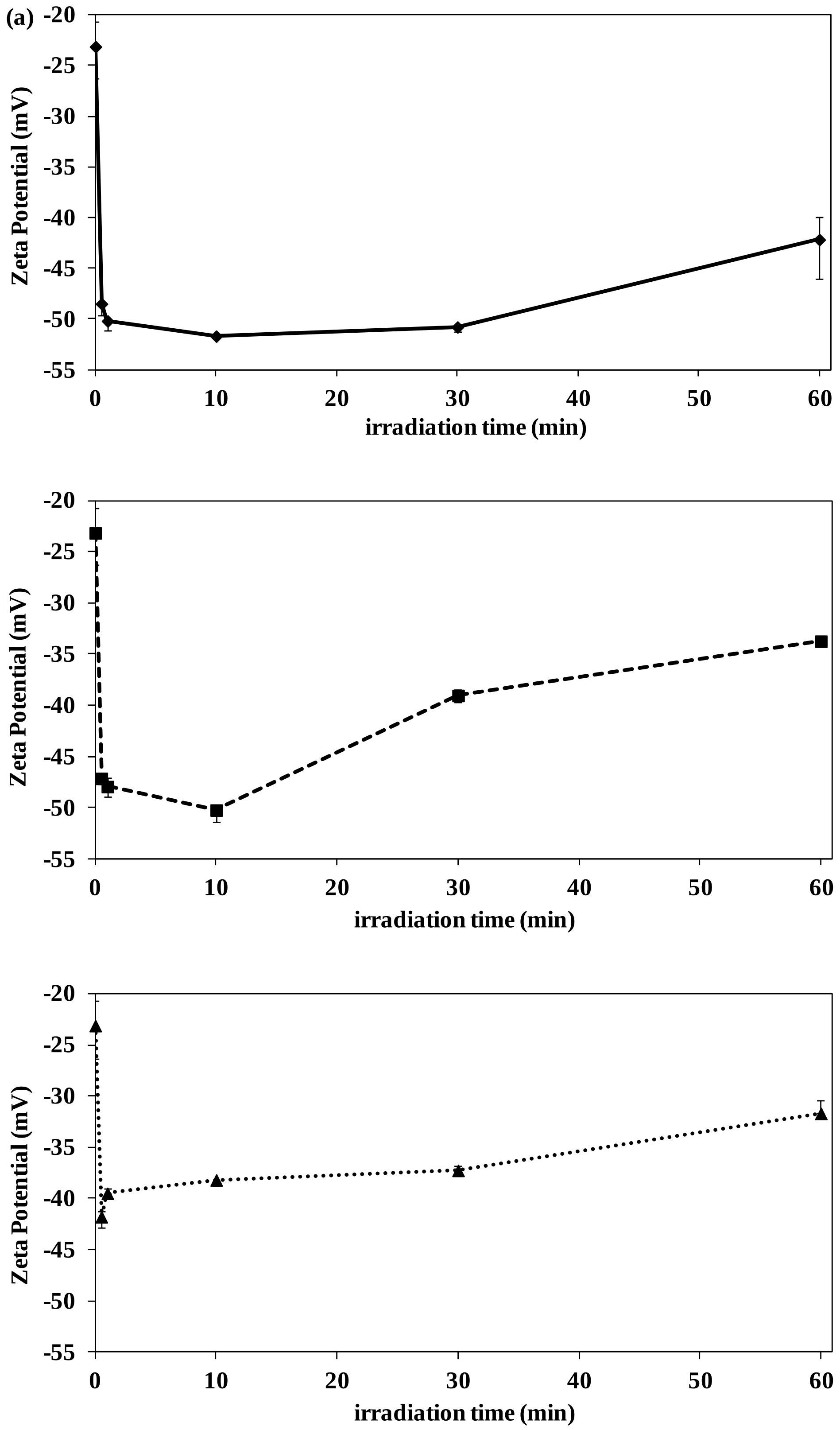


Figure 4.16 Zeta potential of pristine SWCNHs and treated SWCNHs with different irradiation time and pressure of (a) 1, (b) 10 and (c) 20 mbar.

Particle size as shown in Figure 4.17 revealed the particle size of SWCNHs dispersion decrease with initial irradiation time, approximately 320 nm for the pristine SWCNHs, about 201, 202 and 217 for 1 min with pressure of 1, 10 and 20 mbar, respectively. The smaller of particle size would lead to enhance dispersion in deionized water, as show in results of dispersion and zeta potential. For longer irradiation time, particle size of SWCNHs becomes bigger than initial irradiation, approximately 418, 447 and 520 nm for 60 min with difference pressure of 1, 10 and 20 mbar, respectively. This suggests that treated SWCNHs for longer irradiation time can be aggregated via intermolecular hydrogen bonding between two COOH groups as shown in Figure 4.18 [21, 23, 37, 38], leading to aggregation of the treated SWCNHs as can be seen in Figure 4.15: (vi) and low zeta potential, poor dispersion in deionized water. The higher pressure would also enhance the oxidation process, lead to a bigger particle size, low zeta potential and poor dispersion.

The carboxylated SWCNHs were quantitatively analyzed by titration using NaOH to determine the COOH concentrations on the surface of the oxygen plasma treated SWCNHs. As can be seen in Table 4.2, the mol of acidic oxygen-containing surface groups per gram of SWCNHs. The concentration of the COOH groups increase, with increasing irradiation time and pressure.

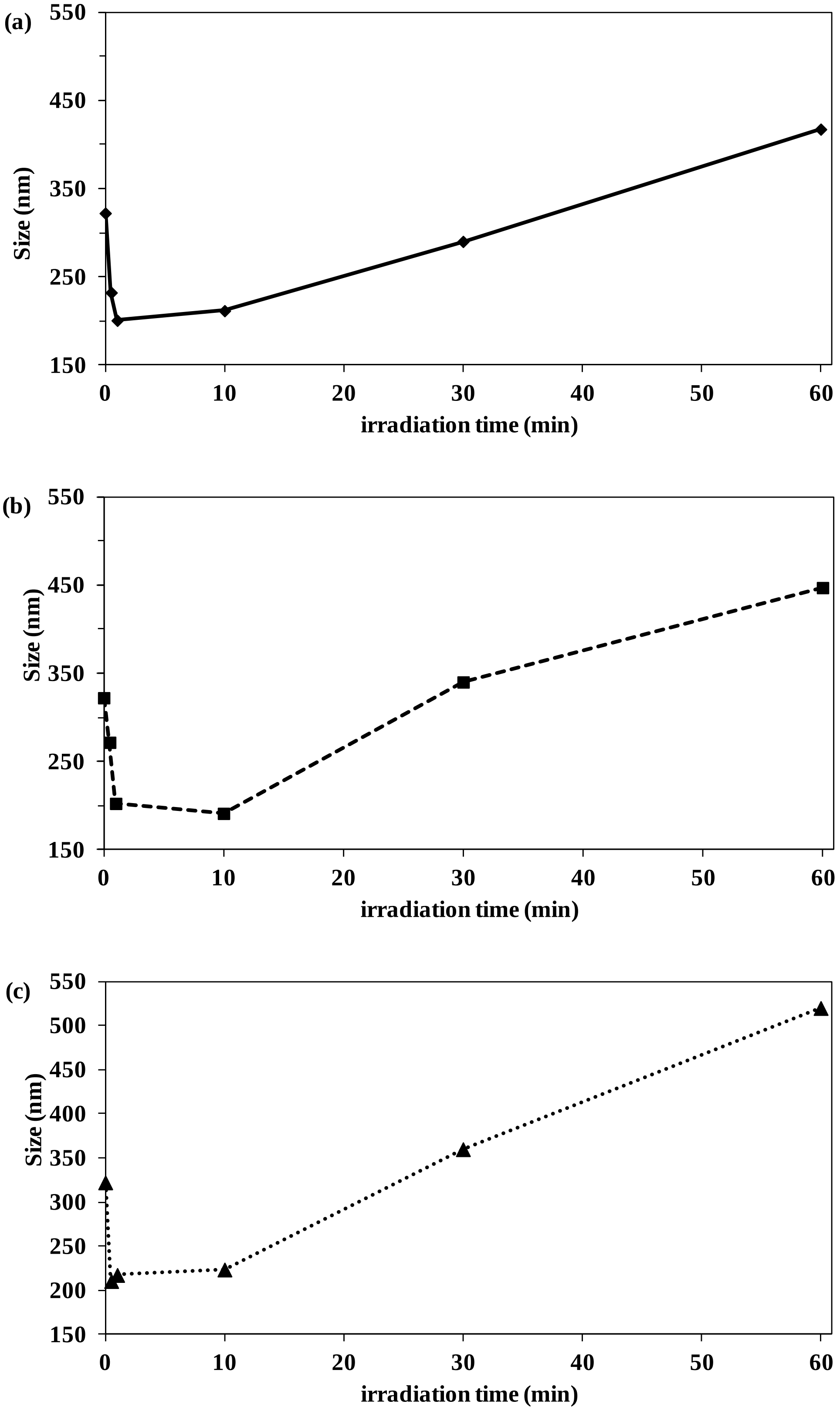


Figure 4.17 Particle size of pristine SWCNHs and treated SWCNHs with different irradiation time and pressure of (a) 1, (b) 10 and (c) 20 mbar.

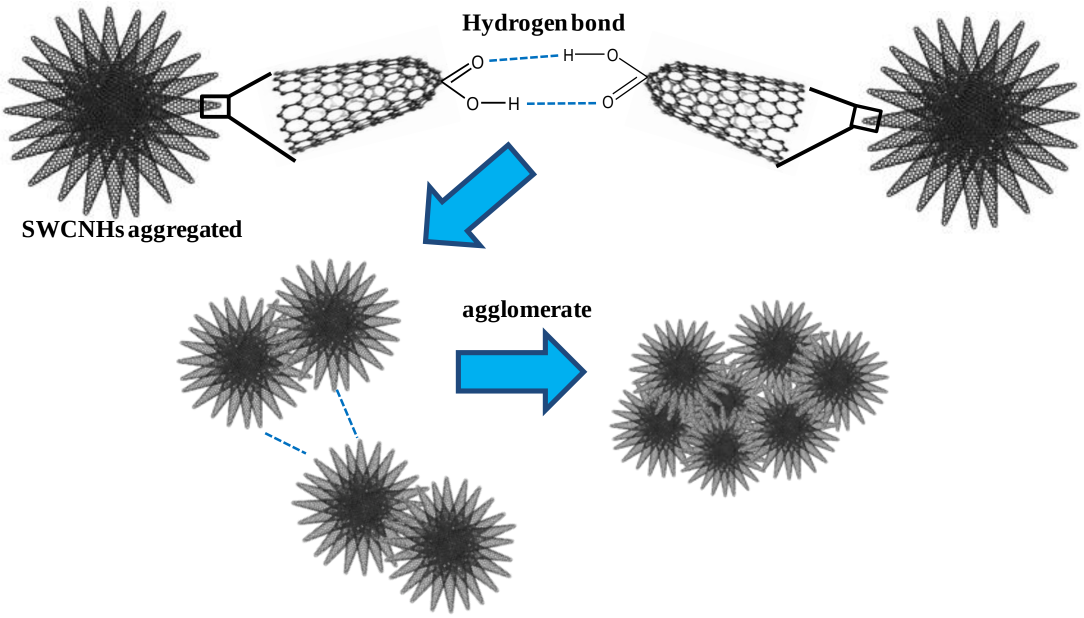


Figure 4.18 Shown schematic representation of the proposed aggregation of SWCNHs via intermolecular hydrogen bonding between two COOH groups.

Table 4.2 Concentrations of carboxylic groups of treated SWCNHs of treatment conditions.

Oxygen plasma treatment conditions	COOH contents (mol/g)
Pristine	0.005
0.5 min x 1 mbar	0.215
1 min x 1 mbar	0.217
10 min x 1 mbar	0.421
30 min x 1 mbar	0.590
60 min x 1 mbar	0.732
10 min x 10 mbar	0.450
10 min x 20 mbar	0.458

4.3 Impregnation of PVPI onto SWCNHs and Its Release

Typical morphology of PVPI-impregnated SWCNHs was observed by TEM image shown in Figure 19. From TEM image, SWCNHs was wrapped by PVPI, not clearly as destructed forms damaged by electron beams.

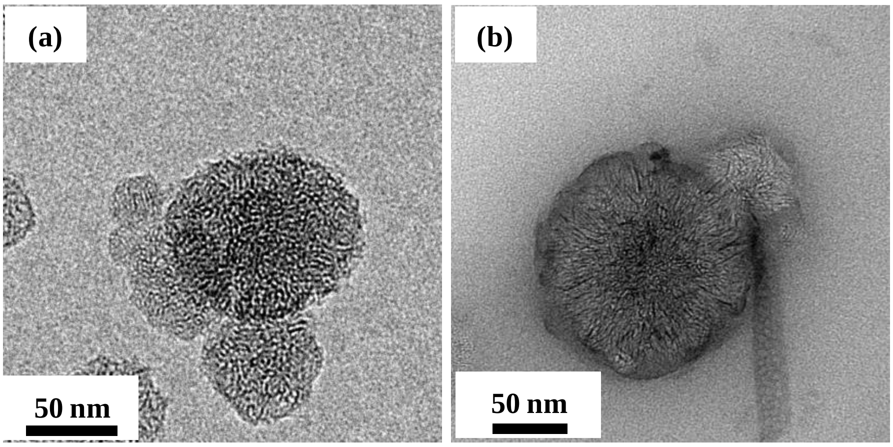


Figure 4.19 Typical TEM images of (a) pristine and (b) PVPI-impregnated SWCNHs.

In Figure 4.20 present EDS spectrum of PVPI-impregnated SWCNHs at 1:1. From the result, it is found that additional iodine peak, compare with pristine SWCNHs (Figure 3.5). These confirm that PVPI exist in the PVPI-impregnated SWCNHs.

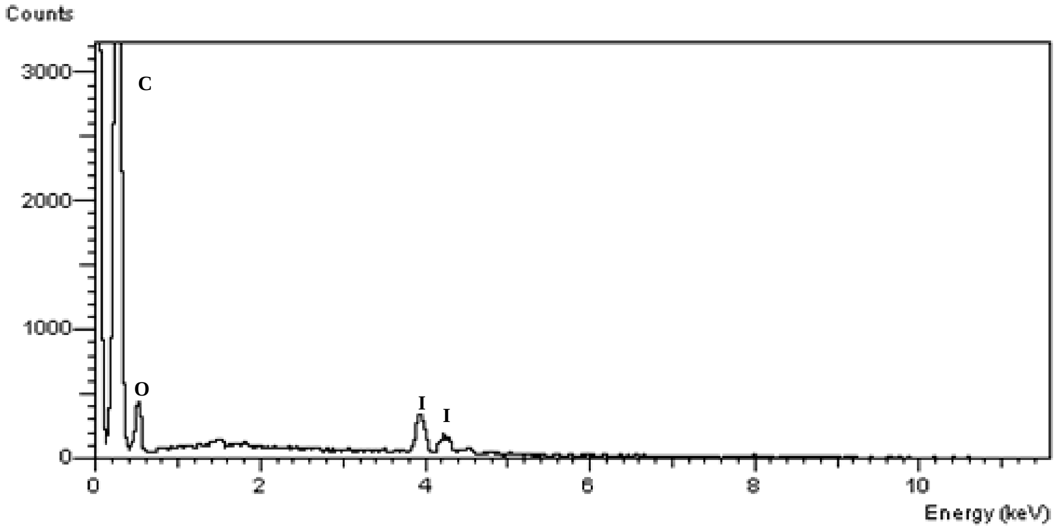


Figure 4.20 EDS spectrum of PVPI-impregnated SWCNHs; ratio 1:1.

The loading of PVPI in SWCNHs was measured with TGA. Pristine and plasma-treated SWCNHs were combusted by TGA, as shown in Figure 4.21(a) and 4.22 (a) respectively, decomposition occurred at around 590 and 820 °C. The peak at 590 °C assigned to the combustion of amorphous and defective carbon. Also peak around 820 °C represented to the degradation of tubular graphene and graphitic carbon[36]. In TGA analysis of pure PVPI in Figure 4.21 (b), degradation occurred at 300, 380 and 520 °C.

The TGA of PVPI-impregnated SWCNHs, pristine and plasma-treated in Figure 4.21 (c) and 4.22 (b). indicated that the PVPI quantities were calculated to be 40 and 42 % respectively, deduct of residual and moisture.

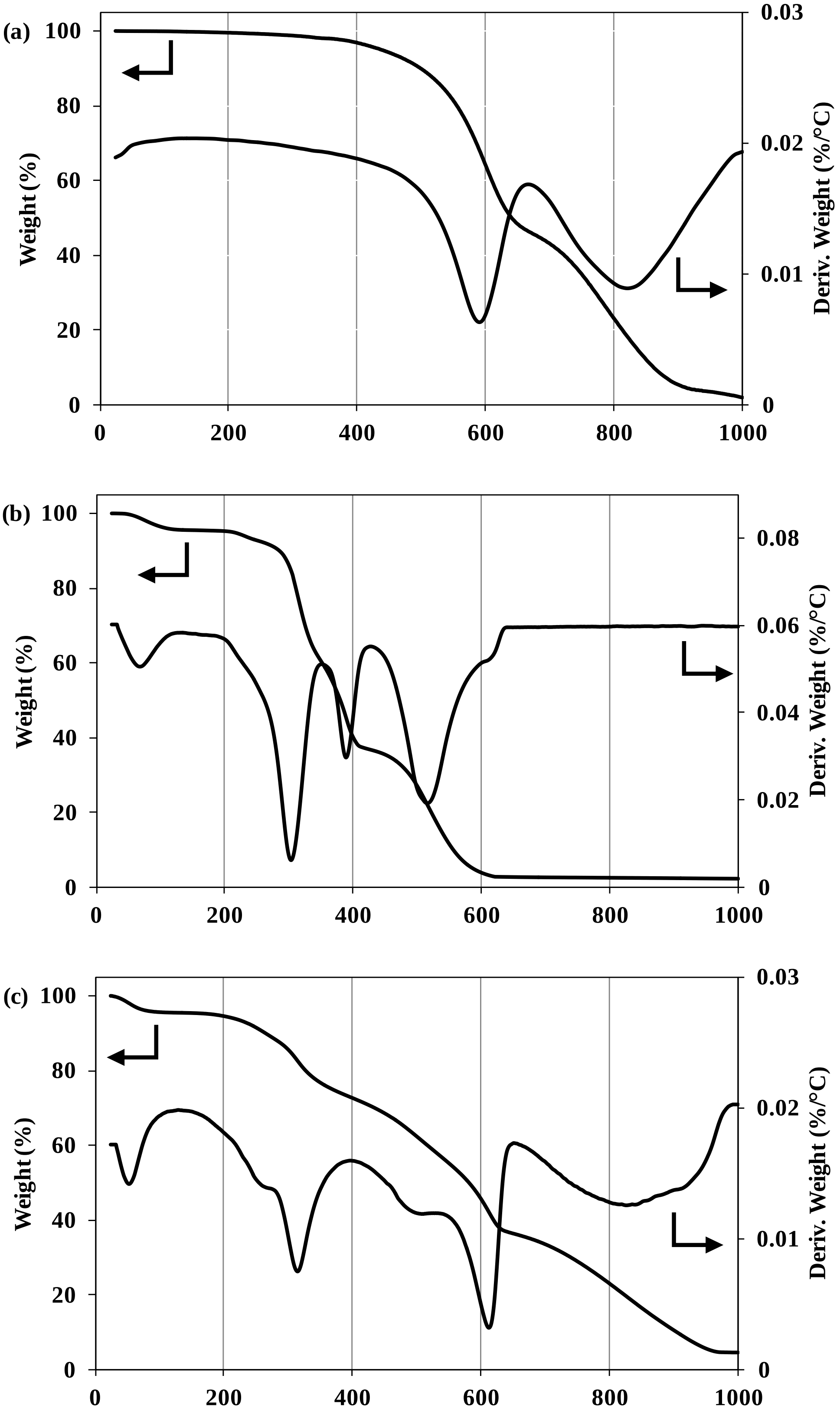


Figure 4.21 Thermogravimetry and differential thermogravimetry curves of (a) pristine SWCNHs, (b) PVPI and (c) PVPI-impregnated SWCNHs

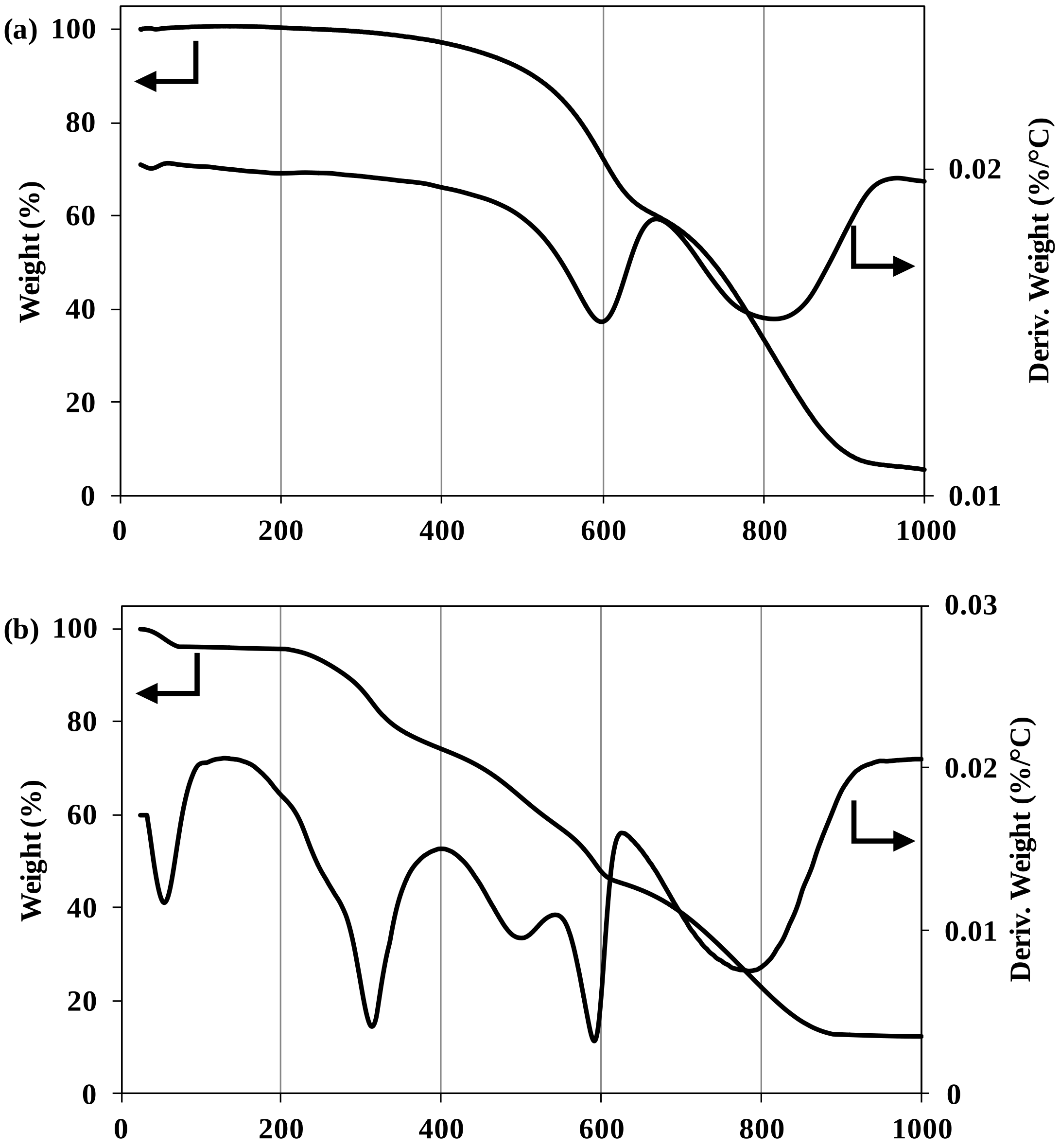


Figure 4.22 Thermogravimetry and differential thermogravimetry curves of (a) plasma-treated SWCNHs and (b) PVPI-impregnated SWCNHs.

4.3.1 Comparisonbetween of PVPI, PVPI-impregnated Pristine SWCNHs and Plasma-treated SWCNHs

In applying PVPI-impregnated SWCNHs, pristine SWCNHs and plasma-treated SWCNHs, to a drug delivery system, the PVPI release needs to be slow release. From result as shown Figure 4.23, it found that the release rate of PVPI from plasma-treated SWCNHs in deionized water was lower than pristine SWCNHs and free PVPI powder. About 360 and 240 min for the PVPI release from plasma-treated SWCNHs and pristine SWCNHs to saturate in deionized water, respectively. For free PVPI was took about 10 min for saturate in deionized water. At initial time, 0 min, the release of PVPI from free PVPI, pristine SWCNHs and plasma-treated SWCNHs were 37.5, 25.6 and 23.1 %, respectively.

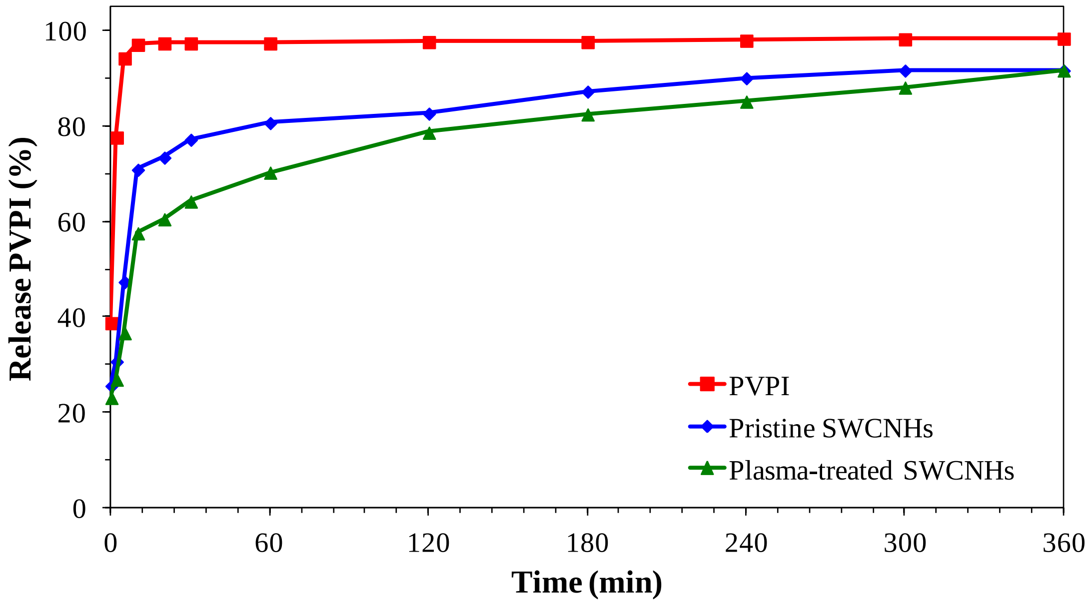


Figure 4.23 Plot showing PVPI released from free PVPI and PVPI-impregnated SWCNHs (pristine and plasma-treated SWCNHs), respectively.

4.3.2 Effect of Mass Ratio of PVPI to SWCNHs

Effect of mass ratio of PVPI to SWCNHs (plasma-treated) as shown in Figure 4.24 found that the increasing mass ratio would lead to fast release of PVPI in initial time. This result would assume that increasing mass ratio would be more wrapped on surface of SWCNHs, as shown schematic in Figure 4.25.

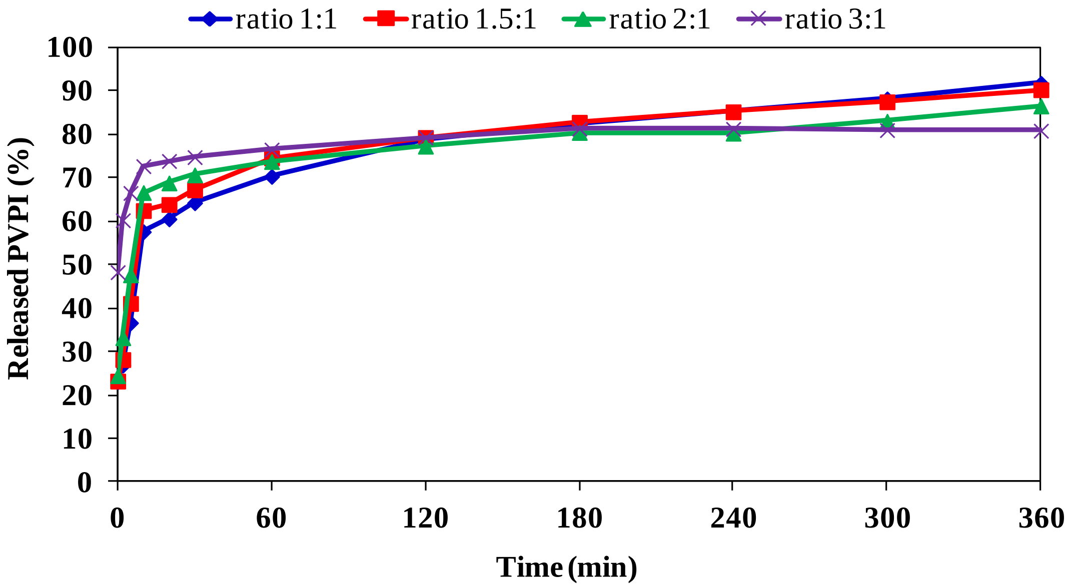


Figure 4.24 Plot showing PVPI released from free PVPI-impregnated SWCNHs (plasma-treated SWCNHs) with different mass ratio.

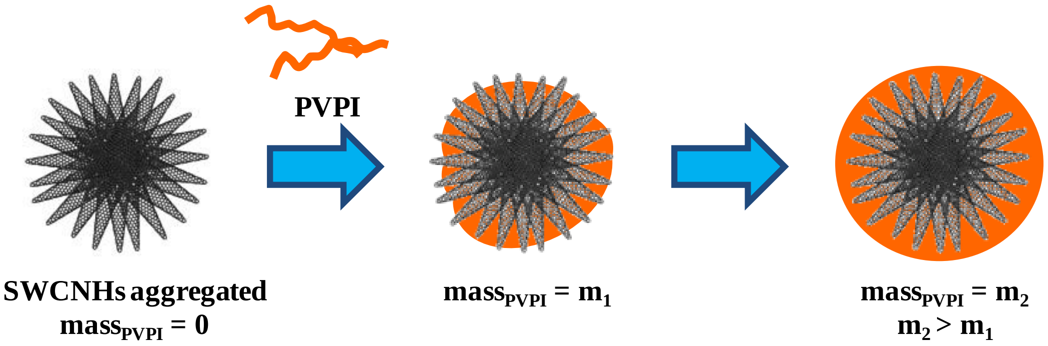


Figure 4.25 Represents schematic of PVPI-impregnated SWCNHs.

Comparison of released PVPI was impregnated on to pristine and plasma-treated SWCNHs with different mass ration of PVPI to SWCNHs of 1:1, 1.5:1 2:1 and 3:1 as shown in Figure 4.26. From result, it found that SWCNHs treated by oxygen plasma could help reduce the desorption rate of PVPI, leading to its slow release. So, this result would suggest that oxygen plasma treated SWCNHs would exhibit an improved capability to contain and release PVPI which was impregnated onto their surface.

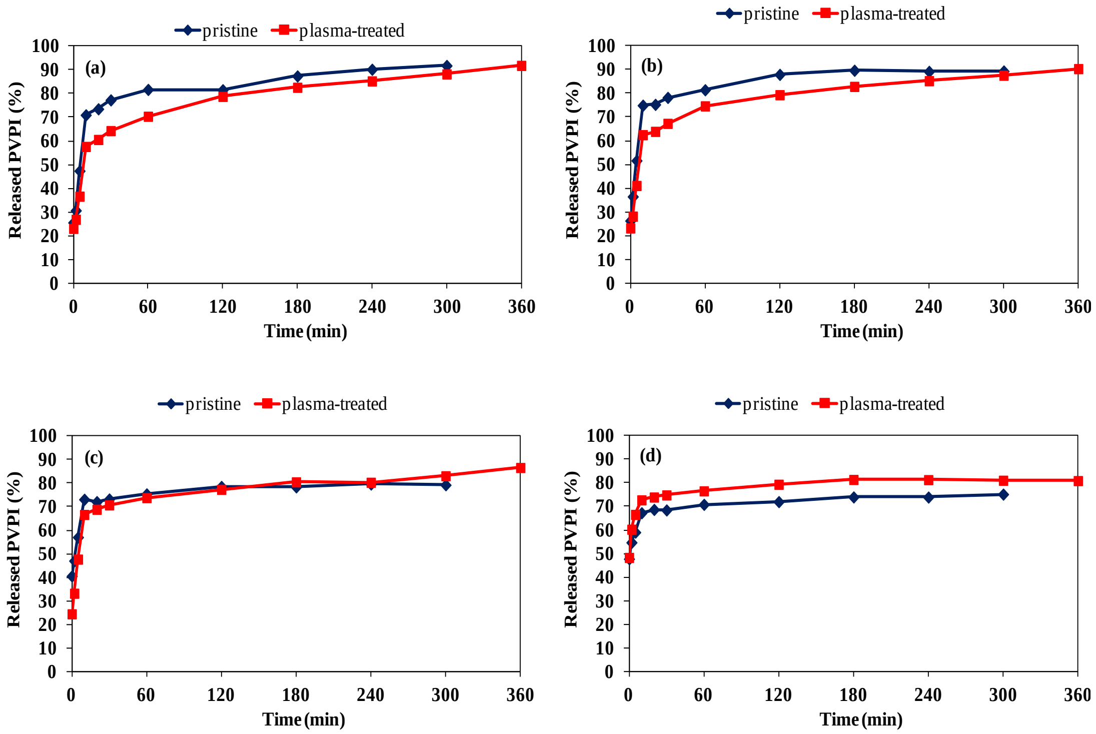


Figure 4.26 Plot showing PVPI released from free PVPI-impregnated SWCNHs compare between of pristine and plasma-treated SWCNHs with mass ratio of (a) 1:1, (b) 1.5:1, (c) 2:1 and (d) 3:1.

4.3.3 Kinetic Model of PVPI Released

Kinetic model, to examine the rate of PVPI released from PVPI-impregnated SWCNHs.

Pseudo first-order equation:

$$\frac{dC(t)}{dt} = k_1 \, (C_0 - C(t)) \tag{2}$$

From eq. 2, integrating if for the boundary condition t = 0 to t = t and C_t = 0 to C_t = C_t, it may be rearranged for linearized data ploting as shown eq. 3:

$$\ln\left(C_0 - C_t\right) = \ln(C_0) - k_1 t \tag{3}$$

Pseudo second-order equation:

$$\frac{dC(t)}{dt} = k \, (C_0 - C(t))^2 \tag{4}$$

From above equation, integrating if for the boundary condition t = 0 to t = t and C_t = 0 to C_t = C_t, it may be rearranged for a pseudo second-order equation as shown eq. 5:

$$\frac{t}{C_t} = \frac{1}{k_2 C_0^2} + \frac{1}{C_0} t \tag{5}$$

C_0 and C_t are concentration at initial and time (t), respectively.

k_1 and k_2 are the rate constant of the pseudo first-order (min^{-1}) and second-order (g/mg·min)

Table 4.3 Coefficients of pseudo first-order kinetic model.

Sample	**Pseudo first-order**	
	k_1 (min^{-1})	**r^2**
PVPI	0.0031	0.2534
Pristine SWCNHs	0.0053	0.7719
Plasma-treated SWCNHs	0.0054	0.9014

Table 4.4 Coefficients of pseudo second-order kinetic model.

Sample	**Pseudo second-order**	
	k_2 (g/mg·min)	**r^2**
PVPI	16.3126	0.9999
Pristine SWCNHs	0.8805	0.9989
Plasma-treated SWCNHs	0.1851	0.9969

From the Table 4.3 and 4.4, the pseudo first-order in not suitable fitted for free PVPI and PVPI-impregnated SWCNHs (pristine and plasma-treated SWCNHs), lower the correlation coefficients (R^2). So the pseudo first-order kinetic model is not well to describe the release process. However, release of pseudo second-order was liner with the correlation coefficients (R^2) higher than 0.99. This study indicated that the pseudo second-order model can describe the release process well as shown in Figure 4.27. Addition, the value of rate constant (**k_2**) represents the rate of the release of PVPI from SWCNHS.

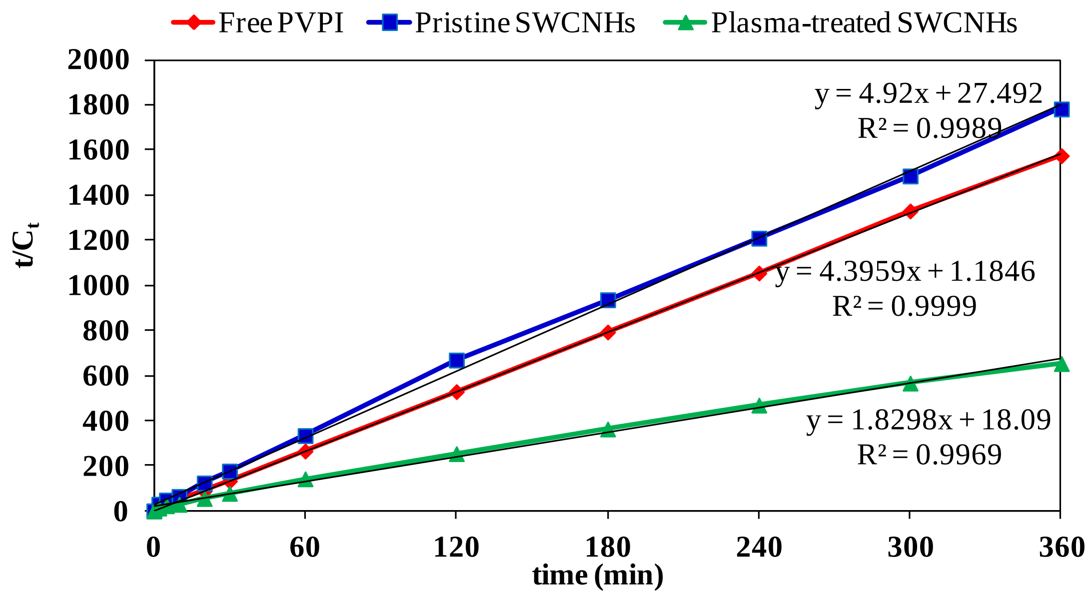


Figure 4.27 Pseudo second-order linear transforms of the free PVPI and PVPI-impregnated SWCNHs.

The Coefficients, rate constants (k_2), of is pseudo second-order kinetic model shown in Table 4.5. A lower rate constants represents slow release of PVPI from plasma-treated SWCNHs.

Table 4.5 Coefficients of pseudo second-order kinetic model.

Ratio	**Pseudo second-order**	
	k_2 (g/mg·min)	**r^2**
1:1	0.1851	0.9969
1.5:1	0.2634	0.9980
2:1	0.2921	0.9994
3:1	1.0984	0.9999

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

In this work, SWCNHs were synthesized by gas-injected arc in water (GI-AIW) method. The arc discharge operation is carried out at 80 A and 24 V. During the arc operation, the anode was moved vertically upward into the hole of the cathode at a controlled speed of 1.5 mm/s. At the same time, nitrogen (N_2) gas was injected downward into the two narrow channels at the top of the cathode at a flow rate of 5 l/min. SWCNHs synthesized by gas-injected arc-in-water (GI-AIW) method were then irradiated by low-temperature plasma for regulating their surface hydrophilicity. Effects of treatment parameters, which are irradiating time, pressure and electricity current were experimentally examined. Polyvinylpyrrolidone-iodine (PVPI) was also impregnated onto the pristine and plasma-treated SWCNHs. It is expected that the plasma-treated SWCNHs could help reduce the desorption rate of PVPI, leading to its slow release. The conclusions of the present research are summarized as follows,

5.1.1 Surface Modification of SWCNHs by Oxygen Plasma Treatment

Oxygen plasma treatment could change the SWCNH surface property. The analytical results based on Raman spectroscopy, FT-IR and zeta potential indicate that plasma irradiation time and pressure could affect the structures of SWCNHs. The SWCNHs after oxygen plasma treatment disperse well in deionized water and do not form aggregation after a long settling time, 1 month.

Comprehensive microscopic analyses reveal that SWCNHs treated by oxygen plasma would have observable aggregate and change structure after treated for 30 and 60 min. The morphology of SWCNHs treated by oxygen plasma between of 0.5 to 10 min was insignificantly changed. However, treatment for 30 and 60 min would result in an observable formation of intimately connecting network of SWCNH aggregates.

These results would suggest that stimulating electric current of 5.5 mA, irradiation time of 10 min and treatment pressure of 1 mbar are appropriate condition for surface modification of SWCNHs by oxygen plasma treatment. Because of these, the morphology of SWCNHs cannot be changed the plasma bombardment without significant change. The zeta potential, size and dispersion image indicated that SWCNHs can be dispersion for longer time.

5.1.2 Impregnation of PVPI onto SWCNHs and Its Release

SWCNHs wrapped with PVPI were experimentally examined and analyzed. The mechanism and rate of PVPI released based on pseudo second-order was verified with the correlation coefficients (R^2). This study indicated that the oxygen plasma treated SWCNHs which were impregnated with PVPI would exhibit an improved PVPI release behavior.

5.2 Recommendation for Future Work

1. Use X-ray photoelectron spectroscopy (XPS) for characterization of SWCNHs treated by oxygen plasma.
2. To study effect of mixture gases of argon and oxygen, it is expected that argon could help reduce oxidation reaction.
3. The others application for plasma-treated SWCNHs should be also investigated.

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APPENDICES

APPENDIX A

SYNTHESIS OF SWCNHS BY GAS-INJECTED ARC IN WATER (GI-AIW) METHOD

Figure A.1 show the influence of the nitrogen gas flow rate on the yield of SWCNHs. The yield is defined as the ratio of the weight of as-grown SWCNHs to the total weight loss of the consumed anode.

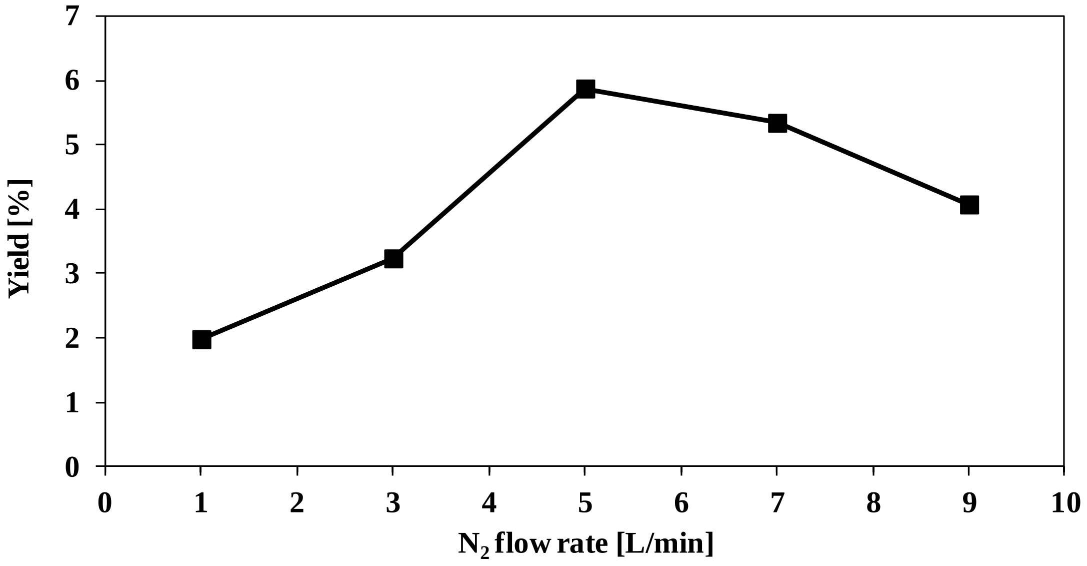

Figure A.1 Influence of nitrogen gas flow rate on the yield of SWCNHs synthesized by GI-AIW.

APPENDIX B

SURFACE MODIFICATION OF SWCNHS BY OXYGEN PLASMA TREATMENT

Typical, oxygen plasma treatment was showed by camera image as shown in Figure B.1.

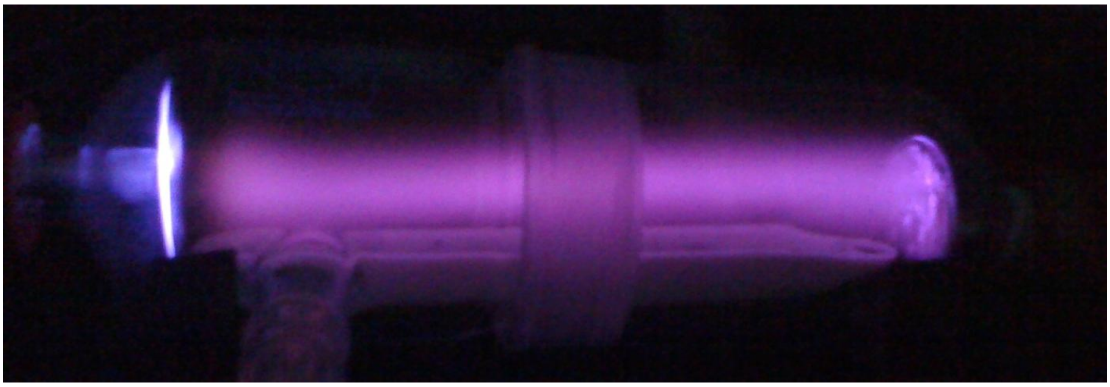

Figure B.1 Camera image of the oxygen plasma treatment.

APPENDIX C

PVPI IMPREGNATED SWCNHS

In Figure C.1 show calibration curves of PVPI and PVP compare with conductivity, respectively.

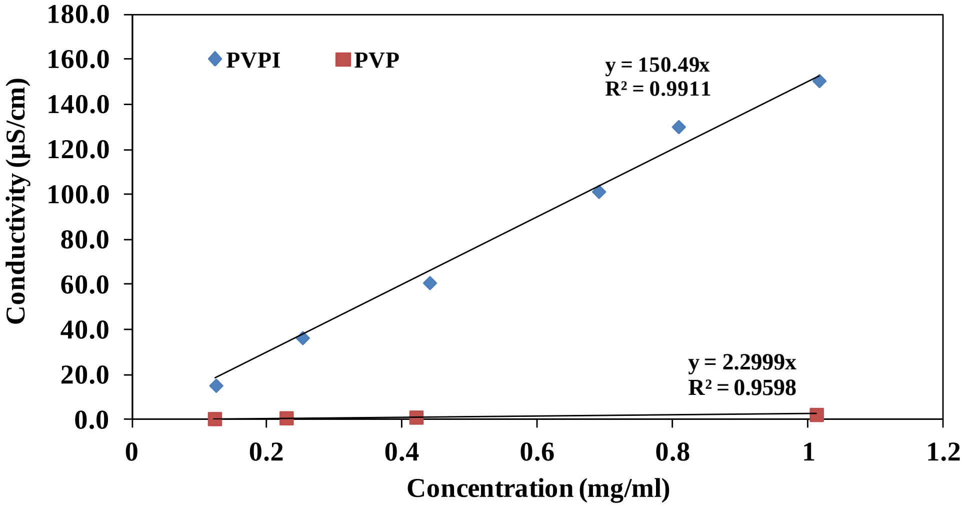

Figure C.1 The calibration cure of PVPI and PVP.

The morphology of PVPI-impregnated SWCNHs with different mass ratio of PVPI to SWCNHs, 1.1, 1.5, 2 and 3 was observed by TEM image shown in Figure C.2, respectively. TEM images are not clearly because of electron beams destructed of PVPI.

Data sheet of experimental of released PVPI, pseudo-first order and pseudo-second order of free PVPI and PVPI-impregnated SWCNHs as shown in Table C. 1, 2 and 3

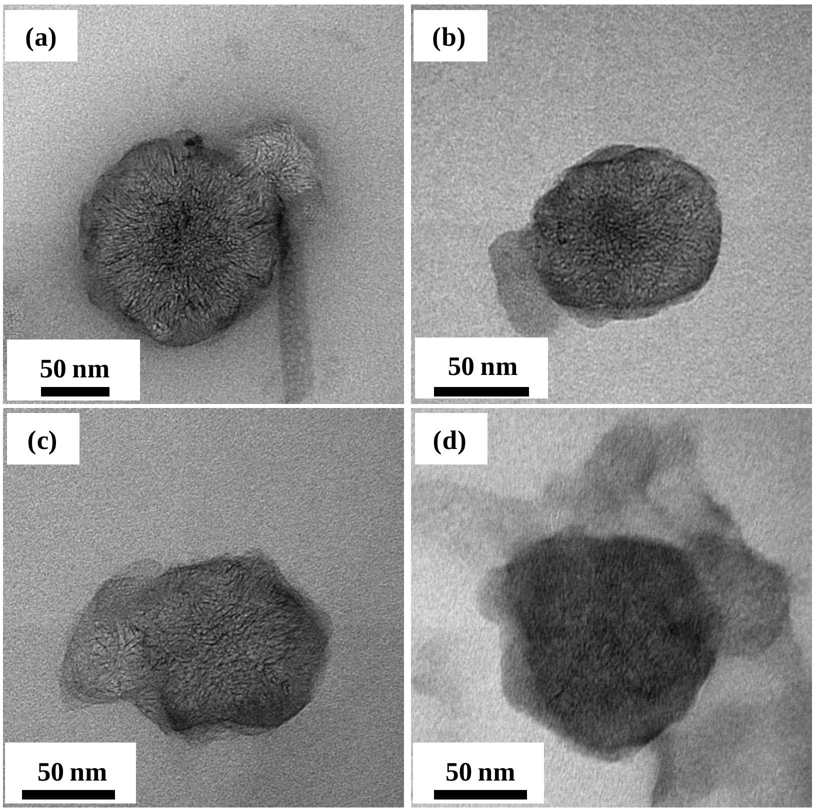

Figure C.2 Typical TEM images PVPI-impregnated SWCNHs with different ratio of PVPI to SWCNHs of (a) 1:1, (b) 1.5:1, (c) 2:1 and (d) 3:1.

Table C.1 Data sheet of experimental of free PVPI.

time (min)	**Cond. (μS/cm)**	**Conc. (mg/ml)**	**Release (%)**	**ln(C/C$_0$)** (pseudo-first order)	**t/C** (pseudo-second order)
0	13.54	0.0900	37.49	0.0000	0.000
2	27.14	0.1803	75.14	0.6954	11.090
5	32.94	0.2189	91.20	0.8890	22.843
10	33.94	0.2255	93.97	0.9189	44.340
20	34.04	0.2262	94.25	0.9219	88.420
30	34.04	0.2262	94.25	0.9219	132.629
60	34.04	0.2262	94.25	0.9219	265.259
120	34.14	0.2269	94.52	0.9248	528.963
180	34.14	0.2269	94.52	0.9248	793.445
240	34.24	0.2275	94.80	0.9277	1054.836
300	33.94	0.2255	93.97	0.9189	1330.200
360	34.38	0.2285	95.21	0.9320	1575.492

Table C.2 Data sheet of experimental of PVPI-impregnated SWCNHs (pristine).

time (min)	**Cond. (μS/cm)**	**Conc. (mg/ml)**	**Release (%)**	**ln(C/C$_0$)** (pseudo-first order)	**t/C** (pseudo-second order)
0	8.5	0.0563	25.61	0.0000	0
2	10.2	0.0675	30.70	0.1812	29.60944
5	15.7	0.1043	47.42	0.6160	47.92675
10	23.5	0.1562	70.98	1.0193	64.0383
20	24.3	0.1617	73.52	1.0544	123.6565
30	25.6	0.1700	77.28	1.1043	176.4589
60	27.0	0.1797	81.69	1.1598	333.8658
120	27.0	0.1794	81.54	1.1580	668.927
180	28.9	0.1922	87.37	1.2271	936.4439
240	29.9	0.1984	90.19	1.2588	1209.565
300	30.4	0.2019	91.79	1.2764	1485.587
360	30.6	0.2020	91.80	1.2767	1782.178

Table C.3 Data sheet of experimental of PVPI-impregnated SWCNHs (plasma-treated).

time (min)	**Cond. (μS/cm)**	**Conc. (mg/ml)**	**Release (%)**	**ln(C/C$_0$)** (pseudo-first order)	**t/C** (pseudo-second order)
0	20.9	0.1386	23.10	0.0000	0
2	24.3	0.1616	26.93	0.1535	12.37752
5	33.1	0.2201	36.68	0.4624	22.72119
10	52.0	0.3458	57.64	0.9145	28.91444
20	54.7	0.3635	60.59	0.9643	55.01706
30	58.1	0.3859	64.31	1.0239	77.75029
60	63.5	0.4223	70.38	1.1141	142.0909
120	71.1	0.4726	78.76	1.2266	253.932
180	74.6	0.4956	82.59	1.2742	363.2262
240	77.0	0.5117	85.28	1.3061	469.0597
300	79.7	0.5294	88.23	1.3402	566.6987
360	82.9	0.5509	91.82	1.3800	653.4625

APPENDIX D

LIST OF PUBLICATION

Oral Presentation:

Piyapong Lerkprasertkun, Kajornsak Faungnawakij, Chantamanee Poonjarernsilp, and Tawatchai Charinpanitkul "Effect of N_2 gas flow rate on synthesizing yield of single-walled carbon nanohorns via gas-injected arc-in-water method" Oral Presentation of the German-Thai Symposium on Nanoscience and Nanotechnology GTSNN2011: GREEN NANOTECHNOLOGY FOR THE FUTURE, Nakon Ratchasima, Thailand, September 13 – 16, 2011.

Proceeding:

Piyapong Lerkprasertkun, Kajornsak Faungnawakij, Chantamanee Poonjarernsilp, and Tawatchai Charinpanitkul, "Single-walled carbon nanohorns treated by plasma irradiation for slow release of PVPI" Proceeding of the 6th Pure and Applied Chemistry International Conference 2012 (PACCON 2012), Changmai, Thailand, January 11 – 13, 2012.

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