SYNTHÈSE DE NANOTUBES DE CARBONE MONO-PAROIS MODIFIÉS CHIMIQUEMENT PAR L’INJECTION D’AMMONIAC GAZEUX À CONTRE-COURANT DANS UN PROCÉDÉ À PLASMA THERMIQUE INDUCTIF

SYNTHESIS OF CHEMICALLY-MODIFIED SINGLE-WALLED CARBON NANOTUBES BY COUNTER-CURRENT AMMONIA GAS INJECTION INTO THE INDUCTION THERMAL PLASMA PROCESS

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To my parents

"Science is a way of thinking much more than it is a body of knowledge"

Carl Sagan
RÉSUMÉ

Les nanotubes de carbone mono-parois (SWCNTs) sont très peu dispersibles dans les solvants et ils ont besoin d'être chimiquement modifiés avant leur utilisation dans beaucoup d'applications. Ce travail se concentre sur la synthèse du matériau des SWCNTs chimiquement modifié par une approche in situ. Les objectifs principaux de cette recherche sont : 1) explorer le procédé chimique in situ pendant la synthèse des SWCNTs et 2) examiner de manière approfondie l'effet de l'environnement réactif sur les SWCNTs.

Les effets du type de catalyseur et son contenu sur le produit fini des SWCNTs, synthétisé par plasma thermique inductif (PTI), ont été étudiés pour remplacer le cobalt (Co) toxique dans la matière première. À cet égard, trois mélanges de catalyseurs différents (c.-à-d. Ni-Y₂O₃, Ni-Co-Y₂O₃, et Ni-Mo-Y₂O₃) ont été utilisés. Les résultats expérimentaux ont montré que le type de catalyseur affecte la qualité des SWCNTs. Une qualité similaire peut être produite lorsque la même quantité de Co est remplacée par le Ni. En outre, des résultats observés dans les travaux expérimentaux ont été explicités par les résultats des calculs thermodynamiques.

La thermogravimétrie (TG) a été utilisée tout au long du travail pour caractériser les échantillons de SWCNTs. La TG a tout d'abord été normalisée par l'étude des effets des trois principaux paramètres instrumentaux (rampe de température, RT, la masse initiale de l'échantillon, MI, et le débit de gaz, D) sur le T₀sett et largeur à mi-hauteur (LMH) obtenu à partir de graphiques TG et TG dérivés de noir de carbone, respectivement. Par conséquent, un plan factoriel à deux niveaux a été prévu. L'analyse statistique a montré que l'effet de RT, MI, et à un degré moindre D est significatif sur la LMH et négligeable sur T₀sett.

Une méthodologie a ensuite été développée sur la base de la synthèse des SWCNT en utilisant le système PTI, à travers une approche chimique in situ. L'ammoniac (NH₃) a été choisi et injecté à contre-courant dans le réacteur PTI à trois débits différents et en utilisant quatre types de buses différentes. La simulation numérique a indiqué un meilleur mélange du NH₃ dans le réacteur PTI lorsqu'une buse particulière a été utilisée. Les résultats expérimentaux montrent l'augmentation d'intensité de D-bande dans les spectres Raman d'échantillons SWCNTs lors de l'injection du NH₃. Le NH₃ pourrait augmenter la teneur en azote du produit fini de SWCNTs jusqu'à 10 fois. L'échantillon des SWCNTs traitée avec 15% vol de NH₃ a montré une dispersion accrue dans le diméthylformamide et l'isopropanol. Les nanostructures de carbone en forme d'oignon et plane, ont aussi été observées.

Une caractérisation complémentaire sur l'échantillon des SWCNTs traités par NH₃ à 15% vol., a indiqué une modification de la surface des nanotubes, où des tubes métalliques ont montré une plus grande réactivité avec NH₃ que les semi-conducteurs. Le modèle, y compris le champ d'écoulement thermique du réacteur et la cinétique de décomposition thermique de NH₃ a suggéré une modification de surface des SWCNTs en deux étapes dans laquelle les nanotubes réagissent premièrement avec les espèces intermédiaires de H et de NH₂. Le NH₃ s'adsorbe ensuite chimiquement sur les nanotubes. Le modèle a également suggéré que les espèces intermédiaires comme le NNH et le N₂H₂ jouent un rôle principalement en conduisant la décomposition du NH₃ plutôt que la modification chimique des SWCNTs.

Mots-clés : Nanotubes de carbone mono-parois, Plasma thermique inductif, Synthèse, Thermogravimétrie, Cinétique, Mécanique des fluides numérique, Thermodynamique, Modification chimique, Fonctionnalisation
**ABSTRACT**

Pristine single-walled carbon nanotubes (SWCNTs) are poorly dispersible and insoluble in many solvents and need to be chemically modified prior to their use in many applications. This work is focused on the investigation of the synthesis of chemically modified SWCNTs material through an *in situ* approach. The main objectives of the presented research are: 1) to explore the *in situ* chemical process during the synthesis of SWCNT and 2) to closely examine the effect of a reactive environment on SWCNTs. Effects of the catalyst type and content on the SWCNTs final product, synthesized by induction thermal plasma (ITP), were studied to replace toxic cobalt (Co) in the feedstock. In this regard, three different catalyst mixtures (i.e. Ni-Y₂O₃, Ni-Co-Y₂O₃, and Ni-Mo-Y₂O₃) were used. Experimental results showed that the catalyst type affects the quality of the SWCNT final product. Similar quality SWCNTs can be produced when the same amount of Co was replaced by Ni. Moreover, the results observed in this experimental work were further explained by thermodynamic calculation results.

Thermogravimetry (TG) was used throughout the work to characterize the SWCNTs product. TG was firstly standardized by studying the effects of three main instrumental parameters (temperature ramp, TR, initial mass of the sample, IM, and gas flow rate, FR) on the T onset and full-width half maximum (FWHM) obtained from TG and derivative TG graphs of carbon black, respectively. Therefore, a two-level factorial statistical design was performed. The statistical analysis showed that the effect of TR, IM, and to a lower extent, FR, is significant on FWHM and insignificant on T onset.

A methodology was then developed based upon the SWCNTs synthesis using the ITP system, through an *in situ* chemistry approach. Ammonia (NH₃) was selected and counter-currently injected into the ITP reactor at three different flow rates and by four different nozzle designs. Numerical simulation indicated a better mixing of NH₃ in the ITP reactor when a certain nozzle was used. The experimental results showed the increase of D-band intensity in the Raman spectra of SWCNT samples upon the NH₃ injection. NH₃ could increase the nitrogen content of the SWCNTs final product up to 10 times. The SWCNTs sample treated with 15 vol% NH₃ showed an enhanced dispersibility in Dimethylformamide and Isopropanol. Onion-like and planar carbon nanostructures were also observed.

Complementary characterization on the SWCNT samples treated by 15 vol% NH₃ indicated the surface modification of nanotubes. Metallic tubes showed a higher reactivity with NH₃ than semiconducting ones. The model including the reactor thermo-flow field and NH₃ thermal decomposition kinetics suggested a two-step SWCNT surface modification in which nanotubes firstly react with H and NH₂ intermediates and later, NH₃ chemisorbs on the nanotubes. The model also suggested that the intermediate species, like NNH and N₂H₂, play a role primarily in driving the NH₃ decomposition rather than the chemical modification of SWCNTs.

**Keywords:** Single-walled carbon nanotube, Induction thermal plasma, Synthesis, Thermogravimetry, Kinetic, Computational fluid dynamic, Thermodynamic, Chemical modification, Functionalization.
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\(A_\theta\)  tangential component of magnetic vector potential (T m)
\(C_D\)  drag coefficient
\(\bar{C}_h\)  chiral vector
\(C_p\)  specific heat of fluid at constant pressure (J/kg K)
\(C_\mu\)  constant in turbulence model
\(C_1\)  constant in turbulence model
\(C_2\)  constant in turbulence model
\(c_p\)  specific heat of particle injected (J/kg K)
\(C_i\)  volume fraction constant
\(C_r\)  time scale constant
\(D_k\)  binary diffusion coefficient of species \(k\) (m\(^2\)/s)
\(E_\theta\)  tangential component of electric field (V/m)
\(F_L\)  Lorentz force (N/m\(^3\))
\(f\)  frequency applied to RF induction coil (Hz)
\(g^0\)  standard free Gibbs energy
\(G_1\)  product of the turbulent viscosity and viscous dissipation terms (kg/m s\(^3\))
\(h\)  specific enthalpy of fluid (J/kg)
\(h_c\)  heat transfer coefficient of fluid (W/m\(^2\) K)
\(H_r\)  radial component of magnetic field intensity (A/m)
\(H_z\)  axial component of magnetic field intensity (A/m)
\(J_{\text{coil}}\)  coil current density (A/m\(^2\))
\(J_{\text{ind}}\)  induced current density (A/m\(^2\))
\(K\)  turbulent kinetic energy (m\(^2\)/s\(^2\))
\(k_B\)  Boltzmann constant (J/K)
\(m\)  mass flow rate (kg/s)
\(P_{\text{ohm}}\)  heat generation by ohmic heating (W/m\(^3\))
\(p\)  static pressure of fluid (Pa)
\(Pr\)  Prandtl number of fluid
\(Pr_\nu\)  constant in turbulence model
\(Pr_K\)  constant in turbulence model
\(Pr_t\)  turbulent Prandtl number
\(R\)  universal gas constant (J/mol K)
\(R_{\text{rad}}\)  radiational loss taken into account by using net emission coefficient (W/m\(^3\))
\(S_{C_i}\)  turbulent Schmidt number
\(T\)  temperature of fluid (K)
\(\bar{T}\)  translation vector
\(T_{\text{onset}}\)  temperature at which material starts to lose weight
\(u\)  axial velocity of fluid (m/s)
\(v\)  radial velocity of fluid (m/s)
\(\nu\)  kinematic viscosity (m\(^2\)/s)
\(w\)  swirl velocity of fluid (m/s)
\( Y_k \) mass fraction of species \( k \)

ITP induction thermal plasma

TG thermogravimetry

Greek letters

\( \varepsilon \) dissipation rate of turbulent kinetic energy \((m^2/s^3)\)

\( \kappa \) laminar thermal conductivity of fluid \((W/m K)\)

\( \kappa_{eff} \) effective thermal conductivity of fluid \((W/m K)\)

\( \kappa_t \) turbulent thermal conductivity of fluid \((W/m K)\)

\( \gamma_i \) activity coefficient

\( \mu \) laminar viscosity of fluid \((kg/m s)\)

\( \mu_{eff} \) effective viscosity of fluid \((kg/m s)\)

\( \mu_t \) turbulent viscosity of fluid \((kg/m s)\)

\( \mu_0 \) magnetic permeability of free space \((N/A^2)\)

\( \zeta^* \) length fraction of the fine scales: * denotes fine-scale quantities

\( \rho \) mass density of fluid \((kg/m^3)\)

\( \sigma \) electrical conductivity \((\Omega^{-1} m^{-1})\)

\( \tau \) viscous stress tensor \((N/m^2)\)
CHAPTER 1. Introduction

1.1 Nanotechnology

The term ‘nano’ in nanotechnology originates from the Greek word *Nanos* meaning dwarf. In metrology, 1 nanometer (nm) is equal to $1 \times 10^{-9}$ m. Hence in material science, nanotechnology deals with a variety of structures of matter having at least one dimension in the nanometric range [Poole and Owens, 2003].

1.2 Carbon

Carbon, one of the most abundant elements, is sixth in the periodic table with an atomic mass of 12.011 g and an atomic number 6. Carbon is considered a non-metallic element with a $1s^2 2s^2 2p^2$ electron configuration. It possesses four electrons in the valance shell and can hold up to four extra electrons to become saturated. Therefore, carbon forms many versatile compounds with different size and shapes. Three main natural allotropes of carbon are amorphous carbon, graphite, and diamond. There are also different synthetic allotropes of carbon. Among those, fullerene and carbon nanotubes are the most well-known species. Figure 1.1 illustrates these five different allotropes of carbon.

![Allotropes of Carbon](image)

**Figure 1.1** Five different allotropes of carbon.

Fullerene and Nanotube structures were drawn using Nanotube Modeler© JCrytalSoft v. 1.7.3
From a chemical point of view, carbon atoms bind together in a planar sp² (C=C) or spatial sp³ (C-C) hybridization. In perfect graphite, fullerene, and nanotube, carbon atoms bind with sp² hybridization while in diamond and amorphous carbon, the hybridization is sp³. From a physical point of view, carbon can make a 0D, 1D, 2D, or 3D spatial configuration which makes it a very interesting element to study. Four main allotropes of carbon are summarized in Table 1.1.

<table>
<thead>
<tr>
<th>Allotrope</th>
<th>Dimension</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fullerene</td>
<td>0D</td>
<td>sp²</td>
</tr>
<tr>
<td>Nanotube</td>
<td>1D</td>
<td>sp²</td>
</tr>
<tr>
<td>Graphene*</td>
<td>2D</td>
<td>sp²</td>
</tr>
<tr>
<td>Diamond</td>
<td>3D</td>
<td>sp³</td>
</tr>
</tbody>
</table>

* A single-layered graphite

The nature of bonding of carbon atoms and their spatial configurations affect drastically the chemical and physical properties of each allotrope. For instance, graphite with the 3D configuration and sp² hybridization has soft mechanical strength compared to that of diamond having an extraordinary strength, with the 3D configuration and the sp³ hybridization.

1.3 Carbon nanotubes

The first evidence of carbon nanotube may have been observed in 1952 by Radushkevich and Lukyanovich [Monthioux and Kuznetsov, 2006]. They reported the formation of thread-like nuclei and co-twisted threads during the production of carbon black deposits on Fe, in the presence of flowing CO gas at 600 °C. However, they implied no explanation for such an observation and brought no evidence for such thread-like structures to be carbon nanotube. This is due to the low resolution of transmission electron microscope (TEM) at that time. Two decades later, in an attempt for the synthesis of carbon fiber by pyrolysis of benzene and ferrocene, single- and multi-shell hollow tubular carbon structures with diameters from few to tens of nanometers were observed [Oberlin et al., 1976; Terrones, 2003]. At that time, the research community was interested in micron size materials, so no attention was drawn to this interesting observation. Therefore, the discovery of carbon nanotube has been ascribed to
Sumio Iijima who was the first to publish an article reporting the formation of helical microtubules of graphitic carbon with diameters ranging from 4 to 30 nm and 2 to 50 in number of graphitic layers. This was discovered during his attempts to synthesize fullerene using an arc-discharge evaporation method [Iijima, 1991]. His report clearly indicated a definitive method for the synthesis of what is called today ‘multi-walled carbon nanotube’ (MWCNT). Two years later, in 1993, Iijima and Ichihashi [Iijima and Ichihashi, 1993] and Bethune et al. [Bethune et al., 1993] reported for the very first time the synthesis of single-shell carbon nanotubes of ~1 nm diameter, which was later named ‘single-walled carbon nanotube’ (SWCNT). Both of these newly engineered nanostructures of carbon have garnered immense attention from the carbon research community due to their very unique structures: a very high aspect ratio making them very close to an ideal 1D structure. In the same era, researchers from other fields have also been attracted to work on carbon nanotubes (CNTs) leading to grow this new field of research much faster than expected. In the past twenty years, a large amount of work has been devoted to the optimization and improvement of the synthesis methods, characterization, chemistry, and applications of CNTs. Figure 1.2 represents the contribution of the research community in the field of CNTs for the past twenty years. As shown in Figure 1.2, the number of published scientific articles has exponentially increased over the past two decades implying the importance of CNTs in materials science and showing that the field of carbon nanotubes is very active.

Figure 1.2 Number of annual publications on CNTs per year, from 1992–2012. Data collected from Science Finder database
1.4 Thermal plasma

Plasma is the fourth state of matter constructed essentially by atoms (neutral particles), ions and electrons. The main characteristic of plasma is that it is electrically conductive due to the considerable number of free charge carriers. Interestingly, plasma of certain gases (e.g., H₂) at a high temperature ($10^6$ K) can be even more electrically conductive than metals at room temperature. Plasmas can be placed into two distinct groups: i) thermal plasma, and ii) non-thermal plasma. In thermal plasma, the electron temperature approaches the temperature of the heavy particles (i.e., neutrals and ions) and therefore, the plasma is in a local thermodynamic equilibrium (LTE). While in non-thermal plasma, the electron temperature is much higher than the temperature of the heavy particles and therefore this type of plasma, which strongly deviates from kinetic equilibrium, is not at LTE [Boulos et al., 1994; Boulos, 1991]. Accordingly, non-thermal plasma is also called non-equilibrium plasma. Different types of plasmas exist which are either naturally generated or man-made. They can be classified according to the electron temperature and density. Some of these natural or man-made plasmas are illustrated in Figure 1.3.

Figure 1.3 Different types of plasmas from naturally generated to man-made: 1) Solar corona, 2) Ionosphere, 3) Flames, 4) Thermonuclear fusion plasma, 5) Glow and RF discharges, Fluorescent lamp, 6) High pressure Arc and RF discharges, Shock waves.
Adapted from [Boulos et al., 1994]
Thermal plasma technology covers a wide range of applications including: i) thermal plasma coating such as plasma spraying, wire arc spraying, and thermal plasma chemical vapor deposition, ii) cutting, iii) fine and ultrafine powder synthesis, iv) powder densification and spheroidization, v) waste-treatment vi) thermal plasma metallurgy [Fauchais and Vardelle, 1997; Pfender, 1999]. The main devices widely used in the aforementioned applications for generating thermal plasma are direct current (DC) plasma torches, and radio frequency (RF) inductively coupled plasma torches. Choosing plasma-generating device for a certain application is tightly related to the processing condition and a good compatibility between the processing requirements and the characteristic of the device. The main characteristics of these two thermal plasma-generating devices are summarized in Table 1.2.

Table 1.2 Typical characteristics of DC plasma and RF induction torches

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>RF induction torch</th>
<th>DC plasma torch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total gas flow rate</td>
<td>High c</td>
<td>Low (&lt;100 slpm a)</td>
</tr>
<tr>
<td>Commonly used gases</td>
<td>Wide range of gases</td>
<td>Ar, He, H$_2$, N$_2$, oxidizing</td>
</tr>
<tr>
<td></td>
<td>with almost no limitation c</td>
<td>gas (only with cold copper electrodes) a</td>
</tr>
<tr>
<td>Maximum temperature (K)</td>
<td>10 000 a</td>
<td>12 000 a</td>
</tr>
<tr>
<td>Operating pressure (kPa)</td>
<td>25-400 c</td>
<td>20-500 c</td>
</tr>
<tr>
<td>Velocity (m/s)</td>
<td>10-20 a</td>
<td>400-600 a</td>
</tr>
<tr>
<td>Residence time (ms)</td>
<td>10-20 a</td>
<td>0.5 a</td>
</tr>
<tr>
<td>Hot core volume (cm$^3$)</td>
<td>60-300 b</td>
<td>~ 0.4 a</td>
</tr>
<tr>
<td>Average energy efficiency (%)</td>
<td>50 c</td>
<td>70 c</td>
</tr>
<tr>
<td>Local power density</td>
<td>Low a</td>
<td>High a</td>
</tr>
</tbody>
</table>

a [Boulos, 1991]
b [Boulos, 1992]
c [Fauchais and Vardelle, 1997]

1.4.1 RF induction plasma torch

As shown in Figure 1.4, the RF induction plasma torch mainly consists of three concentric tubes: (i) a confinement tube which is constructed either by quartz (Power plate < 30 kW) or ceramic (30< Power plate <150 kW) and surrounded by 3 to 7 turns of the induction coil, (ii) a quartz tube separating sheath gas from central gas, and (iii) an injection probe [Fauchais and Vardelle, 1997]. The role of the turned-coil is to generate a magnetic field inside the ceramic tube. The upper part of the torch is the gas distributor that introduces the plasma-forming
gases into the torch. The sheath gas is employed in order to protect the confinement tube’s wall from hot plasma gas. The plasma-forming gas, the central gas, is introduced into the torch from the center. An adjustable water-cooled probe is placed at the centre of the ceramic tube for effective introduction of gaseous, liquid, or solid feedstock materials into the plasma discharge at the center. To sustain the plasma, a minimum amount of power has to be applied which depends on the frequency of the power supply and also on the gas composition [Fauchais and Vardelle, 1997]. The schematic diagram of the RF induction plasma torch along with its typical temperature profile is depicted in Figure 1.4. Compared to DC plasma torches, RF induction torches have some advantages [Boulos et al., 1994; Fauchais and Vardelle, 1997] which make them suitable especially in the nanostructure synthesis, these include:

- A good flexibility in choice of plasma forming gases from inert to very reactive ones.
- A better mixing of reactants in the plasma due to the axial injection.
- A longer residence time allowing for a larger amount of feedstock to be treated.
- A large plasma volume with a longer residence time makes the RF induction torch suitable for in-flight melting process of metals and ceramic powders at high throughput.

![Schematic of an RF induction plasma torch along with its typical temperature profile.](image)

Adapted from [Moradian et al., 2010]
1.5 Problematic and context

Carbon nanotubes hold great promise in many applications such as polymer composites, as reinforcements, in nanoelectronic devices, as electron emitters and field emission transistors, in energy storage, probes, sensors, and biological applications such as drug delivery and tissue engineering [Ajayan and Zhou, 2001; Baughman et al., 2002; Eder, 2010; Endo et al., 2008; Harris, 2009; Krueger, 2010; Popov, 2004]. This is because of the outstanding physicochemical properties of carbon nanotubes along with their unique 1D structure. However, there has been a big obstacle in taking advantage of these unique properties in target applications. It is their poor processability. There has been an immense amount of research in the past two decades on functionalizing CNTs and up to now, a wide variety of methods has been proposed and developed for effective surface functionalization in order to enhance their solubility, functionality, and processability. Most of these methods are based on wet chemistry (also known as solution-based chemistry) in which usually milligram amounts of CNTs material is subjected to higher amounts of reactive chemicals. Hence, it is a batch process. The first problem which arises from wet chemistry-based methods is the considerable amount of the waste materials that they produce. In addition to the resulting low yield of the process which is mainly due to the partial loss of the starting sample during the process, the waste products have to be further treated. The waste production of these methods will be much more intense when the scaling up is taken into consideration. These methods are considered complex since they follow several time-consuming steps such as premixing, stirring, centrifuging, filtering, rinsing and drying. Besides the additional cost of each step to the final CNTs products, following all these steps at the optimum conditions is not an easy task and may be the main reason why these methods are mostly limited to the laboratory scale. An alternative functionalization process is cold plasma technology which has been shown in the literature to be effective for the surface chemistry of CNTs [Khare et al., 2005; Khare et al., 2002b; Khare et al., 2002a; Khare et al., 2004b; Khare et al., 2004a; Plank et al., 2003; Valentini et al., 2005]. Beside the advantages it offers such as fast reaction time (in an order of several minutes) and a cleaner process, this method is subjected to some issues:

- The chemistry is mostly limited to the surface of CNTs sample.
• Scaling up is a challenging task.
• Controlling operating parameters for the best chemistry is not an easy task since the reaction takes place only on the surface of the sample.
• The pricey operation unit adds extra cost to the final CNTs products.
• Limited chemistry

Although there has been a large number of work on the chemical modification of SWCNTs materials, the proposed methods including wet chemistry and cold plasma are essentially post-treatment processes. Post-processing adds extra cost to the final product and in the case of CNTs, the functionalization process can augment the price of the final product up to seven times (source: Sigma-Aldrich®).

Worldwide use of SWCNT materials in many applications urges developing reliable, safe and continuous synthesis method at a large scale. Since their discovery in 1993, it has been a real challenge to design and develop a synthesis method answering all these needs. The first introduction of an ITP synthesis system [Kim et al., 2007] demonstrated a promising method for continuous large scale synthesis of SWCNT materials with high production rate (i.e., kg/day) using a 60 kW power unit. Moreover, the only limitation for scaling up ITP synthesis system is mainly related to the available highest power unit in the market working at 1MW (TEKNA Inc. CANADA). A simple calculation indicates that the proposed ITP system has the potential to be roughly scaled up by a factor of 16 to produce a few tons of SWCNT per year which will be a real breakthrough in the carbon nanotube market. However, there are concerns related to the health issues of nanomaterials (e.g. the effect of SWCNTs on humans) which forces reconsideration of the minimization of nanomaterials exposure in the work place. Therefore, in designing and developing future synthesis procedures one must also consider occupational health and safety (OHS) issues in addition to the technical priorities [Alinejad et al., 2012a]. The early study showed that high quality SWCNTs can be synthesized by a mixture of solid carbon black and metal catalysts in which Co is one of the catalysts forming the mixture [Kim et al., 2007]. Although synthesizing high quality SWCNTs is of great interest, a recent toxicological study has indicated high cytotoxicity of cobalt particles [Alinejad et al., 2012a]. Using highly toxic cobalt in the feedstock of SWCNT materials,
which will remain in the final product, has been the major bottleneck of the product. In addition to the use of non-toxic materials in the feedstock, the setup itself plays an important role in increasing OHS risks. The first setup used by Kim et al. (2007) is not a closed system meaning that the exposure is quite probable in the work place especially during the sample recovery and the cleaning process. Scaling up such a system means much higher exposure risks; too high to be tolerated by workers and authorities.

In carbon nanotube material synthesis, characterization of the final product is an important step. Some characterization techniques are very specific while others are more general and used more frequently. Among these general techniques, thermogravimetry (TG) is one which is frequently used for carbon nanotubes materials mainly due to its simplicity in characterizing the metal content [Geng et al., 2002; Moon et al., 2001], purity [Itkis et al., 2005], and thermal stability [Landi et al., 2005; Lima et al., 2009; Yu et al., 2005]. Although it was one of the first techniques used to characterize CNTs [Pang et al., 1993], no systematic study has been performed on this technique in order to closely examine the influence of instrumental parameters and also the sampling on the final results. In reviewing the literature, it was found that TG parameters vary amongst studies, and in some studies go unmentioned, implying that their direct effect on the final results of TG has not fully been considered. For instance, the initial mass of CNT samples characterized using TG has been reported in a wide range from 1 to 10 mg [Itkis et al., 2005; Landi et al., 2005; Yu et al., 2005]. Additionally, other studies have not mentioned the applied gas flow rate at all [Hu et al., 2003; McKee and Vecchio, 2006]. In order to widely use the TG technique for CNT materials and produce reliable TG data, its standardization is essential and must be considered [Decker et al., 2009]. Moreover, using TG for the purity evaluation is of great interest, compared to other techniques such as high resolution scanning electron microscopy (HRSEM) or near-infrared (NIR) spectroscopy, because it is the only technique that can be used for direct purity evaluation of SWCNT materials. However, TG is very straightforward and promising only when the CNT samples show a simple TG behavior. In the case of as-produced SWCNT materials, including those grown by the ITP method (used in this project), that are not highly pure and show a very complex TG behavior [Kim et al., 2009a], the possible use of TG for purity evaluation is hindered.
1.6 Project definition and objectives

The main objective of the present work is to modify in situ the chemistry of SWCNTs produced using the ITP system by studying the effect of the ammonia gas addition into the SWCNT synthesis environment. By achieving this objective, several advantages are believed to be obtained compared to conventional wet chemistry processes and cold plasma technology. Developing in situ chemistry enables minimization of costs of the SWCNT functionalization process since the whole process takes place at the same time and same place as the synthesis process. In situ process is expected to also increase the overall energy efficiency of the synthesis process since the heat of reaction is supplied by the main plasma gas stream in the ITP reactor. Towards the main objective, several specific objectives are taken into consideration: i) To investigate the possible effects of the reactive synthesis environment on the morphology and structural quality of SWCNT final product, ii) to study the reactivity of SWCNTs material with ammonia at high temperature in the ITP reactor, iii) to investigate the effect of different types of ammonia injections on the thermo-flow field of the ITP reactor by a 3D model, and iv) to develop a full 2D model based on coupled computational fluid dynamic (CFD)- kinetics of ammonia thermal decomposition in order to predict the concentration profile of reactants during decomposition of ammonia in the ITP reactor.

To perform in situ chemistry in the ITP system, ammonia is chosen as the reactive gas. The choice of ammonia is made based on the following criteria:

- The effectiveness of ammonia in functionalizing SWCNTs has been already proven [Felten et al., 2005; Khare et al., 2004b].
- The presence of N/H-containing functional groups has valuable applications in biology and polymer composite [Chen et al., 2004; Ramanathan et al., 2005a; Ramanathan et al., 2005b; Richard et al., 2003].
- N/H functional groups can act as anchor sites for grafting of other groups as well.
- Ammonia is used in the gas phase therefore less influence is expected on the thermo-flow field of the reaction system compared to when liquid or solid chemicals are used.
• Thermodynamic and transport properties of ammonia along with its decomposition kinetics have been widely studied and established enabling a full model of reaction system to be developed.

• Gas phase chemicals are preferred due to a better control of the mixing process in the ITP reactor.

In defining the in situ SWCNTs chemical modification project, some hypotheses are initially considered in order to approach the best practice for effective chemistry. To our best knowledge, the proposed project is new and no similar work has been performed so far by other research groups on SWCNTs. Therefore, the parameters affecting this process are not well known and need to be defined.

Ammonia addition into the ITP synthesis system is to be performed by a counter-current injection process from the base of the reactor. In contrast to the co-current flow, which is dominated by the main flow, it is believed that the counter-current flow enables better control on the velocity field of the reacting flow which in turn enables the elongation of residence time of reactants in a desired place. The choice of injection place is also critical since the effective growth region of SWCNTs is in the temperature range starting from liquid formation down to the end of eutectic temperature, and growth must be terminated before anchoring functional groups [Gorbunov et al., 2002]. In the case of a carbon-nickel system, the eutectic point is 1 600 K and the temperature at the base of the ITP reactor is not more than 900 K [Kim et al., 2009b]. Therefore, the base of the reactor is selected as the starting point for the injection process in order to avoid perturbing SWCNTs growth while having effective ammonia decomposition. With this in mind, the parameters changed during the in situ chemistry of SWCNTs material are the gas flow rate, the injection place, the mixing, and the initial temperature of ammonia. The mixing is primarily controlled by injecting ammonia through four different nozzle designs. Three different ammonia flow rates (i.e., 9, 18 and 28 slpm) are tested. The ammonia is injected at room temperature using a water cooled probe and for higher temperatures an in situ preheating process through a non-water cooled insert tube is used.
Numerical modeling of a chemical process gives valuable information that cannot always be obtained through experimental work. Depending on the setup used for such a chemical process, the use of numerical simulation is sometimes inevitable. In the case of the ITP reactor designed for effective SWCNT synthesis, the setup limits in situ measurements. This is because of the very high temperature of the reacting flow, the graphite insert inside the reactor, and also the in-flight powders limiting any direct spectroscopy measurements. As a result, an attempt is made to develop a numerical simulation for the thermal decomposition of ammonia in the ITP reactor. Since it is believed the chemical modification is directly affected by this decomposition process, predicting the concentration profile of the reactive species in the ITP reactor will not only give valuable insight about the obtained results of experimental work but it will also be a proper tool for further progress such as optimization and scaling up of the process. In this regard, to model the reacting flow, a 2D computational numerical fluid dynamic (CFD) approach using ANSYS/FLUENT v.13 code is developed for the prediction of the thermo-flow field inside the ITP reactor and is further coupled with the kinetics of the process using CHEMKIN/Add-In code. Moreover, it is believed that mixing can affect the thermo-flow field of the reactor. Therefore, the effect of mixing during the ammonia injection process is studied by developing a 3D model in which the injection of ammonia through a certain nozzle is numerically simulated using ANSYS/FLUENT v.13 code.

Another objective is to replace the toxic cobalt catalyst (Co) which has been used to produce high quality SWCNTs using the ITP method with a less toxic metal. The effective synthesis of SWCNTs requires a good body of knowledge about the effect of catalysts used. Catalysts play an important role in the synthesis of SWCNTs due to the fact that the main SWCNT growth mechanism is via the catalyst particles [Celnik et al., 2008; Gorbunov et al., 2002; Guo et al., 1995]. A wide range of catalysts have been tested for the synthesis of SWCNTs by different methods and their role and effects have been widely studied [Moisala et al., 2003]. However, because of the novelty of the ITP system only a limited number of catalysts have been tested so far [Kim et al., 2007]. Since each synthesis method has its own unique characteristic it is neither feasible nor rational to expand the obtained results from one particular synthesis system to another one. It has been reported that any changes in the nature of the catalyst can directly alter the SWCNT quality [Moisala et al., 2003]. Therefore, to make any change in the
type or amount of catalyst in the feedstock a comprehensive study seems inevitable. In this regard, a series of synthesis experiments are performed using the ITP system to closely examine the influence of three different transition metal catalysts including, Co, Ni, Mo at different ratios, on the SWCNTs final product. Moreover, a thermodynamic study using FACTSAGE code (v.6.2) is performed on predicting the reaction system in the gas and liquid phases. Therefore, the effects of the catalyst type and content on the SWCNTs final product are investigated by i) performing thermodynamic calculations, with the same conditions as the experimental part, on the reaction system in both gas and liquid solution phases using FACTSAGE code, ii) testing six different catalyst mixtures on the synthesis of SWCNTs by the ITP system, and iii) characterizing structural quality and morphology of the SWCNT samples synthesized using six different catalyst mixtures.

An appropriate characterization technique is essential to closely examine any changes in the synthesized SWCNT samples. The proper use of a material characterization technique needs a full knowledge about not only the material properties but also the instrumental limitations and parameters which can affect the final results. A non-standardized method in which the effects of instrumental and sampling parameters are unknown can give misleading results. Besides, the material properties are highly dependent on their primary size so that when it comes to nanometric range the change may not be disregarded [Poole and Owens, 2003]. The SWCNT samples are characterized by thermogravimetry (TG) technique in this work. The objective is therefore to standardize this technique prior to its use for ITP-grown SWCNTs material. Initial mass of sample, gas flow rate, and temperature ramp are three main parameters which are assumed to affect the TG behavior of as-produced SWCNTs material. Therefore, to investigate how the TG is affected by these three parameters, a two-factorial design is planned to statistically conclude their effect on two response variables i.e., $T_{\text{onset}}$ and full-width half maximum (FWHM), which are respectively measured from TG and derivative TG graphs of nano-sized carbon black (CB). The obtained data is then analyzed by analysis of variance (ANOVA) using Design-Expert software v. 6. Moreover, to characterize in detail the complex TG behavior of as-produced ITP-grown SWCNTs, TG analysis is performed on the SWCNT samples at three different purity levels: as-produced (industrial grade), thermally oxidized (moderate purity), and acid-treated (high purity).
1.7 Original contributions
The SWCNTs synthesis field has been the subject of many studies since the discovery of SWCNT in 1993. By a rapid look at the literature, one can realize the large size of the research which has been devoted to SWCNTs synthesis. Although there have been many advances in SWCNTs synthesis in many aspects, poor dispersibility and solubility of SWCNTs material in many solvents still remains a problem. The only solution proposed so far to overcome this problem is through post-treatment processing in which the as-produced SWCNTs are further processed and chemically modified by an appropriate method. Therefore, the main originality of the present work arises from the fact that the synthesis and the chemical modification of SWCNTs are simultaneously performed in the ITP system at a large scale (i.e., kg/day), i.e. in situ, for the first time. Moreover, 2D numerical modeling of the reacting flow in the ITP reactor including the kinetics and mixing of ammonia is developed for the first time. SWCNTs are also synthesized for the first time with an Mo catalyst and with new catalyst ratios in the mixture using the ITP system. Towards the characterization of the SWCNTs material using TG, the effect of different instrumental and sampling parameters not studied so far on the final TG results are investigated and discussed.

1.8 Thesis structure
This thesis consists of eight chapters. Chapter 1 is a brief introduction to carbon nanotubes, and thermal plasma. The problematic, objective, and project definition are discussed in this chapter as well.

Chapter 2 comprises a literature review on the structure, properties and application of carbon nanotubes and, in particular, single-walled carbon nanotubes (SWCNTs), synthesis methods, growth mechanisms, and their chemical modification processes.

Chapter 3 is complementary to the experimental setup and procedure described in chapter 6.

Chapter 4 describes the first article included in this thesis on studying experimentally and theoretically the effects of different type of metal catalysts (i.e., Ni, Co and Mo) and their content on the SWCNTs final product.
Chapter 5 describes the second article of the thesis in which a standard procedure for TG analysis of SWCNT materials based on a statistical experimental design is proposed and the effects of three main TG parameters (i.e., temperature ramp, initial mass of the sample, and gas flow rate) on the final results are explained. A simple method for purity evaluation of SWCNTs material having complex TG behavior is also proposed in this article.

Chapter 6 includes the third article specifying a detailed experimental procedure of counter-current ammonia injections into the ITP reactor for an effective in situ chemical modification of the final SWCNTs material. A 3D numerical simulation is performed to study the effect of two different types of ammonia injections on the thermo-flow field of the ITP reactor.

Chapter 7 focuses on the findings presented in the fourth article of the thesis based on the effect of ammonia addition into the synthesis environment on the surface chemistry of SWCNTs material. A 2D numerical model including the kinetics and mixing of ammonia in the ITP reactor is also developed in this chapter.

Chapter 8 is devoted to the overall conclusions and future work of the present work.
CHAPTER 2. Literature review

2.1 Carbon nanotubes

Carbon nanotubes are mainly categorized in two groups: i) multi-walled carbon nanotubes (MWCNTs) and ii) single-walled carbon nanotubes (SWCNTs). Another group can also be considered, so-called double-walled carbon nanotubes (DWCNTs) which are indeed MWCNTs constructed with only two co-axial graphene layers. Although these groups have many things in common, they also possess unique characteristics and properties and have been separately studied. The main focus of this chapter is on SWCNTs.

2.2 SWCNTs structure

The SWCNT structure can be seen as a graphene layer which is rolled up in a way that one edge is attached to its symmetry, as shown in Figure 2.1. Although this definition does not imply anything about the real formation mechanism of SWCNT, it can explain the structural characteristics of SWCNT.

![Figure 2.1: Rolling up a graphene sheet to SWCNT.](https://www.jmtour.com)

Adapted from James M. Tour group at Rice University: www.jmtour.com.

The chirality, the way that a graphene sheet is rolled up into a cylinder, can directly affect the properties of SWCNTs. In general, two main types of nanotubes can be created: i) achiral: including armchair and zigzag (Figure 2.2a and b, respectively) and, ii) chiral tubes, (Figure 2.2c). A chiral vector, Ċₙ, which spans the circumference of a cylindrical nanotube and is
formed by the rolled up graphene sheet, can be defined to uniquely determine the structure of SWCNT, as shown in Figure 2.3. The chiral vector can be written as (2.1):

$$\vec{c}_h = n\vec{a}_1 + m\vec{a}_2$$

(2.1)

where n and m are integers. The nanotube diameter, $d_t$, is directly related to the length of the chiral vector via (2.2):

$$|\vec{c}_h| = \pi d_t$$

(2.2)

The orientation of the chiral vector is determined with the so-called chiral angle, $\theta$, which can be calculated via (2.3):

$$\tan \theta = \frac{\sqrt{3} m}{2n+m}$$

(2.3)

The nanotube diameter can be determined as follows:

$$d_t = \frac{a \sqrt{n^2+mn+m^2}}{\pi}$$

(2.4)

where $a$ is equal to 2.36 Å. From equation (2.1) to (2.4), one can conclude that a SWCNT can be typically described with only two integers, n and m, and can be written as (n,m) (zigzag (n,0), and armchair (n,n)). For instance a (4,2) SWCNT can be obtained by rolling up the unit cell, shown in Figure 2.3, along the translation vector. The (4,2) SWCNT will then have a theoretical diameter of ~ 0.4 nm [Dresselhaus et al., 1996].
Figure 2.2  Schematic of three different types of SWCNT, (a) armchair, (b) zigzag, and (c) chiral.
Reprinted with permission from [Dresselhaus et al., 1996], © 1996, Elsevier

Figure 2.3  Unit cell of CNT on un rolled graphene sheet, with the chiral vector, $\vec{c}_h$, and its perpendicular translation vector, $\vec{T}$.
Reprinted with permission from [Dresselhaus et al., 1996], © 1996, Elsevier
2.3 Carbon nanotubes properties

SWCNTs consist of only carbon atoms arranged in a crystalline structure very close to that of graphene. The length and diameter of SWCNT can reach up to ~3 mm [Hata et al., 2004] and a few nanometers (0.6–3 nm) [Baughman et al., 2002], respectively, depending on the synthesis method. For instance, SWCNTs synthesized with the arc-discharge method possess a narrow diameter distribution of ~1.2 to 1.6 nm with a length exceeding a few micrometers whilst those synthesized with another method, the so-called high pressure carbon monoxide (HiPCO), have shown a wider diameter distribution (i.e., 0.5–2.5 nm) with a length of several micrometers. As-produced SWCNTs are mainly in a form of a bundle containing tens to hundreds of nanotubes. This arises from a very high Van der Waals interaction force of about 0.5 eV/nm [Dyke and Tour, 2004a]. However, individual SWCNTs are occasionally observed in the as-produced soot or can be synthesized with a specific method [Kong et al., 1998]. Since the aspect ratio (i.e. length over diameter) associated to SWCNTs is quite high (> 1000), they are real examples of one-dimensional structures which have been considered perfect candidates to be studied in solid state physics where the behavior of matter in one-dimension is of interest. In this regard, the SWCNT properties have been extensively studied through both theoretical and experimental approaches since the time they were first identified. Through this extensive research, SWCNTs have shown exceptional properties which in turn resulted in more studies to investigate why these materials exhibit extraordinary properties. Experimental measurements along with many theoretical predictions have resulted in determining the mechanical, electronic, thermal, optical, and chemical properties of these newly engineered nanomaterials. Among these properties, mechanical, electronic, thermal, and chemical properties of SWCNTs will be presented in more details in the following paragraphs because of their importance in potential applications. Some interesting properties of SWCNTs are summarized in Table 2.1.
Table 2.1 Physical properties of individual SWCNT

<table>
<thead>
<tr>
<th>Properties</th>
<th>Comparison</th>
<th>Reference</th>
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<tbody>
<tr>
<td><strong>Mechanical</strong></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Young’s modulus</td>
<td>1.25 TPa</td>
<td>Steel: 0.21 TPa</td>
</tr>
<tr>
<td>Elasticity modulus</td>
<td>1.4 TPa(^a)</td>
<td></td>
</tr>
<tr>
<td>Elasticity strength</td>
<td>6(^a), 20(^b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50-500 GPa</td>
<td>Steel: 2GPa</td>
</tr>
<tr>
<td><strong>Thermal</strong></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td>Conductivity (W/m K)</td>
<td>3 500(^a), 7 000(^b)</td>
<td>Diamond: 2 000-2 500</td>
</tr>
<tr>
<td>Stability</td>
<td>Up to 800°C (in air)</td>
<td>Graphite: 450-650</td>
</tr>
<tr>
<td></td>
<td>2 800°C (in vacuum)</td>
<td></td>
</tr>
<tr>
<td>Expansion</td>
<td>negligible</td>
<td></td>
</tr>
<tr>
<td><strong>Electronic</strong></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Resistivity</td>
<td>5–50 (\mu) (\Omega) cm</td>
<td>Copper: 1.7 (\mu) (\Omega) cm</td>
</tr>
<tr>
<td>Current density</td>
<td>(10^9) A/cm(^2)</td>
<td>Copper: (10^6) A/cm(^2)</td>
</tr>
</tbody>
</table>

\(^a\),\(^b\): data from experiment and theoretical calculation, respectively.

A) [Baughman et al., 2002; Coleman et al., 2006; Harris, 2009; Krueger, 2010; Salvetat et al., 1999; Wu et al., 2008]

B) [Balandin, 2011; Eder, 2010]

C) [Baughman et al., 2002; Eder, 2010]

2.3.1 Mechanical properties

The unique crystalline structures of carbon nanotubes are formed by very strong Carbon-Carbon (C-C: sp\(^2\)) bonds residing in a seamlessly rolled-graphene sheet. Since sp\(^2\) C-C covalent bonds are much stronger than C-C sp\(^3\), like that seen in diamond, it has been expected that these nanomaterials could have exceptional mechanical properties. In traditional
mechanics, the mechanical properties of a material are specified by defining a series of moduli, such as Young's modulus, and elastic constants in a microscopic environment where all material dimensions lay in the same scale, usually much higher than the molecular scale. In the case of a nanotube, one scale is in the macroscopic range (length > 1\,\mu m, and in some cases up to millimeters) while its diameter does not exceed a few nanometers. Therefore, much more care has to be taken into account in characterizing nanotube properties. Although the direct measurement of CNTs mechanical properties is a challenging assignment, CNTs Young's modulus has been obtained experimentally and reported in the literature. The first experimental studies were performed by Treacy et al. [Treacy et al., 1996] on MWCNTs, and Krishnan et al. [Krishnan et al., 1998] on SWCNTs, using the same method. The average Young's modulus values \( \bar{Y} \) were shown to be 1.8 and 1.25 TPa, respectively. Since then, different experimental approaches have been developed to directly measure the Young's modulus of CNTs and they have given mostly the same values as those reported in the first instance [Salvetat et al., 1999]. However, the main factor varying the \( \bar{Y} \) value within literature has been found to be more related to the nature of CNT sample than the experimental measurement approach. For instance, using the same experimental measurement method, the \( \bar{Y} \) value measured for CNTs synthesized by chemical vapor deposition (CVD) was one to two orders of magnitude smaller than those synthesized with high temperature methods such as laser ablation or arc-discharge [Salvetat et al., 1999]. This observation implies that the mechanical properties of CNTs are largely affected by the structural defects i.e. structural imperfection, since CVD-grown CNTs normally have a higher degree of structural defects compared to those grown by laser ablation. As a matter of fact, the absolute values for the mechanical properties of CNTs come from the theoretical calculations based on the molecular dynamic simulation. The unique structure of CNT allows the prediction of mechanical properties through well-established molecular dynamic simulation which can be further compared to the experimental measurements. Unlike the experimental measurement obliged to be performed on limited numbers of tubes having different structural defects, theoretical calculations can be performed on a perfect, well-defined, defect-free nanotube which allows the prediction of the highest mechanical properties that a carbon nanotube can achieve. Moreover, it allows the study of the influence of parameters such as nanotube diameter, \( d_t \),
and chirality, $\tilde{C}_h$, on the mechanical properties which is not feasibly achievable through experimental measurements. In this regard, the first theoretical study was reported by Lu [Lu, 1997] who predicted the Young's modulus and elastic properties of both SWCNTs and MWCNTs. Theoretical calculation has shown that the Young's modulus of an isolated SWCNT can reach up to 1.26 TPa, independent of its diameter and chirality for nanotubes of $d_t > 0.6$ nm. The theoretical studies and experimental measurements appear to confirm each other indicating very unique and exceptional mechanical properties for CNTs. It is now well-established that the CNTs possess a Young's modulus higher than any other known material. Because of their high strength and capability in distorting the relaxing stress, SWCNTs exhibit very high flexibility even at room temperature [Salvetat et al., 1999].

### 2.3.2 Electronic properties

The nanometric scale of CNTs along with the unique electronic structure of the graphene layer results in their unusual electronic properties, unlike any other material. Unlike their mechanical properties, electronic properties of CNTs are highly and tightly related to their chirality. Specifically, it is the geometric structure of CNT which controls its electronic properties. SWCNTs with the structure $(n,n)$ (i.e., armchair), are always metallic while those with the structure $(n,m)$ (with $n-m=3i$, $i=\text{integer}$), are small-gap semiconductors only if $i\neq0$, and large-gap semiconductors, only if $i=0$. All nanotubes having an $n-m=3i$, $i\neq0$, can be considered metallic at room temperature because of their small gap. Therefore, electronic properties of CNTs, i.e. metallic or semiconductive, can be generally defined according to the equations 2.5 and 2.6, respectively.

\[
|n - m| = 3i, i \neq 0 \tag{2.5}
\]

\[
|n - m| = 3i \pm 1, i \neq 0 \tag{2.6}
\]

There have been an immense amount of experimental studies on SWCNTs in order to further investigate their electronic properties [Bockrath et al., 1997; Ebbesen et al., 1996; Issi et al., 1995; Langer et al., 1996; Odom et al., 1998; Tans et al., 1997; Wildoer et al., 1998]. Electronic transport in metallic SWCNTs happens without scattering, known as ballistic
transport. This is the main reason why metallic SWCNTs can carry very high currents, i.e., about 10,000 times more than normal metals, with almost no heating [Baughman et al., 2002]. Throughout these studies, it has been established that the electronic properties of SWCNTs are very sensitive to their geometric structure as well as their chemistry. The electronic properties of SWCNTs are found to be drastically altered by structural defects (e.g., pentagons, heptagons, or vacancies) and dopant species in the carbon network [Dresselhaus et al., 2004a].

2.3.3 Thermal properties

Thermal properties of carbon nanotubes have been discussed and reviewed [Balandin, 2011; Dresselhaus et al., 2004a; Dresselhaus et al., 2004b; Hone et al., 1999], and in this section nanotubes thermal conductivity is explained in detail.

Thermal properties of carbon materials are unique among solid materials. Since they form different allotropes, they possess a wide range of thermal characteristics. For instance, thermal conductivity noticeably changes with the type of carbon allotropes from a very low value, for amorphous carbon (0.01 W/m K), to a high value (2,000 W/m K), for diamond. Thermal properties of materials change when at least one dimension approaches nanometric scales. Therefore, a very exceptional thermal conductivity was speculated for carbon nanotubes since the very beginning. Indeed, both theoretical calculations and experimental measurements have revealed a very high thermal conductivity for carbon nanotubes. To explain the reason for such high thermal conductivity, even exceeding that of in-plane graphite, one needs to understand the basics of heat conduction in solid materials, and specifically, in crystalline structures. In crystalline solids, the phonons\(^1\) and electrons are responsible for heat conduction. In metals, it is the electrons which carry most of the heat while in carbon materials, it is carried by phonons. The reason is the strong C-C sp\(^2\) bonds that efficiently transfer the heat through their vibrations in the lattice. The thermal transport in a solid can be diffusive or ballistic. The diffusive transport happens when the mean-free path of the phonons is smaller than the size of the sample and consequently scattering is dominant for the phonons. In ballistic transport, the mean-free path is larger than the size of the sample and the heat is transported through the

---

\(^1\) Phonon, a quasi-particle, is the quantum of structural vibration in a lattice
solid without scattering. In carbon nanotubes, both types of transport have been observed. At room temperature the mean free path is about 750 nm for a nanotube with a length of 2 µm therefore, the heat transport is still diffusive while at very low temperatures (T< 30 K) the mean-free path becomes long enough that ballistic transport is dominant [Balandin, 2011]. Thermal conductivity (K) in carbon nanotubes is size-dependent. That is K increases as the tube diameter decreases. Molecular dynamic calculations have predicted a very high K for individual SWCNTs, on the order of 7 000 W/m K [Balandin, 2011]. However the value measured experimentally is very scattered. Values of K vary by the experimental method applied for the measurement. For example, the value for K measured by the thermal method is in the range of 1 750 – 5 800 W/m K while electrical method gives it in a range of 3 000 –7 000 W/m K [Balandin, 2011]. Nonetheless, the highest experimentally measured value of SWCNT thermal conductivity is in the order of 7 000 W/m K [Balandin, 2011]. This is exceptionally higher than any other allotrope of carbon.

2.3.4 Chemistry

SWCNT can be viewed as a macromolecular form of carbon, known as “Ladder polymer”, varying in diameter and length. A pristine SWCNT constructed from a perfect graphene sheet is relatively chemically inert. However, because of the curvature in the geometric structure of SWCNT, the π-orbitals of carbon atoms are misaligned resulting in a local strain. Because of this local strain, SWCNTs are anticipated to be more reactive than a graphene sheet which is flat [Niyogi et al., 2002]. A perfect free-standing SWCNT constructed only by carbon atoms is shown in Figure 2.4a. The end cap of SWCNT is assumed to be constructed by a hemispherical fullerenic structure whereas the side-wall is constructed from the graphene sheet. Because of this assumption, SWCNT chemistry accordingly originates from that of fullerene and a curved-sheet of graphene. Consequently, to fully study the chemistry of SWCNTs, knowledge about the chemistry of fullerene and graphite is necessary. As mentioned earlier, the nature of the carbon-carbon bonds in graphitic structures are essentially sp²-hybridized that form trigonal planar geometry. A planar configuration with a pyramidalization angle of \( \theta_p = 0^\circ \) is therefore strongly preferred for this type of atomic structure, while sp³-hybridized carbon atoms need \( \theta_p = 19.5^\circ \) to maintain its tetrahedral
molecular structure [Ouyang et al., 2001]. For fullerene \( C_{60} \), a spherical folding structure of sixty carbon atoms, \( \theta_p = 11.5 - 11.6^\circ \) is calculated which is essentially close to that of tetrahedral hybridization. Therefore, for a certain SWCNT, (5,5) as shown in Figure 2.4, the end cap and sidewall show a pyramidalization angle of \( \sim 11.6^\circ \) and 6.0°, respectively [Ouyang et al., 2001]. The \( \pi \)-orbital misalignment is graphically explained in Figure 2.4c. The bond between two adjacent carbon atoms, C1-C4, in the network of \( C_{60} \) fullerene and (5,5) SWCNT is red-colored, as shown in Figure 2.4c. To realize the \( \pi \)-orbital misalignment, one can look at the red-line bond between two adjacent carbon atoms exactly from the angle shown in the rectangular in Figure 2.4c. By looking at \( C_{60} \), as well as some of carbon atoms in SWCNT, one can see that the \( \pi \)-orbital is perfectly aligned (i.e., \( \phi = 0^\circ \)), as shown by the solid-line circle in Figure 2.4c While, for some other carbon atoms in the SWCNT, the misalignment in the \( \pi \)-orbital with \( \phi = 21.3^\circ \) is clearly observable, as shown in the dashed-line circle in Figure 2.4c. Therefore, the chemistry of SWCNT arises from both the pyramidalization angle and the \( \pi \)-orbital misalignment. The reason can be explained as follows: the strain in the carbon atom network, like in fullerene and SWCNT, drives the chemical reactivity and is due to the structural folding. In fullerenic structures the \( \pi \)-orbital is aligned therefore the strain is mainly due to the pyramidalization. Since the saturation of carbon atoms through a reaction is Accelerated by the relief of this strain, the addition chemistry is strongly favored by fullerene. However, in the case of the SWCNT sidewall, the strain is predominantly due to the \( \pi \)-orbital misalignment rather than the pyramidalization and the relief of this strain controls the addition reactions with the nanotubes sidewall.
Selectivity

A SWCNT sample consists of different nanotube types varying in diameter and chirality. The chemical reaction is selective to the diameter and/or chirality of the nanotube. Knowing that the $\pi$-orbital misalignment angle and the pyramidalization angle scale inversely with the nanotube diameter, the SWCNT’s reactivity is expected to be affected by its diameter where the smaller diameter tubes are generally more reactive than the larger diameter tubes [Banerjee et al., 2005]. The higher reactivity of smaller diameter tubes has been experimentally observed. For instance, Raman spectroscopy on SWCNT samples after an ozonolysis process clearly shows that smaller diameters tubes have a greater tendency to react with ozone. This is because the intensity of the features in the low wave-number regions corresponding to the smaller tubes is decreased compared to that of the features of larger tubes [Banerjee and Wong, 2002]. The same trend in Raman data has been observed after the in situ thermal
oxidation of ITP-grown SWCNTs implying the higher reactivity of small diameter tubes with oxygen [Shahverdi et al., 2012]. In addition to diameter selective chemistry of SWCNTs, the chirality selectivity has also been observed. A solution phase reaction of SWCNTs with osmium tetroxide (OsO₄) in the presence of oxygen and UV irradiation was found to be selective to metallic tubes. A possible reason for such selectivity is that the reactants are transported to the nanotubes sidewall by an intercalation process. This electron transfer process is believed to occur much easier for metallic tubes through formation of an intermediate charge-transfer complex [Banerjee and Wong, 2004b]. A higher reactivity for metallic tubes with nitronium (NO₂⁺) salt has been also reported [An et al., 2005]. However, the higher reactivity of metallic tubes is not always the case since Miyata et al. (2006) showed a higher reactivity of semiconducting nanotubes with hydrogen peroxide (H₂O₂) where metallic tubes were oxidized much slower compared to semiconducting tubes [Miyata et al., 2006]. Therefore, it is suggested that the selective chirality reactivity of SWCNTs is strongly related to the type of reactants. The reaction selectivity of SWCNTs is a very interesting property since it can help to preferentially prepare a sample containing mostly metallic tubes or semiconductive ones. This possibility has been clearly indicated through the work of [Zhang et al., 2006a] where they showed the effective etching of metallic nanotubes from samples treated by methane plasma at 400 °C, leaving behind only semiconductive tubes. This is an important breakthrough since their potential applications sometimes require a sample containing purely semiconducting tubes in field effect transistors (FETs) [Zhang et al., 2006a], or metallic tubes as nanometer-size conductors [Miyata et al., 2006].

**Surface area**

SWCNTs surface area is directly influenced by their unique structure. They can be individual or in a bundle, open-end or closed-end. In an individual tube with a closed-end, the only available area is its external surface. Inversely nanotubes with open-end can accept foreign molecules or atoms in their cavity. This is why open-end SWCNTs are expected to exhibit a higher surface area than those with closed-end. Indeed, the higher surface area of opened-end SWCNTs has been experimentally observed where nitric acid treatment leads to the opening of the SWCNTs end caps increasing its surface area by two fold [Hu et al., 2003]. In the case
of bundled SWCNTs, due to the Van der Waals interactions, they are packed together so that extra space is created among adjacent tubes. Therefore, four possible adsorption sites are expected for bundled SWCNTs: (i) the hollow interior of nanotubes, (ii) the empty space between the nanotubes, (iii) the grooves created between two adjacent tubes, and (iv) nanotubes exterior surface [Agnihotri et al., 2005].

2.4 SWCNT applications

Many interesting applications can be conceived for carbon nanotubes thanks to their exceptional properties. Their unique quasi-one-dimensional characteristic along with their exceptional mechanical, electronic, thermal, optical, and chemical properties have attracted considerable attention for their use in a wide variety of applications. The application of nanotubes has been the subject of much research in which the efforts have been dedicated to the optimum use of intrinsic CNTs properties for a particular reason. Since application of CNTs is an active field, it has been extensively reviewed through recent publications [Ajayan and Zhou, 2001; Baughman et al., 2002; Endo et al., 2008; Harris, 2009; Krueger, 2010; Popov, 2004]. To date, a wide range of applications have been proposed for CNTs. Their use in electronic devices, polymer composites, sensors, energy storage, and biology [Krueger, 2010] has become possible through intensive work by researchers and manufacturers all around the world. Among many potential applications for CNTs, those that seem more promising will be presented in the following sections.

2.4.1 CNTs-polymer composites

CNTs exhibit high strength, yet are very flexible, light weight, and are highly conductive. They have been found to be very promising candidates as fillers in polymers matrices. It is very common to add fillers to the polymer in order to enhance its mechanical properties and conductivities. A huge amount of studies have been done on the use of CNTs in polymers to make the next generation of high performance composites. Once the incorporation of CNTs in polymers is successfully achieved one can expect better mechanical, electronic, and thermal properties from bulk polymers. However, this is not an easy task since CNTs cannot be easily incorporated into a polymer matrix due to their poor processability and lack of effective
interaction with a polymer matrix. That is why the CNTs chemical functionalization process is an inevitable step prior to their use in polymer composites. There are some good publications reviewing advances in carbon nanotube-based nanocomposites, all indicating a good progress and radiant future [Grady, 2011; Khare and Bose, 2005; Moniruzzaman and Winey, 2006; Pandey and Thostenson, 2012; Rahmat and Hubert, 2011; Xie et al., 2005]. For instance adding only small amounts of nanotubes (<0.1 wt%) into the polymer matrix can enhance the electrical conductivity of the composite by several orders of magnitude compared to the host polymer [Moniruzzaman and Winey, 2006]. The electrical percolation threshold has been reported at $2.5 \times 10^{-4}$ wt % and conductivity at 2 S/m at 1 wt % CNT in epoxy matrices [Sandler et al., 2003]. Moderate enhancement in thermal conductivity and thermal stability has been achieved in carbon nanotube/polymer composites [Moniruzzaman and Winey, 2006]. The interface between CNT and polymer matrix is important in defining final properties of the CNT-based composite [Khare and Bose, 2005]. With the aid of CNTs surface modification, which results in improved dispersion, a significant reinforcing effect of CNTs on the mechanical properties of the composite is anticipated [Khare and Bose, 2005]. Polystyrene composites with functionalized SWCNT have demonstrated a percolated SWCNT network structure at 1 vol % SWCNT which is due to the improved compatibility between the SWCNTs and the polymer matrix [Cynthia et al., 2002]. Addition of chemically modified CNTs to the polymers have shown the best results in terms of enhancement of the composite mechanical properties such as toughness and Young’s modulus [Coleman et al., 2006].

2.4.2 Electronic devices

Once a high electric field (10 V/cm) is applied on a solid surface with a negative electrical potential, electrons are emitted from the solid into vacuum by the quantum mechanical tunneling effect. This phenomenon is called field emission of electrons. Since electric fields concentrate at the sharp points, an extremely high field can be obtained on a sharp tip of a very thin needle [Saito and Uemura, 2000].

One of the most promising applications for CNTs is related to the electron field emission devices. It is because the combination of CNTs characteristics such as very small size, high strength, high electrical conductivity, and chemical stability make CNTs very ideal field
emitters used in flat panel display, electron guns in electron microscopes and microwave amplifier. CNTs and especially SWCNTs emitters have shown advantageous current density, threshold electrical field and longer life time compared to conventional emitters such as Mo or Si [Ajayan and Zhou, 2001]. The main trend in manufacturing transistors by many companies such as IBM, AMD and Intel is based on decreasing the transistors size below 45 or even 30 nm. Therefore, SWCNTs with less than 3 nm in diameter, are considered as promising candidates for the advancement of field-effect transistors (FETs). Recent advances in separating SWCNTs have even more facilitated their use in FETs. Different types of nanotube-FETs such as p-type (mainly semiconducting tubes), n-type and ambipolar have been successfully manufactured [Endo et al., 2008].

2.4.3 Tips probe imaging

CNTs have been used as a tip in probe imaging and also as gas sensors. Their exceptional mechanical properties along with unique one-dimensional geometry make them ideal tips for atomic force microscopy (AFM). The first use of CNTs as AFM tip is back to 1996 where MWCNT was glued to the AFM tip [Dai et al., 1996]. Later, individual and bundled SWCNTs were also successfully attached to the AFM tip [Wong et al., 1998]. Through the experimental work, it has been shown that CNTs-based tips can produce more realistic images with a better resolution compared to the conventional tips such as pyramidal Si tips [Harris, 2009]. Moreover, the use of chemically functionalized-CNT by carboxyl or amine groups as a tip for AFM, has enabled the chemical imaging because the functional groups on the CNT can interact specifically with those group patterned on the sample surface which accordingly makes it possible to carry out chemically sensitive imaging. Use of CNT-based tips for high resolution AFM imaging holds a great promise in biological system [Harris, 2009]. For instance, it allows to image biological molecules such as DNA or Alzheimer disease related amyloid-b-protofibrils with high resolution which is not obtainable with conventional tips [Ajayan and Zhou, 2001].
2.4.4 Sensors

CNTs can sense the changes made physically or chemically to their surroundings. This characteristic has allowed them to be used as chemical and/or physical sensors. They are sensitive to external physical parameters such as temperature, pressure, and mechanical strain [Krueger, 2010]. It has been recently shown that the as-produced SWNCT flexible sheet is highly sensitive to the normal pressure and can be used as pressure sensor [Genest et al., 2012]. In addition to pressure sensors, the use of CNTs as weight sensors (i.e., nanobalance) and flow sensors has been also reported in the literature [Harris, 2009; Krueger, 2010].

CNTs can also respond to their chemical environment by changing their electrical resistivity. It is now possible to detect the type and the concentration as low as ppt (part per trillion) of certain chemicals using CNTs-based sensors. Upon exposure to certain gases (e.g., NO₂, NH₃, CO, etc) the electrical resistance of semiconducting SWCNTs drastically changes in a way (it increases or decreases) and it can be measured. This response is quite fast compared to the conventional sensors and occurs at room temperature, unlike the other sensors which work at higher temperatures (>200°C) [Eder, 2010; Kong et al., 2000; Krueger, 2010]. Recently, it has been shown that even an inert gas can be detected by metallic SWCNTs since their electronic transport is sensitive to collision with the gas molecules [Harris, 2009]. Functionalized-SWCNTs have shown a greater sensitivity compared to pristine ones. Functionalization process has also enabled SWCNT to detect a broader range of chemicals [Harris, 2009].

2.5 SWCNT synthesis methods

Following the introduction of arc-discharge as a method for the synthesis of SWCNTs for the very first time in 1993 by Iijima and Bethune at IBM, many efforts have been devoted to develop new methods and/or to enhance the existing ones. In general, the proposed methods of SWCNT synthesis can be categorized in two main groups: (i) low temperature, and (ii) high temperature [Gavillet et al., 2002]. Chemical vapor deposition (CVD) methods are placed in the first group while arc-discharge and laser-ablation belong to the second group.
2.5.1 Arc-discharge

Arc-discharge method, shown in Figure 2.5 was the first method used for the synthesis of SWCNT by two separate groups in 1993 [Bethune et al., 1993; Iijima and Ichihashi, 1993]. The method is based on establishing a high electrical potential between two rods, so-called anode and cathode. Very high current of electrons created between the cathode and the anode makes the arc consuming the mixture of graphite and transition metal catalysts on the anode. Since the arc has a very high electrical energy, it can be effectively converted to heat in the presence of gaseous atmosphere turning the gaseous atmosphere into thermal plasma with a temperature exceeding several thousand Kelvin. With a proper configuration and operating conditions, one can produce SWCNT using a mixture of graphite powder and proper catalysts like nickel in the anode. The synthesized SWCNT containing soot is then collected on the water-cooled cathode as shown in Figure 2.5.

![Arc-discharge apparatus for the synthesis of SWCNT. Adapted from [Saito et al., 1996], © 1996, American Institute of Physics](image)

2.5.2 Laser-ablation

The laser-ablation method was introduced in 1995 by Guo et al. at Rice University [Guo et al., 1995]. The method is based on direct evaporation of transition-metal/graphite composite rods by high energy laser beam to produce SWCNT from the condensing vapor in a tubular reactor heated up to 1200 °C in a furnace. The rubbery deposit containing SWCNTs is finally
collected on a water-cooled Cu rod. The schematic of this method with its main components is illustrated in Figure 2.6. With laser-ablation method, the problem of high quantity amorphous carbon production during the synthesis of SWCNT by arc-discharge method was solved. Therefore, this method offers a very high quality and purity SWCNTs compared to those synthesized with arc-discharge. However, the rate of production is very low (i.e, g/day) and scaling up the process is very costly. Based on the idea of laser-ablation method, solar furnace apparatus has been developed to produce SWCNT. The method follows the same procedure as laser-ablation in which the laser beam is replaced by concentrated solar energy [Laplaze et al., 1998].

![Figure 2.6 Oven laser-vaporization apparatus for synthesis of SWCNTs. Adapted from [Guo et al., 1995], copyright © 1995, Elsevier](image)

2.5.3 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is generally referred to a chemical process in which a volatile or decomposable precursor in a controlled atmosphere is decomposed or even reacts on a substrate in order to make a thin film or produce high purity solid materials. The first use of CVD in the synthesis of SWCNT was reported in 1996 [Dai et al., 1996]. In their attempt to synthesize SWCNT, pre-formed nanoscale molybdenum was placed in a quartz boat and heated up to 1200 °C in flowing. CO was then introduced as carbon feedstock while the operating temperature was kept at 1200 °C and a total pressure of ~ 114 kPa was maintained during the operation. It was then shown that the process had successfully synthesized individual SWCNTs. The simplified schematic of CVD process is shown in Figure 2.7. It is
worth mentioning that carbon feedstock used in CVD has not been limited to CO as many other hydrocarbon precursors have shown to effectively produce SWCNT including benzene, ethylene, methane etc. [Su et al., 2000].

Other CVD-based methods have also been developed for the SWCNT synthesis which can be mainly divided into two categories [Kingston and Simard, 2003]: 1) supported-catalyst growth such as that developed for the first time by Dai et al. (1996) and ii) floating (or gas-phase) growth in which the catalyst and carbon source are co-injected into the reaction system either in gas phase or as an aerosol. The well-known CoMoCAT® process developed by the research group of Prof. D. Resasco [Kitiyanan et al., 2000] and recently commercialized by SouthWest NanoTechnologies Inc (SWeNT) falls into the first category. In this process, the Co-Mo mixture supported on SiO₂ beads in the presence of flowing pure CO at 700-950 °C and at total pressure of 1 to10 atm can produce SWCNTs of high purity with narrow size distribution. This process has enabled the mass production of SWCNTs through the catalytic approach. On the other hand, pyrolysis [Cheng et al., 1998] and high pressure carbon monoxide (HiPCO) methods [Nikolaev et al., 1999] can be placed in the second category.

![Figure 2.7 CVD apparatus for the synthesis of SWCNTs](image)

2.5.4 Induction thermal plasma (ITP)

Radio-frequency induction thermal plasma or briefly induction thermal plasma (ITP) method is a technique that has been used for a long time for the effective and high rate production of nano-sized materials especially metals, metal oxides and ceramics. It is particularly used for
the synthesis of highly spherical nano-sized powder in a narrow size distribution. In 2007, a paper was published by the research group of Prof. Soucy at Université de Sherbrooke in which an ITP system was effectively applied for the synthesis of high quality SWCNT-containing soot at industrial scale (i.e., kg/day) [Kim et al., 2007]. However, the first use of the ITP system for the CNT synthesis goes back to 2003 when Cota-Sanchez observed the presence of one CNT in the synthesized soot in his attempt for production of fullerene [Cota-sanchez, 2003]. Further improvement in the method enabled high quality-quantity synthesis of SWCNT through the work of Kim et al. (2007). The synthesis experimental setup used in their work along with its main components are schematically illustrated in Figure 2.8. The method can be essentially placed in the category of high temperature synthesis method since the highest temperature in the system exceeds 10,000 K. Along with many advantages linked to the ITP method compared to other methods, such as a very high production rate, yet high quality SWCNTs comparable to that synthesized with laser ablation, its design has the flexibility in performing in situ chemistry which has not been yet applicable in other SWCNT methods.

Figure 2.8    Schematic of ITP setup used to produce high quality SWCNTs containing soot at large scale. Reprinted with permission from [Kim et al., 2007], © 2007, IOP science
The detailed information about the ITP synthesis setup will be presented in Chapter 3: Material and method.

Different SWCNT synthesis methods are compared and summarized in Table 2.2.

Table 2.2 Advantages and disadvantages of various SWCNT synthesis methods. Adapted from [Eder, 2010]

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc-discharge</td>
<td>Good structural quality</td>
<td>Low yield, moderate purity (60-70 wt%),</td>
<td>Rotating electrode, Magnetic field, Liquid N₂, Water-assisted</td>
</tr>
<tr>
<td></td>
<td>(low defect), easy design, high efficiency</td>
<td>random diameter, not easily scalable</td>
<td></td>
</tr>
<tr>
<td>Laser-ablation</td>
<td>Excellent structural quality (very low defect), control over diameter</td>
<td>Costly, not scalable, very low production rate (g/day)</td>
<td>Ultra fast electron laser, pulsed laser</td>
</tr>
<tr>
<td>CVD</td>
<td>High yields, high purity, scalable, control over tube’s length, chirality, alignment and pattern growth</td>
<td>Low structural quality, needs post-treatment to remove substrate</td>
<td>Plasma enhanced, Laser assisted, Fluidized bed, HiPCO, Super growth</td>
</tr>
<tr>
<td>ITP</td>
<td>Excellent structural quality (very low defect), continuous, scalable, high production rate (kg/day), possibility of in situ chemistry, large-area flexible SWCNT sheet</td>
<td>Industrial grade purity (40-50 wt%), random diameter</td>
<td>In situ purity enhanced (60-65 wt %)</td>
</tr>
</tbody>
</table>
2.6 SWCNT Growth mechanisms

There has been considerable amount of work on defining a complete and reliable mechanism for SWCNT nucleation and growth, in view of the fact that a detailed knowledge of the growth mechanism is fundamental for the controlled synthesis of certain types of SWCNT. Up to now, several mechanisms have been proposed in order to explain the nucleation and growth of SWCNT with different methods of synthesis and varying operating conditions. Since SWCNT is only formed in the presence of catalysts, the catalytic growth mechanism of SWCNT has been studied separately from that of catalyst-free growth obtained for MWCNT. It is believed that the presence of catalyst affects noticeably the way that a SWCNT is formed. The role of catalyst in SWCNT synthesis has been found to be very important regardless of the method used. The methods which use catalyst to produce SWCNT can be generally divided into low temperature and high temperature methods [Gavillet et al., 2002]. CVD methods are essentially placed in the first category since the maximum temperature does not exceed 1200 °C. In these methods, individual SWCNTs are directly grown on pre-formed nanoscale metal catalysts supported by substrate while the scenario is completely different for the high temperature methods. Unlike the CVD methods for which nanoscale catalysts are pre-formed, the formation of nanoscale catalysts and SWCNT happen simultaneously in the synthesis environment in high temperature methods. In the following paragraphs different SWCNT mechanisms will be discussed in details.

2.6.1 Vapor-Liquid-Solid mechanism

The first model explaining the formation and growth mechanism of SWCNT in high temperature methods was first proposed by Saito et al. [Saito et al., 1994], and is widely known as VLS (Vapor-Liquid-Solid) model. Upon high temperature treatment of feedstock containing carbon source and metal catalysts, a vapor consisting of metal/carbon atoms is generated. High cooling rate of this vapor essentially results in supersaturation of that vapor which in turn results in formation of carbon-saturated metallic droplets (i.e., carbon-catalyst alloy). As the temperature of droplets decreases, the excess carbon atoms segregate to the surface of the metal droplets and solidify, forming either SWCNT or graphitic shell depending on the operating condition. To explain the transformation of segregated carbon atoms into
either SWCNT or graphitic shell, the model proposes the formation of intermediate flakes of graphite containing few tens of carbon atoms on the surface. In order to saturate the dangling bonds in their structure, flakes curl and close their open ends. The model then suggests the formation of SWCNT roots on the catalyst nanoparticles from the random assembly of the flakes (i.e., nucleation of SWCNT). The SWCNTs roots will then be fed by carbon atoms from the supersaturated catalyst particle to continue their growth. The schematic of the model is shown in Figure 2.9a. The model was later extended by [Gavillet et al., 2002] through experimental and theoretical studies. Their experimental results supported the proposed mechanism based on VLS model in which in a given SWCNT bundle, the nanotubes nucleate in a cooperative manner and their growth takes place on the same metal particle surface. Furthermore, using quantum molecular dynamic (QML) simulation, it was shown that the diffusion-segregation process occurring at the surface of metal particle is the key phenomenon causing carbon atoms to be incorporated at the root of growing nanotubes (i.e., root growth mechanism). Different scenarios explained by this model are depicted in Figure 2.9b. Based on VLS model, other mechanisms have been recently proposed [Celnik et al., 2008].

![Figure 2.9](a) Schematic of the nucleation and growth of SWCNT in high temperature method, and (b) extended VLS model. Either long bundle or sea-urchin like structure has been experimentally observed. Adapted from (a) [Saito et al., 1994], and (b) [Gavillet et al., 2002], © 2002, Elsevier

### 2.6.2 Scooter mechanism

The so-called "Scooter" mechanism explaining the high yield and uniform results obtained by laser-ablation was proposed by [Thess et al., 1996]. The schematic of this mechanism is
shown in Figure 2.10. Briefly, a single catalyst atom (e.g., Ni, Co) initially adsorbs with strong chemical bond to the open edge of a curving single-layered graphite not having more than 50 atoms. The metal atom can stay adsorbed at the operating temperature (1200-1500 °C) if the bound energy is > 2 eV and may be replaced by another incoming catalyst atom. The metal atom having sufficiently high electronegativity avoids the formation of fullerene by scooting around the open edge of the curved sheet. This scooting process helps annealing any carbons structures that are not energetically favorable and keeps the tube open. The resultant is a prolonged fullerenic structure in a form of tubule, as shown in Figure 2.10. The model cannot explain all the phenomena associated to the formation of SWCNT such as observation of catalyst nanoparticles or very small diameter SWCNTs. However, it can explain the role of catalyst and the reason why certain types of catalysts can produce SWCNT.

2.6.3 Solid-Liquid-Solid mechanism

Unlike the VLS model in which the formation of vapor is an essential condition, in solid-liquid-solid model (SLS model) proposed by [Gorbunov et al., 2002], the existence of carbon vapor is not considered necessary. Instead, the model suggests that condensed amorphous
carbon supplies the carbon atoms for the growing SWCNT. In this model, SWCNT growth is considered as a condensed state transformation of one to another form of solid carbon. The schematic diagram of SLS model is illustrated in Figure 2.11. As shown in the model, molten catalyst (e.g., Ni) is surrounded by amorphous carbon. That amorphous carbon supplies the carbon atoms to the molten particle by dissolution process, as shown in Figure 2.11, with the following sequence: (1) the excess carbon atoms come to the surface of the particle by a precipitation process. During the evolution of these atoms, (2) graphitic structures with defects and dangling bonds are formed on the surface which are not energetically favorable. Therefore, these single-layered graphitic sheets will then (3) be curved, (4) forming the SWCNT nuclei and finally be transformed to (5) a tubular structure, that is SWCNT. The model is not only capable of explaining the importance of temperature since the dissolution and precipitation processes are influenced by temperature, but also it emphasize the role of catalyst on the effective growth of SWCNT.

![Solid-Liquid-Solid (SLS) growth mechanism of SWCNT.](image)

Figure 2.11  Solid-Liquid-Solid (SLS) growth mechanism of SWCNT. Reprinted with permission from [Gorbunov et al., 2002], © 2002, Elsevier

### 2.7 SWCNT chemical modification

As mentioned earlier, carbon nanotubes and specially SWCNTs have very exceptional properties that make them very promising candidates to be used in many applications. However, as explained in section 2.3.4, pristine SWCNT is chemically inert and insoluble in
most solvents limiting their manipulation. Although they can be dispersed in some solvents with the aid of sonication, they rapidly precipitate after the sonication process stops. Stable SWCNTs solutions and dispersions are necessary for proper processing and this can only be achieved through proper chemical modifications.

Chemical modification processes can be categorized according to the place where the functional groups are attached to the SWCNT surface. As shown in Figure 2.12,(a) anchoring can be at defect sites like the open-end, vacancies or structural defects (e.g. Stone-Wales defect [Miyamoto et al., 2004]) which are the energetically favored place for the functional groups to attach to SWCNT, (b) sidewall of SWCNT, (c) inside the SWCNT cavity (i.e., endohedral) and (d) end-cap of SWCNT having semi-fullerenic structure.

![Diagram](a) Reprinted with permission from [Hirsch, 2002], © WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany, (b) and (c) Nanotube Modeler® JCrystalSoft v. 1.7 .3

Figure 2.12 Different classes of SWCNT functionalization (a) defect site chemistry: 1) open-end, 2) vacancy, 3) structural defect (b) side-wall, (c) endohedral and (d) End-cap.

Defect chemistry, in SWCNTs material, has been the first method successfully applied to chemically modify SWCNTs. The structure of as-produced SWCNT is not perfect and it bears different types of defect. The term "defect" is referred to any imperfection in the graphitic structure of nanotube including: i) structural vacancies with dangling bonds, ii) the open-end tube created during the synthesis process or through chemical process, and iii) structural
imperfection such as: Stone-Wales, heptagons and pentagons in SWCNT atomic network [Lu et al., 2005]. As mentioned earlier, the chemical stability of SWCNT arises from the perfect graphene sheet rolled to tubular form where the carbon-carbon bonds are essentially sp² hybridized. However, when defects are present in the SWCNT structure, the structure loses its aromaticity locally which yields increase relative reactivity. As a result, through chemical processing, reactive moieties can react with these carbon atoms at defective sites. Chemical oxidation of SWCNT in mild conditions such as diluted nitric acid treatment [Zhang et al., 2003] can potentially introduce carboxylic functional groups at the “as-existed” defect sites on SWCNT. It is worth mentioning that harsh chemical conditions such as strong nitric acid reflux can create more defects which in turn make the acid-treated SWCNT more reactive than as-produced one. Although categorizing the SWCNT functionalization process according to the place where moieties graft to SWCNT is informative, it does not give any information about the type of bond created. Moreover, defining the exact place where the functional groups anchored on SWCNT is a challenging work which cannot always be achieved. In certain chemical processes, combination of these functionalization strategies can take place making it impossible to place the overall chemical process into one of these categories. In the literature, the functionalization of SWCNT has been more generally categorized according to where the attachment is covalent or non-covalent. If atoms share pairs of electrons their bond is covalent, otherwise it is called non-covalent. Covalent bonds are much stronger than non-covalent bonds and are stable in standard conditions (e.g., room temperature, atmospheric pressure). Up to now, a huge amount of work has been devoted to functionalizing as-produced SWCNTs to make them soluble, more dispersible, and processable by using post-treatment chemical processes. Since there is a wide variety of reactive agents used for effective SWCNT functionalization in the literature and many different functional groups have been attached to SWCNT so far, it is not feasible to list all of these chemicals and groups in this work. Therefore, the emphasis is more on the chemical reactions through which the SWCNT functionalization is achieved.

In most cases, the functionalization process, in which the aim is to graft a certain functional group onto SWCNTs, is performed through a multistep chemical process. In these cases, as-produced SWCNT sample is firstly oxidized or fluorinated through acid treatment or
elemental fluorine, respectively, in order to modify the surface chemistry of nanotubes and make them reactive for grafting the target functional groups. The oxidation can be also achieved through the purification process with strong acids. The obtained tubes after chemical treatment are much more reactive due to the presence of e.g. carboxylic functional groups and can be further chemically processed, mainly through amidation and esterification [Peng and Wong, 2009], in order to graft desired addends to the nanotube. Another approach for pre-activation of SWCNTs is the plasma-activation method. The method is based on the nanotube treatment by noble gas plasma (e.g. Ar) to generate a controlled numbers of defective sites on the nanotubes. By applying this method, Yan et al. (2005) showed that the purified SWCNT has become enough reactive to be further grafted to 1-vinylimidazole under UV irradiation [Yan et al., 2005].

Depending on reaction type and the functional groups, the functionalization process can be direct or indirect. In direct process, as-prepared nanotubes (i.e., raw or purified) are subjected to the chemical reaction through which the nanotubes become functionalized. Some examples of this type of SWCNT functionalization are illustrated in Figure 2.13. Direct chemical functionalization of SWCNT through one of these covalent approaches, depicted in Figure 2.13, has been shown to be possible and effective through the work of many researchers. The first schematic in Figure 2.13 is related to the direct ozonation (or ozonolysis) of SWCNT reported by [Banerjee and Wong, 2002]. In their work, as-prepared HiPCO SWCNTs suspended in methanol (MeOH) were subjected to 10% O\textsubscript{3} in oxygen mixture at pressure of ~3 psi and temperature of -78 °C. This chemical process allowed ozonide intermediates to be generated and further attach to the nanotubes. Through additional works, they showed that the ozonized-SWCNTs can be then utilized as ligands to grow in situ the quantum dots (e.g., CdSe, CdTe) which further leads to creation of carbon nanotube-nanocrystal assembly [Banerjee et al., 2005]. The reaction of SWCNT with ozone at room temperature has also been studied through in situ Infrared (IR) spectroscopy [Mawhinney et al., 2000]. They showed the possibility for oxidation of SWCNT by ozonation leading introduction of oxygenated functional groups, mainly esters and quinones on the nanotubes. The second schematic in Figure 2.13 shows the hydrogenation of SWCNT by the modified Birch reduction method. In this process, the premixed pristine SWCNT-Lithium powder was firstly treated by liquid
ammonia at 220 K and further treated in the re-condensed ammonia vapor in the presence of
ethanol. Their results showed that the proposed dissolved metal reduction method could
successfully introduce atomic hydrogen on the sidewall of nanotubes [Pekker et al., 2001].
Another metal reduction reaction method using alkali metal naphthalides in tetrahydrofuran
(THF) was also shown to be effective for SWCNT hydrogenation [Engtrakul et al., 2012].
Hydrogenation of as-produced SWCNT has been also achieved by direct treatment of
nanotubes by atomic hydrogen generated using a radio frequency (RF) H$_2$ glow discharge (i.e.,
H$_2$ cold plasma) at very low operating pressure (< 1 Torr) [Khare et al., 2002a; Ruffieux et al.,
2002; Zhang et al., 2006b]. Scheme number 5 and 7–9, shown in Figure 2.13, represent the
covalent chemical modification of SWCNT sidewall by cycloaddition chemistry. Addition
reactions to the SWCNT sidewall are among the most important functionalization methods
which are accompanied by the formation of sp$^3$ carbon atoms the sidewall [Wunderlich et al.,
2008]. Different cycloaddition chemical reactions can be applied to successfully functionalize
pristine SWCNTs such as carbene or nitrrene [2+1] cycloaddition, Bingel [2+1] cycloaddition,
Diels-Alder (DA) which involves the reaction between 1,3-diene and dienophile, azomethine
ylides or nitrile amine [1,3-dipolar] cycloaddition and azide photochemistry [Karousis et al.,
2010; Tasis et al., 2006]. Radical addition chemistry on SWCNT has been studied on several
occasions through various approaches by which the covalent SWCNT functionalization with
different functional groups was successfully achieved, as shown in Figure 2.13 by number 4
and 6, for instance. In most of these studies diazonim salts (i.e., organic compounds sharing
R=N$^+$X functional groups: R= e.g. alkyl, aryl, X= e.g. halogen) were selected as the main
source for free radicals formation in the reaction medium [Bahr et al., 2001; Dyke et al., 2004;
Marcoux et al., 2004]. For instance, use of aryl diazonium salt in organic media results in
formation of aryl radicals which can graft to the sidewall of carbon nanotube, as shown in
Figure 2.13: scheme number 6. The resulting SWCNTs with this procedure have shown very
good dispersibility in dimethylformamide (DMF) [Bahr et al., 2001]. Moreover, radical
addition chemistry on SWCNT has been also achieved through thermal or photochemical
methods. In these methods, the organic peroxide reactive chemicals such as benzoyl peroxide
are thermally or photo-chemically decomposed in the presence of SWCNTs and the resulting
free radicals (e.g., phenyl) attach directly to the nanotube sidewall [Peng et al., 2003b; Umek
et al., 2003]. Another successful route for addition chemistry is nucleophilic addition by which the alkylation [Tasis et al., 2006], and the covalent addition of organolithium and magnesium compounds [Wunderlich et al., 2008] onto the SWCNTs sidewall have been achieved.

![Diagram of various covalent SWCNT functionalizations](image)

**Figure 2.13** Various covalent SWCNT functionalizations.
Adapted, reprinted with permission from [Banerjee et al., 2005], © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In the indirect process, the nanotubes surface is chemically activated prior to the preferred reaction. Widely utilized, the oxidation [Chen et al., 1998; Qu et al., 2002; Wang et al., 2005a] and fluorination [Boul et al., 1999; Khabashesku et al., 2002; Saini et al., 2003] processes enable nanotubes to be further chemically modified through substitution or addition chemistry. The schematic of this type of functionalization through pre-oxidized SWCNT or fluorinated SWCNT is depicted in Figure 2.14. The pristine SWCNT is firstly oxidized by
reacting with strong acids such as H$_2$SO$_4$ or HNO$_3$ or their mixture to introduce oxygen species on the nanotubes, as shown in Figure 2.14a. Subsequently, the desired functional groups (e.g., Cl, NH, R) are grafted to the nanotubes via these pre-attached oxygen-based functional groups. The use of strong acid reactions was firstly employed for the purification of as-produced SWCNTs. Since most SWCNT final products contain noticeable amount of impurities including metal catalysts, the acid treatment has been applied to dissolve these impurities. However, through characterization of the purified SWCNT samples, it was found that the SWCNT surface chemistry also changes during the purification process due to the introduction of oxygenated species. Since any additional process may affect the SWCNT surface chemistry, as-produced SWCNT has to be distinguished from those which are processed (e.g., purified), when the SWCNT chemistry comes into consideration. In the case of fluorination, the nanotubes are firstly fluorinated through sidewall derivatization with elemental fluorine and subsequently the obtained fluorinated-SWCNTs will further react with another reagent to attach desired groups on the nanotubes, as shown in Figure 2.14b. The indirect functionalization can be placed in the same category as the defect-site functionalization processes because the pre-formed moieties on the nanotubes create sp$^3$ bonds. Moreover, SWCNT functionalization can be performed prior to the solubilization process which is the case when the solubilization solvent is different from the functionalization solvent. In this regard, the functionalization is firstly performed and the obtained chemically-modified CNTs will be solubilized in the desired solvent, while if the functionalization takes place in the target solvent, the process is called in situ [Bahr and Tour, 2001; Georgakilas et al., 2002]. However, it is necessary to distinguish the term ‘in situ’ in the present thesis. In this work, the word ‘in situ’ refers to any process which takes place simultaneously during the SWCNTs synthesis process and in the same place, in contrast to the post-treatment process, unless otherwise mentioned. As a result, the term in situ functionalization, or chemical modification used in this work refers to the chemical process which is performed during the SWCNTs synthesis and in the same place (i.e., reactor).

Although a great deal of work has been performed on the large-scale gas-phase surface chemical modification of metal-based nanomaterials [Leparoux et al., 2010, Nessim et al., 2009, Pratsinis et al., 2010, Teleki et al., 2009], the main gas phase chemistry which has been
proposed so far for the effective SWCNT functionalization is the post-treatment cold plasma method. Cold plasma method is a chemical process in which a gas or a mixture of gases is transformed to plasma by means of radio-frequency (RF) or microwave sources at low pressures (<0.15 kPa). Generated plasma is reactive enough thanks to the presence of electrons, ions and radicals to modify effectively the surface chemistry of SWCNT by attaching proper functional moieties covalently. This method was firstly used in 2001 when Chen and his co-workers employed RF glow discharge plasma generated from acetaldehyde to activate the surface of vertically aligned CNTs by aldehyde functionalities (i.e., –CHO) to produce a thin coating of polymer [Chen et al., 2001b]. The plasma method has been then widely used for the covalent functionalization of CNTs with various functional groups using different plasma gases (e.g., CF₄, NH₃, O₂, N₂, H₂) [Felten et al., 2005; Khare et al., 2005; Khare et al., 2004b; Khare et al., 2004a; Plank et al., 2003; Shi et al., 2002; Valentini et al., 2005; Zhang et al., 2006b]. The advantage of this method compared to others is that it is rapid and it leaves no waste materials behind, except the exhaust gases. On the other hand, controlling the reaction parameters is a challenging task and the reactions are limited mostly to the surface of SWCNT samples. Scaling up is also another challenge where kilogram amount of SWCNT sample has to be treated.
SWCNT functionalization through (a) oxidation or (b) fluorination.
Adapted, reprinted with permission from [Banerjee et al., 2005], © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
2.8 Conclusion

In conclusion, the physicochemical properties of SWCNTs were shown to be exceptional and promising for many applications in the field of polymer composites, electronic devices, tip probe imaging, and sensors. Their mechanical strength and thermal conductivity surpass any material and their electronic properties are interestingly affected by their structural configuration. Their chemistry originates from both the fullerene and planar graphite. Although they are chemically inert, at certain conditions they can react with reactive agents through which their surface chemistry is modified. Depending on the chemical process, their chemistry can be size-dependent and/or chirality-dependent.

Although there are several methods for the synthesis of SWCNTs, either low temperature-based or high temperature-based, a high temperature-based ITP method holds a great promise in mass production of SWCNTs with a quality comparable to that of laser ablation-grown SWCNTs material which is considered as the best quality material. The mechanism of SWCNTs growth in the ITP system can be best explained by the VLS model. Here, the SWCNTs nucleation begins by the supersaturation of the plasma generated carbon-metal vapour. Their growth continues through a dissolution-segregation of carbon atoms in catalyst droplets.

SWCNTs are relatively inert. Hence, they show a poor processability and functionality which are important characteristics for the development of applications. Therefore, to enhance the functionality of SWCNTs chemical modification is necessary. In this regard, a large number of chemicals have been used to introduce various functional groups directly or indirectly onto SWCNTs. A direct chemical process is performed on as-produced SWCNTs while an indirect chemical process is performed on the previously chemically-treated SWCNTs. In the latter, the desired functional groups are added to as-preformed active sites on the SWCNTs.

Chemical modification of SWCNTs is mainly performed in liquid solution phase or gas phase and, is essentially a post-treatment process in which the as-produced SWCNTs are chemically processed. In the wet chemistry process, the reaction of reactive agents and the SWCNTs material takes place in the liquid solution phase therefore several time-consuming extra steps
are essential such as stirring, centrifugation, filtering, and drying in order to obtain the final product. Accordingly, these processes add substantial cost to the final products. On the other hand, cold plasma processes offer a much faster reaction time but are limited to the surface of the as-produced SWCNTs material, and need an extra costly unit of plasma which will consequently add extra cost to the final product.
CHAPTER 3. Material and method

In this chapter, the material and method used for the synthesis of chemically modified SWCNTs material are described in more details. As mentioned earlier in section 2.5.4, the ITP system was used throughout this work to synthesize high quality SWCNTs material at large scale (kg/day). Due to health concern raised from working with SWCNTs materials, the improvement in the synthesis setup has been necessary in order to minimize the risk of exposure not only during feedstock preparation and synthesis but also during sample collection and cleaning process. Moreover, to perform effectively the in situ chemistry, the modification in the original synthesis setup, shown in Figure 3.1a, was found inevitable. Because of these two reasons the modified synthesis system was built up as shown in Figure 3.1b.

Figure 3.1 Lab-scale SWCNT synthesis system (a) original setup, (b) modified setup
A schematic diagram of the modified setup is shown in Figure 3.2.

To modify the synthesis setup to an enclosed system, the major changes made are as follows:

- The powder feeder was placed in a ventilation system specifically designed for nanomaterials.
- Two glove boxes were added to the system in order to collect the sample from the reactor and filtration system without opening the synthesis system to the laboratory.
environment. This modification also allows for zero-exposure during the cleaning process.

- A sample collection bucket was attached to the bottom of the filtration system inside the glove-box.
- A blow back system was added at the exit of the filtration system in order to facilitate the sample collection inside the bucket without opening the system to the laboratory environment. Moreover, it allows for the continuous production without interrupting the synthesis process.
- A water-cooled probe was placed at the base of the reactor for the counter-current injection of NH₃.
- A Quadrupole mass spectrometer (MS, ThermoStar: Balzers instruments) was connected to the exit of the synthesis system in order to qualitatively and quantitatively monitor the exhaust gas.

The synthesis setup illustrated in Figure 3.2 mainly consists of:

- A 50 kW radio frequency (RF) induction thermal plasma torch or simply ITP torch (TEKNA, PS 50) run by an RF power supply (Lapel 60 kW unit).
- A tubular water-cooled reactor constructed from stainless steel having 80 cm long and 15 cm internal diameter (ID).
- A filtration system constructed by three vertically aligned porous metallic tubes with a length of 45 cm and an outer diameter (OD) of 6 cm.

TEKNA-PS 50 plasma torch is an inductively coupled radio frequency plasma generating instrument with a maximum input power of 50 kW and 3 MHz operation frequency. The torch is constructed from a ceramic tube which is covered by five-turn coil. For the sheath gas helium (He), and for the central and the feedstock carrier gas argon (Ar) are selected. The sheath gas is separated from the central gas by a tube made of quartz. A mixture of carbon black and catalysts (i.e., feedstock material) which is carried by Ar, is injected directly into the ITP torch through a high-pressure water cooled probe. Passing through the hot plasma generated by ITP torch, the injected feedstock is effectively vaporized. The generated vapour
experiences a rapid cooling process while it passes through the reactor resulting in formation of SWCNTs containing soot. The synthesized SWCNT containing soot will be then separated from the gas phase inside the filtration system and collected on the porous tubes in a form of flexible sheet. To have a higher temperature profile inside the reactor, two graphite inserts are installed into the reactor. The first one at the top of the reactor has a length of 50 cm and ID of 8 cm while the second one at the bottom of the reactor has a length of 30 cm and ID of 10 cm. Through many synthesis experiments, it has been found that the optimum SWCNT quality is achieved when the graphite insert temperature at the top of the reactor reaches 800 °C. Therefore, prior to each synthesis experiment the preheating process was performed ranging between 20 to 30 minutes to reach 800 °C. The operating condition of this preheating process is summarized in Table 3.1.

Table 3.1 ITP operating conditions during the preheating process

<table>
<thead>
<tr>
<th>Sheath gas (slpm)</th>
<th>Central gas (slpm)</th>
<th>Carrier gas (slpm)</th>
<th>Power (kW)</th>
<th>Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar/H2: 85/11</td>
<td>Ar: 25</td>
<td>Ar: 5</td>
<td>40</td>
<td>67</td>
</tr>
</tbody>
</table>

When the system reaches the proper temperature, the Ar/H2 plasma is switched to He/Ar plasma and the operating conditions are changed to that is presented in Table 3.2.

Table 3.2 Typical ITP operating conditions during the synthesis of SWCNT

<table>
<thead>
<tr>
<th>Sheath gas (slpm)</th>
<th>Central gas (slpm)</th>
<th>Carrier gas (slpm)</th>
<th>Power (kW)</th>
<th>Pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He: 123 or 135</td>
<td>Ar: 25</td>
<td>Ar: 5</td>
<td>40–45</td>
<td>67</td>
</tr>
</tbody>
</table>

During each synthesis test, the inlet and outlet temperature of each cooling water circle were measured by thermocouples and data was acquired by Labview software. The temperature measurement allows for energy balance calculation in order to investigate the overall energy efficiency of the synthesis process. A typical averaged data table archived by Labview during the synthesis process (at 45 kW, He: 135 slpm, Ar: 30 slpm) is summarized in Table 3.3. Since during the in situ chemical process, the plasma operating conditions were kept constant the calculated energy efficiently is representative for all the tests.
Table 3.3  Cooling water flow rate, inlet and outlet temperature of each ITP component

<table>
<thead>
<tr>
<th>Component</th>
<th>Flow (slpm)</th>
<th>T_in (°C)</th>
<th>T_out (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torch</td>
<td>21.1±0.1</td>
<td>18.4±0.1</td>
<td>29.1±1.4</td>
</tr>
<tr>
<td>Probe</td>
<td>3.2±0.1</td>
<td>20.6±0.1</td>
<td>26.6±1.2</td>
</tr>
<tr>
<td>Reactor</td>
<td>7.8±0.1</td>
<td>18.4±0.1</td>
<td>34.2±1.8</td>
</tr>
<tr>
<td>Filter</td>
<td>14.6±0.1</td>
<td>18.4±0.1</td>
<td>19.7±0.8</td>
</tr>
</tbody>
</table>

To calculate the overall energy efficiency of ITP synthesis system, it is necessary to calculate the heat loss from each component in Table 3.3 via the following equation:

\[ \text{Heat loss} = \text{water inlet mass} \times C_p \times (T_{\text{out}} - T_{\text{in}}) \]  \hspace{1cm} (3.1)

Considering the water density to be 998.3 (kg/m³) at 20 °C and the specific heat to be 4.183 (kJ/kg K), the total heat loss is equal to 27 kW and accordingly the total energy efficiency with a 45 kW input power is equal to 40%. This calculation indicates very well that any in situ chemistry will noticeably improve the total energy efficiency of the ITP synthesis system since the heat necessary for such reactions are provided in situ by the synthesis system.

For instance, decomposition of only 1 mole of ammonia for the chemical modification of SWCNTs needs 45 kJ, calculated using FACTSAGE software v.6.3, which is a considerable amount of energy.

The counter-current injection process was performed using different nozzles at the tip of the probe and the produced SWCNT samples were preliminary analyzed with nitrogen (N) elemental analyzer (TCH-600, LECO). Different nozzles used in this work are illustrated in Figure 3.3.
Along with these four different nozzles, ammonia was also injected without nozzle through water-cooled probes having ID of 2 and 1 mm. In order to preheat the injected ammonia gas, an interchangeable tube was inserted into the water-cooled probe.
CHAPTER 4. Synthesis of single-walled carbon nanotubes using induction thermal plasma technology with different catalysts: thermodynamic and experimental studies

Avant-propos

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Contribution to the document: The experimental works, as well as the thermodynamic studies were performed by Ali Shahverdi and Yasaman Alinejad under the supervision of Prof. G. Soucy and Prof. N. Faucheux. Drafting of the manuscript was also performed by Ali
Safety concerns with previous reactor design commands new reactor design and components. Non-trivial adaptation of operating parameters for production of high quality SWCNTs using new ITP reactor urged a systematic study to be performed. Meanwhile, it was chosen to modify the precursors to reduce the toxicity. As such, this Chapter includes a systematic study through both the experimental and the theoretical approaches on the catalyst type and content affecting the quality of SWCNTs synthesized using the ITP method.

The results presented in this article were obtained from the SWCNT samples synthesized by the new ITP system shown in Figure 3.1b. However, the preliminary experiments were initially performed with the old ITP system shown in Figure 3.1a. The summary of these preliminary tests is given in Table 1.

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Feedstock</th>
<th>Concentration (wt %)</th>
<th>Power (kW)</th>
<th>Pressure (kPa)</th>
<th>Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YA-PhD-14</td>
<td>Ni-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.0-0.5-97.5</td>
<td>45</td>
<td>67</td>
<td>5</td>
</tr>
<tr>
<td>YA-PhD-17</td>
<td>Ni-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.6-7.5-89.6</td>
<td>40</td>
<td>67</td>
<td>17</td>
</tr>
<tr>
<td>YA-PhD-18</td>
<td>Ni-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>5.2-94.8</td>
<td>40</td>
<td>67</td>
<td>21</td>
</tr>
<tr>
<td>YA-PhD-19</td>
<td>Ni-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>12.0-3.0-85.0</td>
<td>45</td>
<td>67</td>
<td>3</td>
</tr>
<tr>
<td>YA-PhD-20</td>
<td>Ni-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>12.0-3.0-85.0</td>
<td>45</td>
<td>67</td>
<td>15</td>
</tr>
<tr>
<td>YA-PhD-9</td>
<td>Ni-Mo-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.6-2.6-7.5-87.2</td>
<td>40</td>
<td>67</td>
<td>12</td>
</tr>
<tr>
<td>YA-PhD-10</td>
<td>Ni-Mo-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.6-2.6-7.5-87.2</td>
<td>40</td>
<td>67</td>
<td>21</td>
</tr>
<tr>
<td>YA-PhD-15</td>
<td>Ni-Mo-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.6-2.6-7.5-87.2</td>
<td>40</td>
<td>67</td>
<td>18</td>
</tr>
<tr>
<td>YA-PhD-11</td>
<td>Ni-Co-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.6-2.6-7.5-87.2</td>
<td>40</td>
<td>67</td>
<td>25</td>
</tr>
<tr>
<td>YA-PhD-13</td>
<td>Ni-Co-Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-CB(Monarch280)</td>
<td>2.6-2.6-7.5-87.2</td>
<td>40</td>
<td>67</td>
<td>16</td>
</tr>
</tbody>
</table>
The obtained samples were characterized mostly with HRSEM and Raman spectroscopy to closely examine the effect of the catalysts and the plasma power on the SWCNT final product. The findings of these experiments enabled to further perform the synthesis experiments with the new setup. The synthesis experiments performed with the new setup (not presented in this article) are summarized in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Feedstock</th>
<th>Concentration (wt %)</th>
<th>Powers (kW)</th>
<th>Pressure (kPa)</th>
<th>Duration (min)</th>
</tr>
</thead>
</table>
| PAS01    | Ni-Co-Y$_2$O$_3$-  
CB(Monarch280)     | 2.6-2.6-7.5-87.2     | 40          | 67             | 20             |
| PAS02    | Ni-Co-Y$_2$O$_3$-  
CB(Monarch280)     | 2.6-2.6-7.5-87.2     | 40          | 67             | 20             |
| PAS03    | Ni-Co-Y$_2$O$_3$-  
CB(Monarch280)     | 2.6-2.6-7.5-87.2     | 40          | 67             | 20             |
| PAS06    | Ni-Co-Y$_2$O$_3$-  
CB(Monarch280)     | 2.6-2.6-7.5-87.2     | 45          | 67             | 29             |
| PAS12    | Ni-Y$_2$O$_3$-     
CB(Monarch280)      | 5.2-7.5-87.2         | 40          | 67             | 40             |
| PAS13    | Ni-Y$_2$O$_3$-     
CB(Monarch280)      | 5.2-7.5-87.2         | 43          | 67             | 20             |
| PAS14    | Ni-Y$_2$O$_3$-     
CB(Monarch280)      | 2.0-2.0-87.2         | 43          | 67             | 29             |

The chemical equilibrium of the reacting synthesis system which is presented in this article was calculated based on the minimization of the Gibbs free energy of the system using FACTSAGE code v.6.2. The total Gibbs energy for a closed system at equilibrium state is minimum, so that we can say the rate of the possible changes at given temperature and pressure is zero. According to the FACTSAGE software documentations, the Equilib module calculates the conditions for multiphase, multicomponent equilibria, through Gibbs energy minimization. The total Gibbs free energy of a system can be expressed by following equation:

$$G = \sum_{\text{gas}} n_i (g_i^0 + RT \ln P_i) + \sum_{\text{liquid}} n_i g_i^0 + \sum_{\text{solution}} n_i (g_i^0 + RT \ln X_i + RT \ln \gamma_i)$$
where \( n_i, P_i \) and \( X_i \) are mole, gas partial pressure and mole fraction respectively. In the above equation, \( g_i^0 \) is standard molar Gibbs energy and \( \gamma_i \) is the activity coefficient.

**Titre français:**

Synthèse de nanotubes de carbone mono-parois par plasma thermique inductif utilisant différents types de catalyseurs : études thermodynamiques et expérimentales.

### 4.1 Résumé

Les effets du type et de la quantité de trois mélanges de catalyseurs (i.e., Ni-Y\(_2\)O\(_3\), Ni-Co-Y\(_2\)O\(_3\), et Ni-Mo-Y\(_2\)O\(_3\)) sur la synthèse de nanotubes de carbone mono-parois (SWCNTs) par un procédé plasma thermique inductif ont été examinés afin d’évaluer leurs influences individuelles sur la production de SWCNT. Les calculs thermodynamiques, en gaz et en particulier dans la phase de la solution liquide, ont également été réalisés afin de mieux comprendre les effets des catalyseurs sur la production de SWCNT. La caractérisation des SWCNTs synthétisées qui a été réalisée par différentes techniques dont la spectroscopie Raman, microscopie électronique à balayage à haute résolution (MEB-HR) et l’analyse thermogravimétrique (ATG) a clairement montré que la meilleure qualité de SWCNTs est obtenue en utilisant le mélange de catalyseur de Ni-Co-Y\(_2\)O\(_3\).

### 4.2 Abstract

The effects of the type and quantity of three catalyst mixtures (i.e. Ni-Y\(_2\)O\(_3\), Ni-Co-Y\(_2\)O\(_3\), and Ni-Mo-Y\(_2\)O\(_3\)) on single-walled carbon nanotubes (SWCNT) synthesis by induction thermal plasma process have been examined in order to evaluate their individual influences on SWCNT production. Thermodynamic calculations, in gas and particularly in liquid solution phases, have also been performed to better understand the effects of the catalysts on the production of SWCNT. Characterization of the synthesized SWCNT by different techniques including Raman spectroscopy, high resolution scanning electron microscopy (HRSEM) imaging and thermogravimetric analysis (TGA) clearly indicated that the best quality of SWCNT was achieved using Ni-Co-Y\(_2\)O\(_3\) catalyst mixture in the feedstock.
4.3 Introduction

Due to the very exceptional thermal, mechanical and electrical properties of single-walled carbon nanotubes (SWCNT) discovered by Iijima in 1993 [Iijima and Ichihashi, 1993], much attention has been attracted to this novel nanostructured material. It has a broad range of applications in different fields such as sensors [Cao and Rogers, 2009; Genest et al., 2012], polymers [Breuer and Sundararaj, 2004; Ci et al., 2008], microelectric devices [LeMieux et al., 2009], and biomedical engineering [Fadel et al., 2010; Zanello et al., 2006]. Different methods have been developed for the synthesis of SWCNT including arc discharge [Iijima and Ichihashi, 1993], laser ablation [Guo et al., 1995], chemical vapor deposition (CVD) [Dai et al., 1996], and induction thermal plasma [Kim et al., 2007]. These methods can be divided into two main categories depending on their catalytic or catalyst free synthesis. In catalytic synthesis methods, the presence of catalysts, mainly transition metals, in the feedstock or on the support plate is inevitable [Moisala et al., 2003]. In laser ablation and arc discharge methods high temperature heating of the target, made from graphite-catalyst mixture plate, followed by a rapid cooling rate process of the generated vapor results in the formation of high quality SWCNT. However, in the induction thermal plasma method (ITP), the formation of SWCNT is based on the direct evaporation of feedstock materials containing carbon black (CB) and a mixture of catalysts in the high temperature plasma plume. For CVD methods, hydrocarbon decomposition takes place over the supported catalyst particles which indeed act as active sites for the nucleation of SWCNT [Dai et al., 1996]. Since different phenomena occur in various synthesis methods, it is somehow impossible to adopt a unique mechanism for the SWCNT formation. Among all suggested mechanisms so far, the nucleation and growth of SWCNT based on carbon-catalyst interaction [Celnik et al., 2008] is more suited for the gas phase methods. Indeed, in the gas phase, SWCNT formation includes several steps (a) decomposition of catalysts and carbon source, (b) nucleation and growth of catalyst nanoparticles, (c) carbon diffusion or solubilization into the metal particles and (d) precipitation and solidification in the form of SWCNT. In this mechanism, diffusion and solubilization of carbon atoms into the catalyst liquid droplets is a key factor. The rate of dissolution is mainly dependent on the type of catalyst, temperature, and the presence of other solutes. For example, it has been shown that small amount of sulfur can reduce the surface
tension of liquid metal which favors the higher solubility of carbon [Flint, 1965]. It has been shown experimentally that the solubility of carbon in different catalysts varies notably. For example, the solubility of carbon is high in Mo and Fe, while it is very low in Cu [Moisala et al., 2003]. Therefore, it is expected that changes in the type of catalyst can distinctly affect the formation of SWCNT. Although the efficiency of different catalysts in production of SWCNT with the other methods of synthesis has been intensively studied, no systematic experimental study has been conducted on the effect of the type and quantity of catalysts on the SWCNT synthesis by ITP.

In the present work, since the solubility of carbon and the gas phase composition of plasma are expected to affect the SWCNT synthesis, a complete thermodynamic study on a wide temperature range (500-5 000 K) was carried out in order to fully understand the effect of the type and quantity of catalyst on the gas-phase during the synthesis of SWCNT by ITP process. The operating temperature window was limited to T< 5 000 K since at higher window temperature of plasma the system is noticeably far from the equilibrium state. It is expected that at lower temperatures considered in this work, thermodynamic studies will help to better understand the effect of different catalysts on the synthesis of SWCNT.

Following the thermodynamic study, the effect of three different catalyst mixtures on the SWCNT synthesis by ITP was experimentally studied. Along with Yttrium oxide (Y₂O₃), Ni, Co, and Mo have been selected due to their high efficiency in production of SWCNT using catalytic synthesis methods [Moisala et al., 2003]. Moreover, since there is controversial data about the toxicity of metallic catalysts in the literature [Machado et al., 2011; Sakai et al., 2002; Tessier and Pascal, 2006], it is important to find less harmful catalysts that are capable of producing high quality SWCNT.

4.4 Thermodynamic calculations

Theoretical thermodynamic study was carried out using FACTSAGE 6.2 software on the different carbon-catalyst mixture systems summarized in Table 4.1. To study the solution phase, particularly in liquid state the FSstel database was selected for the calculations. For the gas phase, the FACT53 database was considered without taking into account the inert gases
(Ar, He). Moreover, the presence of sulfur in the CB was not neglected since it can alter the quality of SWCNT [Alinejad et al., 2010]. For these series of calculations, two groups of mixture were considered and their results were compared. In Group 1 (i.e. MIX 1, 2 and 3) three different mixtures of catalysts were considered with a constant total amount of catalysts (i.e., 5.2 wt. %). In fact, the Co content present in MIX 1 was replaced by the same amount of Ni in MIX 2 and by the same amount of Mo in MIX 3 so that the total metallic catalyst content remained constant. Group 2 which includes MIX 4, MIX 5 and MIX 6, contains mixtures with different ratios of Ni-Y$_2$O$_3$ and Ni-Mo-Y$_2$O$_3$.

4.5 Experimental procedure and setup

SWCNT were synthesized at large-scale using ITP system (feed stock injection rate of 2 g/min), as shown in Figure 4.1. Detailed information about the experimental setup can be found in the previous paper [Kim et al., 2007]. The physical properties of the feedstock materials are summarized in Table 4.2. The same mixture compositions used for thermodynamic calculations (Table 4.1) were used in the experimental studies.

Table 4.1 Feedstock material content in weight percent (wt. %) used for the synthesis of SWCNT

<table>
<thead>
<tr>
<th>MIX No</th>
<th>Ni</th>
<th>Co</th>
<th>Mo</th>
<th>Y$_2$O$_3$</th>
<th>CB</th>
<th>S*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>2.6</td>
<td>2.6</td>
<td>0.0</td>
<td>7.5</td>
<td>87.3</td>
<td>2</td>
</tr>
<tr>
<td>2*</td>
<td>5.2</td>
<td>0.0</td>
<td>0.0</td>
<td>7.5</td>
<td>87.3</td>
<td>2</td>
</tr>
<tr>
<td>3*</td>
<td>2.6</td>
<td>0.0</td>
<td>2.6</td>
<td>7.5</td>
<td>87.3</td>
<td>2</td>
</tr>
<tr>
<td>4£</td>
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<td>0.0</td>
<td>0.0</td>
<td>3.0</td>
<td>85.0</td>
<td>2</td>
</tr>
<tr>
<td>5£</td>
<td>5.2</td>
<td>0.0</td>
<td>0.5</td>
<td>7.5</td>
<td>86.8</td>
<td>2</td>
</tr>
<tr>
<td>6£</td>
<td>1.3</td>
<td>0.0</td>
<td>3.9</td>
<td>7.5</td>
<td>87.3</td>
<td>2</td>
</tr>
</tbody>
</table>

* wt. % of sulfur in CB, * Group 1, £ Group 2
Figure 4.1 Schematic diagram of an ITP system designed for large-scale synthesis of high quality SWCNT

The synthesized SWCNT samples were characterized by means of Raman spectroscopy, X-ray diffraction (XRD, PANALYTICAL-X'Pret Pro MPD), thermogravimetric analysis (TGA, SETSYS 2400) and high resolution scanning electron microscopy (HRSEM, S4700, Hitachi). Raman spectroscopy was performed with Ar laser ($\lambda_{\text{ext}} = 514$ nm). TG was performed according to the protocol provided in [Shahverdi and Soucy, 2012].

Table 4.2 Properties of the materials used for the production of SWCNT

<table>
<thead>
<tr>
<th></th>
<th>Size</th>
<th>Purity (%)</th>
<th>$T_{\text{melting}}$(°C)</th>
<th>$T_{\text{vaporization}}$(°C)</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>2μm</td>
<td>99.9</td>
<td>1 455</td>
<td>2 913</td>
<td>Cerac (CANADA)</td>
</tr>
<tr>
<td>Co</td>
<td>2μm</td>
<td>99.9</td>
<td>1 495</td>
<td>2 927</td>
<td>Sigma-Aldrich (CANADA)</td>
</tr>
<tr>
<td>Mo</td>
<td>2μm</td>
<td>99.9</td>
<td>2 623</td>
<td>4 639</td>
<td>Sigma-Aldrich (CANADA)</td>
</tr>
<tr>
<td>CB</td>
<td>45nm</td>
<td>98.0</td>
<td>N/A</td>
<td>3 642</td>
<td>Grade: M280, Cabot Inc.(USA)</td>
</tr>
<tr>
<td>$Y_2O_3$</td>
<td>5μm</td>
<td>99.9</td>
<td>2 425</td>
<td>4 300</td>
<td>Hermann C.Starck (THAILAND)</td>
</tr>
</tbody>
</table>
4.6 Results and discussion

4.6.1 Thermodynamic study

Thermodynamic calculations were performed on different SWCNT feedstock mixtures summarized in Table 4.1. The results of thermodynamic calculations in gas phase and liquid solution phase on Group 1 are depicted in Figure 4.2.

Figure 4.2 Thermodynamic equilibrium composition in gas phase (left-side) and liquid solution phase (right-side) of (a), (b) MIX 1, (c), (d) MIX 2 and (e), (f) MIX 3
The comparison of the total gas phase of each mixture revealed that the total gas phase was poorly affected by the type of metallic catalysts since it ended at almost the same temperature with the same pattern for all the mixtures. Nonetheless, slight differences were observed at the temperature where the total gas phase was terminated for the three mixtures. For example, a more extended gas phase at lower temperature was observed for the MIX 3, MIX 1, and MIX 2 respectively. Details of gaseous species are illustrated under the gas phase (total) curve (Figure 4.2, red curve). The concentration and evolution pattern of the most important precursors of SWCNT (i.e. C_i, i= 1 to 5) seemed not to be affected by the change in the catalyst mixtures. The exothermic reaction of Y-C along with other reactions such as Y-S, Y-O and Ni-S can be considered as a key phenomenon to improve the yield of SWCNT synthesis process since the released heat increases the temperature locally and enhances the supersaturation of carbon in liquid solution phase [Kim et al., 2009b]. The heat released due to Y-C and Y-S reactions will be higher as their concentrations in gas phase are higher compared to other reactions, as seen in Figure 4.2a, c and e. Figure 4.2b, d and f show the liquid solution phase formed during the high temperature plasma process of feedstock materials in Group 1. The graphs show that Y did not participate in liquid solution in contrast to the metallic catalysts (i.e., Ni, Co and Mo). The liquid solution was formed abruptly for all mixtures as seen in Figure 4.2. However, for MIX 3, (Figure 4.2 f), Ni content gradually increased up to a point (around T= 2 800 K) where it became the main solvent, while Mo started to diminish at 2 500 K due to solidification. The whole liquid solution phase solidified at a temperature lower than 1 500 K. The presence of liquid solution phase containing metals in such a wide range of temperature compared to the pure liquid metals is due to the solubilization of carbon which lowers the solidification temperature of metals [Gorbunov et al., 2002; Krivoruchko and Zaikovskii, 1998]. The liquid solution phases depicted in Figure 4.2 showed also that along with the presence of liquid metals as solvent, and carbon as a solute, the other species including O, S and NiS exist in all liquid solutions. Compared to other species, a high degree of solubilization for carbon in liquid metals favored the formation of SWCNT. Interestingly, Mo compared to other catalysts can markedly elongate the existence range of liquid solution phase about 1 000 K.
The calculated liquid solution phase of MIX 1 and MIX 2 are depicted in Figure 4.3. The Mole-Temperature graphs of S and O for both mixtures were quite the same indicating that their solubility was the same in Ni and Co. However, three main differences between the liquid solution phase of MIX 1 and MIX 2 were observed (Figure 4.3). The first difference was the solubility pattern of C which started at a higher content for MIX 1 and ended at the same content as MIX 2. This observation firstly suggests that the solubility of C was enhanced by Co in the binary system of Ni-Co compared to unary Ni system. Moreover, taking into account the concentration gradient of C over temperature as a driving force for nucleation of SWCNT [Celnik et al., 2008; Wen et al., 2008], the binary Ni-Co system, having a bigger \( \Delta C/\Delta T \) in the same range of temperature than unary Ni system, eases the nucleation of SWCNT. The second difference was the range of temperature in which the liquid solution phase exists. As shown in Figure 4.3, this temperature range seemed to be slightly wider for MIX 1 than MIX 2. According to the very high temperature gradient and cooling rate along the induction thermal plasma reactor [Kim et al., 2009b], the wider temperature range in which the liquid solution phase exists can increase the time of SWCNT growth leading to a higher quality final product. The third difference is that unlike Ni, Co did not react with S in liquid solution phase which consequently allowed the active catalysts sites to uptake more carbon atoms.

Figure 4.4 and Figure 4.5 show thermodynamic calculations for another mixture of Ni (MIX 4) and two other mixtures of Mo (MIX 5 and MIX 6). Figure 4.4 shows the gas phase and liquid solution phase of MIX 4 in which the amount of Ni and \( \text{Y}_2\text{O}_3 \) was changed. By reducing the amount of \( \text{Y}_2\text{O}_3 \) in the feedstock mixture, the oxygen content was also reduced. The gas phase composition of the feedstock mixture was consequently affected by this change in the oxygen content as observed in the thermodynamic calculation results (Figure 4.4a). On the other hand, the liquid solution phase was more affected by the change in the Ni content. High content of Ni in the gas phase makes the formation of NiS thermodynamically more favorable which in turn may partially compensate the diminution in the heat released by the exothermic reaction of \( \text{Y}-\text{C} \rightarrow \text{YC}_2 \). The shortage of O in the reaction system results in an increase in sulfur cluster (S\(_2\)) followed by the formation of another cluster (S\(_3\)) in the lower temperature regions (\( T< 3000 \text{ K} \)) (Figure 4.4a). The formation of the clusters of sulfur at temperatures
where liquid solution phase exists can reduce the effectiveness of the process since these clusters can compete with carbon precursors in being solubilized into the liquid solution and occupy it and form the soluble NiS. This can be a reason why the amount of S and NiS in the liquid solution phase has been remarkably increased in Figure 4.4b.

![Figure 4.3](image_url)  
Superimposed liquid solution phase of MIX 1 (dashed-line) and MIX 2 (solid-line).

![Figure 4.4](image_url)  
MIX 4 thermodynamic equilibrium compositions in (a) gas phase and (b) liquid solution phase.

The total gas phase and also carbon precursors (C<sub>1</sub>-C<sub>5</sub>) seemed to be independent from the amount of metal catalysts and follow the same pattern, as shown in Figure 4.5. The total heat of dominant exothermic reactions, mentioned above, was poorly affected since the gas phase...
composition did not significantly change between MIX 5, MIX 6, and MIX 3 as shown in Figure 4.2c. The main changes were detectable from the liquid solution phases (Figure 4.5b and d). By adding small amount of Mo (i.e., 0.5 wt. %) the liquid solution phase temperature window and the solubility of solute species were changed compared to MIX 2. By increasing the amount of Mo, the solubility of C was changed compared to MIX 2 which is in total agreement with the experimental observations where the solubility of carbon is very high in Mo [Moisala et al., 2003].

Figure 4.5   Thermodynamic equilibrium composition in gas phase (left side) and liquid solution phase (right side) of (a) MIX 5 and (b) MIX 6
4.6.2 Experimental results

HRSEM images of SWCNT samples synthesized with different feedstock mixtures are depicted in Figure 4.6. All samples represent the existence of SWCNT bundles entwined with impurities including graphitic particles, catalysts and amorphous carbon. HRSEM images demonstrated also the different morphology of SWCNT produced using different types and amounts of catalysts.

To compare the structural quality of SWCNT samples synthesized with different catalyst mixtures, Raman spectroscopy was performed and the results are summarized in Table 4.3. The intensity of tangential vibration mode of graphite at 1 582 cm$^{-1}$ (G-band), over the intensity of disordered sp$^3$ carbon at 1 350 cm$^{-1}$ (D-band), is an informative value for the structural quality assessment of SWCNT [Dresselhaus et al., 2005]. A higher G/D ratio is an indicator for a better quality of SWCNT. The Raman analysis showed that the highest quality of the SWCNT was achieved using MIX 1 in which Co was present. In contrast, the lowest quality of SWCNT was obtained using MIX 6 in which Mo had the highest content. Sample obtained with MIX 2, possessed SWCNT with a lower quality than those produced by MIX 1. Therefore, Ni-Co binary mixture would be a better choice than Ni alone for production of high structural quality SWCNT. Furthermore, Co can be considered as a promoter for the synthesis of SWCNT. The results of Raman analysis for MIX 1 and MIX 2 are in good agreement with the thermodynamic calculations that predicted a superior potential of Ni-Co mixture in the synthesis of higher quality SWCNT. For MIX 4, SWCNT quality seemed similar to that obtained using MIX 2. This observation is in good agreement with the thermodynamic results. Although the increase and decrease in the Ni and Y$_2$O$_3$ contents respectively, could affect the reaction system individually, their overall impact on the SWCNT synthesis seemed to be neutral.
Figure 4.6 HRSEM images of SWCNT samples synthesized with (a) MIX 1, (b) MIX 2, (c) MIX 3, (d) MIX 4, (e) MIX 5 and (f) MIX 6

Table 4.3 Quality assessments of SWCNT synthesized with different catalysts mixtures

<table>
<thead>
<tr>
<th>MIX No.</th>
<th>MIX 1</th>
<th>MIX 2</th>
<th>MIX 3</th>
<th>MIX 4</th>
<th>MIX 5</th>
<th>MIX 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>G/D</td>
<td>15.2</td>
<td>13.6</td>
<td>4</td>
<td>14</td>
<td>4.5</td>
<td>3.8</td>
</tr>
</tbody>
</table>
To closely examine the crystalline structure of SWCNT synthesized with different catalyst mixtures in Group 1, XRD analysis was performed and the results are shown in Figure 4.7.

![XRD patterns of SWCNT samples synthesized with (a) MIX 1, (b) MIX 2, and (c) MIX 3](image)

Figure 4.7 XRD patterns of SWCNT samples synthesized with (a) MIX 1, (b) MIX 2, and (c) MIX 3

The XRD analysis revealed that unlike pure Ni and Co, pure Mo did not exist in the final SWCNT product. However, the carbide form of Mo (MoC) was found. This observation suggested the higher tendency of Mo to form carbide than Ni and Co catalysts in the present ITP operating conditions. It should be mentioned that the carbide formation can reduce the yield of the SWCNT synthesis by putting away the active catalysts from the SWCNT nucleation sites. Therefore, the formation of MoC in high quantity during the ITP process is unfavorable and has to be minimized.

To further investigate discrepancies observed between experimental results and thermodynamic calculation for Mo, the temperature profile of the reactor along the central axis was plotted regarding to the numerical simulation of the ITP synthesis system (Figure 4.8) [Kim et al., 2009b]. The eutectic temperature of Mo-C system ($T_{\text{eutectic}} = 2500$ K) [Hugosson et al., 2001] and Ni-C/Co-C ($T_{\text{eutectic}}= 1600$ K) [Kim et al., 2009b] are located at 0.6 and 0.75 m respectively from the torch exit (Figure 4.8). Two temperature zones are depicted in this graph: 3000-2000 K and 2000-1000 K. Since it has been experimentally proven that the optimal synthesis temperature lies 100-200 K below the $T_{\text{eutectic}}$ [Gorbunov et al., 2002; Kataura et al., 2000], the Zone 1 is expected to be a region in the ITP reactor which is more appropriate for the synthesis of SWCNT with Mo catalyst while the Zone 2 is suitable for...
using Ni and Co catalysts. As shown in Figure 4.8, the length of Zone 1 is only 13 cm in the reactor while the length of the Zone 2 is 30 cm. Therefore the nanotubes synthesized with Ni and Co have at least 2.3 times greater residence time in their suitable temperature zone than those synthesized with Mo.

![Figure 4.8 Axial profile of temperature along the centreline of the reactor. Black and white circle denote the eutectic temperature of Mo-C and Ni-C/Co-C systems, respectively](image)

Given that Co and Ni eutectic temperature is almost the same, this observation enables to explain why both Ni and Co produced SWCNT with similar quality but higher than that synthesized using Mo. Therefore, to overcome the problem observed with Mo it is necessary to optimize the ITP operating conditions to obtain similar temperature zone for Mo with the same effective length as Ni and Co.

To characterize the thermogravimetric behavior of each SWCNT sample produced with the feedstock mixtures in Group 1, TG analysis was performed (Figure 4.9). All SWCNT samples demonstrated a multistep weight loss in the temperature range of 200-800 °C indicating the presence of different carbonaceous structures including SWCNT. The mass loss became zero at temperatures above 800° C where the residual mass, attributed to the residual catalyst
content, was calculated to be 15, 12 and 11 wt.% for the SWCNT samples synthesized with MIX 1, MIX 2, and MIX 3, respectively. The mass gain at temperature around 200 °C was due to the oxidation of metal catalysts in the samples which was then followed by a rapid mass loss at a temperature around 350 °C due to the fast reaction of amorphous carbon with oxygen [Shahverdi et al., 2012]. The temperature at which SWCNT samples start to lose weight (T\textsubscript{onset}) seemed to be identical. However, the multistep weight loss event (TG graph) was more identical for the samples synthesized with MIX 1 and MIX 3 than MIX 2. This observation suggested that the ternary mixture of catalysts with the identical catalyst oxide produced SWCNT samples with the same TG behavior while this behavior was slightly changed when the binary mixture was used.

![TG graphs of SWCNT samples synthesized using MIX 1 (dashed-dotted line), MIX 2 (dashed line) and MIX 3 (solid line)](image)

**Figure 4.9** TG graphs of SWCNT samples synthesized using MIX 1 (dashed-dotted line), MIX 2 (dashed line) and MIX 3 (solid line)

### 4.7 Conclusion

The effect of metallic catalysts and their quantity in the feedstock material on the synthesis of SWCNT were thermodynamically and experimentally studied. High quality SWCNT can be produced with a ternary catalyst mixture containing Ni, Co and Y\textsubscript{2}O\textsubscript{3} or with a binary mixture of Ni and Y\textsubscript{2}O\textsubscript{3}. Thermodynamic calculations indicated that type and quantity of metal catalysts would affect more the liquid solution phase formed in the ITP reaction system during
SWCNT production and less the gas phase, while the content of \( \text{Y}_2\text{O}_3 \) changed the gas phase with less impact on the liquid solution phase. Considering the eutectic temperature of the metallic catalyst-carbon system, the effective residence time for Ni/Co was found to be 2.3 times more than Mo in the ITP resulting in a higher quality Ni/Co-grown SWCNT. Thus, Mo potential for the synthesis of SWCNT can be improved through ITP process optimization by increasing the length of higher temperature zone (T > 2 000 K).

**Acknowledgement** This study was supported financially by the Natural Sciences and Engineering Research Council of Canada (NSERC) and Research Chair of Canada (Laboratory of Cell-Biomaterials Biohybrid Systems).
CHAPTER 5. Thermogravimetric analysis of single-walled carbon nanotubes synthesized by induction thermal plasma

Avant-propos

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Contribution to the document: Ali Shahverdi performed the experimental parts, statistical analysis, and drafting of the manuscript under supervision of Prof. G Soucy. This article contributes to the thesis by developing a method for standardization of thermogravimetry (TG) technique used in this work for the characterization of synthesized SWCNT final product. As mentioned in previous chapters, once the nanotube is synthesized, it has to be characterized for different purposes such as catalyst content, thermal stability, morphology, etc. For instance, synthesized SWCNT samples with different catalysts mentioned in previous chapter had to be characterized by TG technique in order to quantify their catalyst content and their thermogravimetry behavior in oxidizing atmosphere after the synthesis process and to detect the presence of functional groups in the SWCNTs sample after the in situ chemical
modification process. Prior to perform any characterization technique with accuracy, a deep knowledge about the instrumental influences and the sampling process is necessary.

**Titre français:**

Analyse thermogravimétrique de nanotubes de carbone mono-parois synthétisés par plasma thermique inductif

**5.1 Résumé**

Une procédure standard d'analyse par thermogravimétrie (TG) de matières carbonées entre autres les nanotubes de carbone mono-paroi (SWCNT) a été développée sur la base d’un modèle statistique pour étudier précisément l’effet de trois paramètres de TG : la rampe de température (RT, °C), la masse initiale (MI) de l’échantillon en mg, et le taux de débit de gaz en sccm sur les résultats de TG. En outre, l’effet de l’échantillonnage y compris la morphologie de l’échantillon et la teneur en humidité sur TG ont été étudiés. Les résultats de la conception statistique ont clairement montré que la TG a été affectée par ces trois paramètres, notamment par la MI et la RT. Fait intéressant, il a été observé que les résultats de TG sont peu affectés par la morphologie d’échantillon et la faible teneur en humidité. Cette étude a également confirmé le potentiel de la TG combinée avec la microscopie électronique à balayage haute résolution (MEB-HR) comme méthode simple et directe pour évaluer la pureté des SWCNTs dans les échantillons, et cela, même avec un comportement complexe de TG tel qu'obtenu pour des échantillons produits par plasma thermique inductif. Une étude complémentaire sur les catalyseurs nanométriques a indiqué que ces types de matériaux peuvent gagner ou perdre de la masse dans un environnement oxydant pendant TG. Une perte de masse de 6% et un gain de masse de 23% ont été observés pour l’oxyde d’yttrium et le nickel pur nanométrique, respectivement. Un simple calcul montre un gain de masse total de 1% en particulier par les catalyseurs dans l’échantillon de SWCNTs pendant la TG.

**5.2 Abstract**

A standard procedure for thermo-gravimetric analysis (TGA) of carbonaceous materials including SWCNTs was developed based on a statistical design to precisely study the effect of
three main thermo-gravimetric (TG) parameters: temperature ramp (°C), initial mass of the sample (mg) and the rate of flowing gas on the TGA results. In addition, the effect of sampling including sample morphology and moisture content on TGA were studied. The results of statistical design clearly showed that TGA was affected by these three parameters and particularly by initial mass and temperature ramp. Interestingly, it was observed that the TGA results are affected insufficiently by the sample morphology and low moisture content. The present study also confirmed the potential of TGA combined with high-resolution scanning electron microscopy (HRSEM) to be a simple and straightforward method for purity evaluation of SWCNT containing sample with a complex TG behavior such as those of induction thermal plasma-grown. A complementary study on nano-metric catalysts indicated that these types of materials enable to gain or lose weight in an oxidative ambient during TGA. A mass loss of 6% and a mass gain of 23% were observed for pure nano-metric yttrium oxide and nickel, respectively. A simple calculation showed a total mass gain of 1 wt. % particularly by the catalysts in the SWCNT sample during TGA.

5.3 Introduction

In material science, thermogravimetry has been numerously applied to characterize thermal decomposition, degradation and stability properties of materials [Corradini et al., 2009; Howell et al., 2010; Howell and Carter, 2010; Howell and Cho, 2010; Martins et al., 2009; Sato et al., 2009; Yoshino and Miyake, 2010]. It has also become a popular technique for single-walled carbon nanotubes (SWCNTs) characterization since their discovery in 1993 by Iijima [Iijima and Ichihashi, 1993]. It has been widely used to study the stability of SWCNT in an inert (e.g., Ar, N₂) or oxidizing atmosphere (e.g., O₂, CO₂) at different temperatures and to measure the catalysts content of these synthetic materials produced with different techniques such as: arc-discharge [Park et al., 2002; Shi et al., 2000], laser ablation [Kingston et al., 2004; Rinzler et al., 1998], chemical vapor depositions (CVD) [Murakami et al., 2003; Su et al., 2000] and induction thermal plasma [Kim et al., 2007]. Moreover, it is used as a rapid and simple method for purity evaluation where the purity is high (i.e., the main product is SWCNT and the remaining is catalyst). Although it is of interest to use TG for other types of SWCNT materials, the problem arises with these materials containing a noticeable amount of
carbonaceous impurities causing a complex TG behavior. One of the most complex products is the induction thermal plasma-grown SWCNTs [Kim et al., 2007]. These materials are a complex mixture of different carbonaceous species and nano-metric metallic catalysts due to an extremely high temperature plasma and very rapid cooling rate (i.e., $3.5 \times 10^5$K/s) [Kim et al., 2007] leading the formation of the complex carbonaceous-metallic mixture. The presence of carbonaceous impurities along with SWCNTs creates a multi-step mass loss in TG graph. Therefore, in derivative graph (DTG) several peaks appear overlapping each other making deconvolution and consequently purity evaluation impossible. In this work, TG combined with HRSEM is performed on the SWCNT sample at three different purities: 1) as-produced sample 2) thermally oxidized sample and 3) acid-treated sample; in order to identify each peak in DTG graph of induction thermal plasma grown-SWCNT, and consequently to evaluate its purity.

To evaluate precisely the purity or even the catalysts content of SWCNT sample, in first step the method used has to be standardized. Although TG has been used over past time, but no systematic study has been done for a particular SWCNT-containing material and only general methods have been proposed which in fact cannot be suitable for all types of SWCNT-containing materials. In this regard, a statistical plan is designed in order to study the influence of different factors including TG-instrumental and sampling parameters on the TG results. Among these parameters, only those having the most affecting role on TG results were selected. For instance, the nature of crucible that has less impact on the TG curves was not considered in this study since the material of construction of the crucible does not react rigorously with the sample containing mainly carbon in the temperature range of 25-1 000 °C [Wendlandt WW, 1986]. In parallel, the influence of sample morphology and sample drying on the TG results were studied.

This is worthy to note that physical and chemical properties of SWCNT-containing materials can be affected by the method used for the synthesis meaning that SWCNT materials synthesized by different methods vary one from another. TG behavior is not an exemption and it is consequently affected by the SWCNTs method of synthesis. One of the main differences of induction thermal plasma-grown SWCNT material from other types is that it contains a
noticeable amount of nano-metric catalysts [Kim et al., 2009b]. Besides, it is believed that the material properties in nano-metric ranges may differ from those of bulk [Poole and Owens, 2003]. Therefore, it is reasonable to expect that the TG result of SWCNT materials can be affected by the presence of these nano-metric catalysts and how it is affected is one of the objectives of the present work.

5.4 Experimental

5.4.1 Synthesis and Purification

SWCNTs material was produced in a sheet form in our laboratory using an induction thermal plasma system [Kim et al., 2007]. A mixture of carbon black (CB), as a carbon source, and micro-metric metallic catalysts including Ni (1 μm), Co (2 μm) and Y₂O₃ (5 μm) was used as a feedstock material. In the first step of purification, the SWCNT sheet was thermally oxidized in the air in order to remove the excess of amorphous carbons at a temperature of 320 °C for 1 hr. In the second step, in order to remove the excess of metallic catalysts and graphitic particles, the oxidized SWCNTs material was further treated with strong acid (i.e., HNO₃ 70%) for 8 hrs and, the solution was eventually centrifuged at 7 000 rpm regarding the protocol provided in [Kim et al., 2009a].

5.4.2 Statistical design

A statistical design was performed using Design Expert (Stat-Ease Inc., v. 7.1.6) to study the influence of operating parameters on the TG results. A factorial plan with three factors and two levels was designed with full-width half-maximum (FWHM) and onset temperature (T_onset) as the responses variable. Three factors involved in the experimental plan were supposed to be the sample initial mass (IM), the gas flow rate (FR) and the temperature ramp (TR). In order to perform the design with minimum error, nano-sized carbon black (< 40 nm) from Cabot, Co. was used as the carbonaceous sample because of the following reasons: (1) To avoid any catalytic reaction during TG, it is important to select a carbonaceous material that has very low impurity content (high purity carbon), since, for instance, it has been confirmed that the presence of metals and metal oxides can cause the catalytic combustions of carbon black
resulting in lowering the maximum temperature of carbon black combustion [Bokova et al., 2005; Ciambelli et al., 1994]. The same TG behaviors have been observed for SWCNTs materials where the behavior of high purity SWCNTs has differed from as-produced SWCNT materials containing metallic catalysts [Cho et al., 2009; Harutyunyan et al., 2002]. (2) TG of this carbonaceous material reveals only one-step mass loss resulting in a more accurate way to monitor the effect of each factor on the final results in comparison with a sample revealing a multi-step mass loss. Table 5.1 summarizes the $2^{3-1}$ factorial design, including low and high-level values used for each factor.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coded factor</th>
<th>Low level</th>
<th>High level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial mass/mg</td>
<td>IM</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Gas flow rate/sccm</td>
<td>FR</td>
<td>20</td>
<td>40</td>
</tr>
<tr>
<td>Temperature ramp/°C</td>
<td>TR</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

**5.4.3 TGA procedure**

TG was performed using a TG instrument from SETARAM Co. (SETSYS 2400). An alumina crucible with a total volume of 170 µl was used and temperature was measured during TG using a Pt-Rh 20 % rode. Regarding the nitridation of metals at high temperatures a mixture of oxygen and argon (20 % - 80 %, respectively) was used instead of air. Except for the statistical study, all TG tests were carried out regarding our reference protocol (i.e., temperature ramp of 10°C/min, initial mass of ~10-12 mg and flow rate of 40sccm). The maximum temperature in TG did not exceed 1000 °C as the most carbonaceous materials in any forms are burnt away from the sample at this temperature in an oxidizing atmosphere. In order to study the influence of nano-sized catalysts, highly pure (> 99.9 %) powders of Y$_2$O$_3$ and Ni, with an average size of < 50 nm and < 100 nm, respectively, were purchased from Sigma-Aldrich Co.

**5.4.4 Sampling**

Induction thermal plasma-grown SWCNT-containing soot produced in a form of sheet was ground to fine powders by means of a stainless steel sieve with a pore size of 780 µm. The
obtained powder having sizes less than 780 μm was then placed in an oven for three consecutive days at a constant temperature of 105°C to remove the moisture content. The same drying process was also employed on the CB powder. Mass of the samples was weighted before and after drying process by means of microbalance and the difference was assigned to the moisture content. TG was finally carried out on both samples before and after sampling regarding to the reference protocol.

5.5 Results and discussion

5.5.1 Sampling

The effects of sampling including drying and morphology (in sheet or powder form), on TG were studied. Figure 5.1 depicts the results of TG for CB materials before and after drying process. As shown for both samples, $T_{onset}$ does not change significantly with the moisture content. Both samples reveal the same mass loss behavior during TG and the same temperature at which the burning rate is maximized. In general, there is no dramatic difference in TG behavior of original and dried CB samples which can be an indicator for low moisture content.

![TG graphs of CB](image)

Figure 5.1   TG graphs of CB (a) original sample (b) dried sample
The same TG test was performed on SWCNT-containing material in its original and sieved-dried forms. The results are illustrated in Figure 5.2. As shown in Figure 5.2a and b, TG graphs of original and sieved-dried SWCNT samples reveal a multiple-step mass loss in the oxygen-argon atmosphere. The mass loss becomes constant for both samples at a temperature around 700°C where ~86 wt. % of their initial mass is lost. Furthermore, $T_{\text{onset}}$ for both samples appears at almost the same temperatures. A very slight difference is observed due to the small amount of moisture in the original sample which helps the catalytic reaction of the sample to get started at a lower temperature. The residual catalyst content in original sample resides at 0.4 wt. % more than that of dried sample which is well below the instrumental deviation (±0.5 wt. %). By taking into account the consistency of TG behaviors, Figure 5.1 and Figure 5.2 suggest that TG results of induction thermal plasma-grown SWCNT are not affected by sampling procedure including drying and morphology.

![Figure 5.2](image-url)

Figure 5.2   TG graphs of SWCNT (a) as-produced (b) sieved-dried
5.5.2 Statistical study

The results of the statistical design on TG data are summarized in Table 5.2 representing three selected factors at two levels and two responses variable named $FWHM$ and $T_{onset}$. The analysis of variance (ANOVA) on these series of experiments was performed and the results, based on the $FWHM$, are shown in Table 5.3. ANOVA was also carried out based on $T_{onset}$, but the model was not significant showing that this variable is not affected by the selected factors. Contradictory to $T_{onset}$, the model is significant for $FWHM$, as shown in Table 5.3 and Figure 5.3, and affected by all selected factors; however, Figure 5.4 shows that the model is more influenced with TR and IM than FR. In addition, $FWHM$ is positively affected by TR and IM factors while FR has a negative effect on $FWHM$. The small influence of FR compared to other factors suggests that the gas flow rate can be selected at any level between 20 and 40 sccm for such sample. However for sample weighing more than 20 mg, the higher flow rate is suggested in order to provide excess oxygen during TG. For the other two factors, IM and TR, much more attention should be considered as TG is noticeably affected by them. It is worth noting that during TG, the consistency of these two factors is necessary for any individual experiment.

Table 5.2 Two responses variable ($FWHM$ and $T_{onset}$) obtained from TG

<table>
<thead>
<tr>
<th>RUN</th>
<th>IM /mg</th>
<th>FR /sccm</th>
<th>TR /°C/min</th>
<th>$FWHM$ /°C</th>
<th>$T_{onset}$ /°C</th>
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<tbody>
<tr>
<td>5</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>101.3</td>
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<tr>
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<tr>
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<td>20</td>
<td>40</td>
<td>10</td>
<td>132.3</td>
<td>446</td>
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</tbody>
</table>
Table 5.3  ANOVA for selected factorial model

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>P-Value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>8038.17</td>
<td>3</td>
<td>2679.39</td>
<td>1282.73</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>IM</td>
<td>3711.77</td>
<td>1</td>
<td>3711.77</td>
<td>1776.97</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>FR</td>
<td>183.17</td>
<td>1</td>
<td>183.17</td>
<td>87.69</td>
<td>0.0007</td>
</tr>
<tr>
<td>TR</td>
<td>4143.23</td>
<td>1</td>
<td>4143.23</td>
<td>1983.52</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Pure Error</td>
<td>8.36</td>
<td>4</td>
<td>2.09</td>
<td></td>
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</tr>
<tr>
<td>Cor Total</td>
<td>8046.53</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*α=0.05

Figure 5.3  Normal plot of residual for FWHM
5.5.3 Purity evaluation

Figure 5.5 shows TG/DTG graph of the induction thermal plasma-grown SWCNT in its original sheet-like soot form. TG clearly indicates a multi-step mass loss event terminated at temperatures over 700°C. For better understanding of such TG behavior, derivative (DTG) graph is also drawn in Figure 5.5. DTG reveals several peaks at a temperature range of 200-700 °C, overlapping each other in a narrow range and making deconvolution very difficult. It is also observed insufficient information about each peak to associate them to a proper carbonaceous material even with a fully deconvoluted DTG graph. In term of purity evaluation, it is necessary to identify each peak in DTG in order to quantify the amount of SWCNT in the sample. As long therefore as this ambiguity is present for DTG of SWCNT samples, the accurate purity evaluation is impossible and further analysis seems necessary. It is well-known that the carbonaceous materials are formed in a limited crystalline structure from amorphous to well-graphitized materials. The previous study on induction thermal
plasma-grown SWCNT confirmed the absence of the other different forms of carbonaceous material such as diamond, fullerenes and MWCNTs [Kim et al., 2009a]. Amorphous carbon, SWCNTs and graphitized particles are the only possible forms of carbonaceous material that are generally synthesized during induction thermal plasma process. Therefore, as soon as the TG behavior of each species being realized, their purity can be directly evaluated from DTG graph. In this regard, the next step was consequently TG conducted on the thermally-oxidized SWCNT sample with the results shown in Figure 5.6. The oxidizing environment at 350 °C ensures the removal of amorphous carbon from the sample [Scaccia et al., 2005; Shi et al., 1999] as shown by HRSEM images in Figure 5.7. In Figure 5.7b, the shapeless materials attributed to amorphous carbon were successfully removed from the sample. This is in total agreement with DTG results, shown in Figure 5.5: first two peaks appearing at 320 and 350 °C in DTG of as-produced SWCNT sample are disappeared in Figure 5.6. The selective oxidation process helps to accurately evaluate the amount of amorphous carbon from DTG of original sample. Next step, TG was performed on SWCNT samples treated with acid and the results are shown in Figure 5.8. The catalyst content is noticeably reduced and two low temperature peaks appear in DTG. The presence of these two peaks is attributed to the acid treatment process where the sample is immersed in the solution for a long period of time and subsequently being washed with de-ionized water for several times. The peak (1) located at the boiling point of water can be related to the remained moisture content while the peak (2) is highly attributed to the detachment of functional groups created during acid treatment process. Interesting observation from Figure 5.8, in comparison with Figure 5.6, is a noticeable decrease in the relative intensity of the last peak (7) and, a noticeable increase in the intensity of peaks (3, 4, 5, and 6) located between 400 to 600 °C. Figure 5.7c clearly indicates that the main species in the acid treated sample are SWCNTs along with the graphitic particles and catalysts which the latter are observed significantly brighter in the SEM image and remain as residual after TG. Consequently, it is reasonable to attribute the last peak in the DTG of original sample to these graphitic particles. It is well-known that the smaller-diameter SWCNT reacts at lower temperature in air based on a higher curvature strain [Borowiak-Palen et al., 2002; Landi et al., 2005]. Hence, other peaks above 400 °C are highly attributed to the burning of SWCNTs at different temperatures due to the wide diameter distribution of SWCNTs in the
sample. There is only a slight shift in the peak positions due to the noticeable decrease in the catalysts content after acid treatment.

Figure 5.5  TG/DTG graphs of as-produced SWCNT with induction thermal plasma

Figure 5.6  TGA/DTG graphs of thermally oxidized SWCNT sample at 350 °C
Figure 5.7 HRSEM images of induction thermal plasma-grown SWCNT at three different level of purities (a) as-produced sample (low purity) (b) thermally oxidized sample (mid purity) (c) sample treated with strong acid (high purity).

Figure 5.8 DTG graph of highly purified thermal-plasma grown SWCNT along with that of its Gaussian peaks. The graph is deconvoluted into 7 peaks.

By assigning all peaks in DTG of original SWCNT sample to a proper carbonaceous species, it is now possible to evaluate the purity of SWCNT from the under-curve surface of Gaussian-Lorentzian peaks in DTG. However, special care has to be considered due to the presence of nano-metric catalysts in the sample. TG of nano-metric yttrium oxide and Ni catalysts are
depicted in Figure 5.9. Ni catalyst exhibits an expected behavior during TG through gaining 23% mass due to its oxidation. The highest oxidation rate appears at a temperature of 382°C which overlaps the peak associated to amorphous carbon in TG of original SWCNT sample, shown in Figure 5.5. However, the small initial amount of Ni in the feedstock material (0.6 at. %) gains only 1.2 wt. % at this temperature. Contradictory to Ni catalyst, TG of nano-Y$_2$O$_3$ exhibits 6% mass loss in the oxidizing environment. By taking into account the initial amount of Y$_2$O$_3$ in starting feed stock material (0.4 at. %), its individual mass loss results in a total mass loss of 0.5 wt. % for the original SWCNT sample. A simple calculation indicates that about 1 wt. % mass gain is achieved during TG of original SWCNT sample with nano-metric catalysts (Ni+Y$_2$O$_3$). Such a mass gain must be subtracted from the total mass loss when the purity is evaluated. The contribution of nano-metric catalysts in the final result of TG is more considerable when their content is considerably high in the SWCNT sample and this mass gain/loss attributed to the nano-catalysts affects the accuracy of the results.

Figure 5.9  TGA of nano-metric nickel (<100nm) along with that of yttrium oxide (<50 nm)
5.6 Conclusions

Statistical study clearly showed that TG experimental conditions such as initial mass of sample, temperature ramp and gas flow rate significantly affect the final results. The first two factors have a positive effect while the last one has a negative effect on FWHM and the TG results are affected more noticeably by first two factors. Other parameters such as sample morphology and moisture content have shown negligible effect on the TG results of SWCNT materials implying less sensitivity of TG to the sampling conditions than those of instrumental conditions. It was eventually shown that TG combined with HRSEM has a potential for purity evaluation of SWCNT materials with complex behaviors. In this case, TG was performed on SWCNT samples at three different levels of purity to study the multiple mass loss events of the induction plasma-grown SWCNT sample leaded to fully deconvolute its DTG graph. In addition, the presence of nano-metric catalysts in the SWCNT sample clearly showed a total of 1 % mass gain which has to be subtracted from the total mass change in TG. Regarding the type of catalysts, they can gain or lose mass during TG. This mass change is entirely related to the type and initial amount of catalysts in the feed stock material so that the higher the amount of catalysts, the higher mass change is observed.

Acknowledgment This work was partially supported by Le Fonds québécois de la recherche sur la nature et les technologies (FQRNT) and the Natural Sciences and Engineering Research Council (NSERC) of Canada. The author would like to thank Dr.Alireza Hekmat for proof reading of this article.
CHAPTER 6. Counter-current ammonia injection flow during synthesis of single-walled carbon nanotubes by induction thermal plasma

Avant-propos

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Contribution to the document: Ali Shahverdi performed the experimental works, thermodynamic calculations, numerical simulation as well as drafting of the manuscript under supervision of Porf. G. Soucy. This article contributes to the thesis by developing a methodology for the in situ chemical modification of SWCNTs using induction thermal plasma (ITP) system. The results obtained in the fourth chapter clearly indicated the possibility of using a non-toxic feedstock material (i.e., Ni+Y₂O₃+CB) for the synthesis of high quality SWCNT material using the ITP method. Therefore, those findings enabled to further investigate the possibility of performing the in situ chemistry process on SWCNTs. The main contributions of the present article to the thesis are the investigation of the ammonia thermal decomposition behavior in the ITP reactor, studying different experimental conditions of the proposed in situ chemistry process and their effects on the SWCNT final product, and
also studying theoretically the effect of the ammonia mixing process in the ITP reactor by performing a 3D numerical simulation.

In addition to the synthesis tests presented in this article, some other tests were also performed in order to examine other probe designs. These synthesis experiments are summarized in the Table 1. Different types of the nozzle are shown in Chapter 3, in Figure 3.3.

Table 1

<table>
<thead>
<tr>
<th>Test ID</th>
<th>Probe design</th>
<th>Probe position (cm)</th>
<th>Heating wall (cm)</th>
<th>( \text{dNH}_3 ) (vol %)</th>
<th>N content* (%)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAS19</td>
<td>2 mm</td>
<td>30.0</td>
<td>0</td>
<td>5</td>
<td>&lt; 0.2</td>
<td>900</td>
</tr>
<tr>
<td>PAS22</td>
<td>1 mm</td>
<td>30.0</td>
<td>4</td>
<td>5</td>
<td>&lt; 0.2</td>
<td>1025</td>
</tr>
<tr>
<td>PAS23</td>
<td>(a)</td>
<td>40.0</td>
<td>4</td>
<td>5</td>
<td>&lt; 0.2</td>
<td>850</td>
</tr>
<tr>
<td>PAS25</td>
<td>(b)</td>
<td>40.0</td>
<td>0</td>
<td>5</td>
<td>0.30</td>
<td>-</td>
</tr>
<tr>
<td>PAS32</td>
<td>(d)</td>
<td>40.0</td>
<td>7</td>
<td>10</td>
<td>0.53</td>
<td>300-400b</td>
</tr>
<tr>
<td>PAS33c</td>
<td>(d)</td>
<td>40.0</td>
<td>7</td>
<td>0</td>
<td>-</td>
<td>900</td>
</tr>
</tbody>
</table>

* Temperature data not saved by Labview  
\( ^{b} \) Error in temperature reading  
\( ^{c} \) Only Ar was injected  
* SD < 0.01

In test PAS33, only Ar (15 slpm) was injected into the synthesis system to investigate whether the local cooling caused by counter-current injection of gas degrades the quality of SWCNTs or not. The Raman spectroscopy however, indicated that the SWCNTs quality is not degraded.

**Titre français**:

Injection d'ammoniac à contre-courant durant la synthèse des nanotubes de carbone mono-parois par plasma thermique inductif.

**6.1 Résumé**

La production importante de nanotubes de carbone mono-paroi (SWCNTs) a été rendue possible par l'injection de la matière première solide dans le plasma thermique d'Ar-He généré par la torche à induction à haute fréquence. La nature non réactive du plasma d'Ar-He et du carbone solide cause la formation de suie de SWCNTs, cette dernière étant insoluble dans de nombreux solvants et mal intégrée dans les matrices polymériques. Pour mieux comprendre
les effets d'un environnement de synthèse réactif sur les SWCNTs, l'ammoniac gazeux (NH₃) a été injecté à contre-courant dans le jet de plasma par différentes buses à différentes positions dans le réacteur. L'analyse Raman a montré que la qualité des SWCNTs est modifiée de façon évidente lors de l'injection d'ammoniac. L'analyse élémentaire de l'azote sur les échantillons des SWCNTs montre une augmentation maximale de la concentration de 10 fois après injection de NH₃. L'imagerie MET a montré la présence d'une nanostructure du carbone en oignon et planaire dans l'échantillon des SWCNTs obtenus après l'injection de NH₃ (15 vol %). Une amélioration de la dispersion à long terme a été observée pour l'échantillon de SWCNT traité par NH₃ dans le diméthylformamide et l'isopropanol. Enfin, pour établir des réactions ainsi que des espèces possibles à l'état d'équilibre et pour mieux comprendre l'influence de l'utilisation de la buse dans le processus d'injection de NH₃ sur le champ d'écoulement thermique du réacteur à plasma thermique inductif, le système de synthèse a été simulé par un calcul thermodynamique ainsi qu'une méthode CFD (computaitonal fluid dynamic, en anglais), respectivement.

6.2 Abstract

Mass production of single-walled carbon nanotubes (SWCNTs) has been enabled through introducing of solid feedstock into the Ar-He thermal plasma generated by radio-frequency induction torch. The non-reactive nature of Ar-He plasma and solid carbon result in formation of pristine SWCNT final product soot which in the first place is insoluble in many solvents and poorly incorporated in polymers matrix. To better understand the effects of reactive synthesis environment on the SWCNTs material, ammonia gas (NH₃) was counter-currently injected into the main plasma stream with different nozzles and at different positions in the reactor. Raman analysis showed that the quality of SWCNTs was evidently altered upon the ammonia injection. The nitrogen elemental analysis on the SWCNT samples revealed a maximum of 10-fold increase after NH₃ injection. TEM imaging showed the presence of onion like and planar carbon nanostructure in the SWCNT sample obtained after the highest NH₃ concentration (15 vol %). A long-term dispersibility enhancement was observed for the NH₃-treated SWCNT sample in dimethylformamide and isopropanol. Finally, to clarify possible reactions and species at equilibrium state and to better understand the influence of use of
nozzle in the NH$_3$ injection process on the thermo-flow field of the induction thermal plasma reactor, the synthesis system was simulated through a thermodynamic calculation and computational fluid dynamic (CFD) method, respectively.

**Keywords:** Single-walled carbon nanotube, ammonia, synthesis, induction thermal plasma

### 6.3 Introduction

Since its discovery by Iijima [Iijima and Ichihashi, 1993] and Bethune [Bethune et al., 1993], many efforts have been made on the synthesis of single-walled carbon nanotube (SWCNT) owing to its very extraordinary mechanical, thermal and electrical properties [Popov, 2004]. By taking advantage of those extraordinary properties many applications have been developed for the SWCNTs materials in various fields such as polymers [Ci et al., 2008; Sambarkar et al., 2012], biomedical [Fadel et al., 2010; Zanello et al., 2006], sensors [Cao and Rogers, 2009; Genest et al., 2012], microelectronic devices [Baughman et al., 2002], and catalyst supports [Shen et al., 2008]. Since the first SWCNT synthesis method by arc discharge [Iijima and Ichihashi, 1993], many other synthesis methods have been proposed and developed. In general, these methods can be divided in two main categories: low-temperature and high-temperature methods. Low-temperature methods have been mainly developed based on the direct decomposition of hydrocarbons or other gases containing carbon atoms in relatively low-temperature (500-1 100 °C) environment. Chemical vapour decomposition (CVD) [Dai et al., 1996; Kumar and Ando, 2010] processes can be placed in this category. On the other hand, high-temperature methods are based on direct evaporation of carbonaceous materials. Since the evaporation temperature of carbon in solid phase (mainly graphite) is very high (i.e., T$_{\text{sub}}$=3 600 °C), these synthesis systems need to provide a very high temperature environment which has to be followed by a rapid cooling process in order to bring the generated vapour to supersaturation state for the effective nucleation of catalysts/SWCNTs. To achieve a high production yield, the evaporation rate and yield have to be very high so that a very demanding source of power is needed to bring the solid materials to the gas phase. Arc discharge, laser-ablation [Thess et al., 1996] and induction thermal plasma (ITP) [Kim et al., 2007] methods can be placed in this category. In these methods, the temperature exceeds several thousand Kelvin which most of the time forces to use an inert environment (inert
gases). At these temperatures, most species are indeed excited and highly reactive. As such, they could react directly with SWCNT precursors (i.e., C, C_2, C_3, ... ) suppressing the effective nucleation and growth of SWCNT and producing unwanted by-products. Accordingly, the result is a drastic reduction in the yield of synthesis process. Consequently, Ar and He have become most favourable noble gases for high quality production of SWCNT using high-temperature methods. The non-reactive nature of these noble gases together with intrinsic chemical property of carbon in solid phase results in formation of SWCNTs which in the first place are insoluble in many solvents and poorly incorporated in polymer matrices [Hirsch, 2002]. Therefore, any enhancement in dispersibility and processability of SWCNTs materials is expected to improve their possible use in many applications.

Up to now, no systematic study has been performed in order to investigate the effect of reactive gas on the synthesis of SWCNTs-containing soot by high-temperature methods and specifically ITP method. The main goal of this article is to investigate the possible influences that a highly reactive synthesis environment can make on the SWCNTs material and their synthesis process. Therefore, in this work ammonia (NH_3) was selected as reactive gas to be studied in ITP system used for the large-scale production of SWCNTs material. Since NH_3 is a relatively simple molecule constructed only with N and H atoms, the unwanted by-products are expected to be limited. Moreover, the presence of N and H atoms in the structure of CNTs materials has been shown to improve their processability and chemical property which in turn can develop their effective use in many applications such as polymer composites and nanoelectronic devices [Pantarotto et al., 2004; Ramanathan et al., 2005b; Singh et al., 2005]. It has been shown that the soft ion bombardment and harsh chemical conditions (e.g., thermal oxidation, HNO_3 reflux) can introduce disordered carbon atoms (defects) on the sidewall of carbon nanotubes. Since defects are expected to serve as anchor groups for further modification on the surface of SWCNTs, and to be important in the covalent chemistry of SWCNTs, they can be, with a limited tolerance [Chen et al., 2001a; Hamon et al., 1999], considered as promising starting points in further development of SWCNTs chemistry.

For better understanding the effects of reactive environment on the SWCNT synthesis, NH_3 gas was injected counter-currently into the main SWCNTs synthesis flow at two different
positions in the plasma reactor through two different injection nozzle designs and at three different flow rates. Taking into account the formation of reactive species through the decomposition of ammonia, this quantity was measured during the synthesis process by means of Mass spectroscopy (MS). Synthesized SWCNT samples in the presence of NH\textsubscript{3} reactive gas were then characterized by Raman spectroscopy, transmission electron microscopy (TEM) and Nitrogen elemental analyzer in order to evaluate the effect of NH\textsubscript{3} on the structural quality, morphology and chemical composition of SWCNT soot, respectively. Furthermore, the synthesis reaction system of SWCNT in presence of NH\textsubscript{3} was modeled based on thermodynamic calculations and the results were then compared to the experimental results. Finally, thermo-flow field of ITP synthesis system was numerically modeled after NH\textsubscript{3} counter-current injection with and without nozzle in three-dimensions (3D).

6.4 Thermodynamic calculation

The system of C/Ni/Y\textsubscript{2}O\textsubscript{3}/S (97.7, 1.2, 0.4, 0.7 at %) and NH\textsubscript{3} was considered for thermodynamic calculation. Since the inert gases (He, Ar) do not contribute in the reaction at the temperature window that was considered in this calculation (500–5 000 K), they were not taken into account in the calculation. The primary goal of this calculation was to estimate the effect of NH\textsubscript{3} injection on the final product of SWCNT synthesis and then to predict the formation of reactive species and gaseous by-products in the synthesis system. The FACTSAGE 6.3 software code was employed for the thermodynamic equilibrium calculations at a constant total pressure of 66.6 kPa. For the calculation, FactPS and FSstel databases were applied. NH\textsubscript{3} gas stream was added to the calculation at a temperature lower than 2 000 K. Sulphur (S), the impurity of carbon black, was also considered in the calculation because its effect on the synthesis of SWCNT has been observed previously in another study [Alinejad et al., 2010].

6.5 Experimental setup and procedure

SWCNT was synthesized by means of an induction thermal plasma (ITP) system developed for large-scale (kg/day) production [Kim et al., 2007]. For the use of reactive gas in the synthesis process the unit has been modified as illustrated in Figure 6.1. Helium (He) as a
sheath gas and Argon (Ar) as central and feedstock carrier gas were injected into radio-frequency (RF) induction torch (TEKNA-PS50) to form the high energy density plasma using a plate power (i.e., the power provided by the generator to the torch) of ~ 45 kW. The feedstock material was prepared from a mixture of CB (Monarch-280, 45 nm), Ni (Sigma-Aldrich, 2 μm) and Y$_2$O$_3$ (Cerac, 2-4 μm) and then introduced by means of a commercial powder feeder via Ar gas line into the plasma torch. The injected feedstock interacts with the thermal plasma ($T > 10^4$ K) [Kim et al., 2009b] and consequently vaporizes. The generated vapour continues its journey along with the plasma into a water cooled cylindrical reactor with an interior wall made of graphite which is used to enhance the thermo-flow field and to increase the temperature profile inside the ITP reactor. A sudden gas expansion along with high cooling water rate circuit around the reactor wall provides a very high gas cooling rate ($10^5$–$10^6$ K/s) [Kim et al., 2009b] which is necessary for rapid supersaturation of vapour results in a sufficient driving force for the nucleation of the metal nanoparticles followed by SWCNTs nucleation. A suitable temperature profile along the axis of the reactor, then allows SWCNTs to continue their growth from the nucleation sites to several micrometers. The final soot product is then separated from the gas phase by means of a filtration system and recovered in a form of flexible sheet. The synthesis unit and the operating condition applied for this study are depicted in Figure 6.1 and Table 6.1, respectively.
NH\textsubscript{3} in gas form was counter-currently injected into the reactor during the synthesis of SWCNT. For effective NH\textsubscript{3} injection and avoiding untimely decomposition, an adjustable water cooled probe was employed enabling for NH\textsubscript{3} injection in a desired place in the reactor. In synthesis experiments, as summarized in Table 6.2, a non-water cooled interchangeable tube with internal diameter of 1 mm was inserted into the water-cooled injection probe (ID=2 mm) to increase the temperature of NH\textsubscript{3} via \textit{in situ} preheating process for a better
decomposition yield. The inlet of ammonia injection probe is indicated in Figure 6.1. NH\textsubscript{3} was introduced into the reactor via two different nozzles attached to the tip of the non-water cooled interchangeable tube: (1) confined nozzle with 1 mm cross-sectional diameter and (2) wide nozzle with 20 mm cross-sectional diameter, shown in Figure 6.1. Temperature close to the NH\textsubscript{3} injection point (2-3 cm above the tip of the nozzle) was simultaneously measured by K-type thermocouple. Prior to the quantification of gaseous species by using MS, MS was calibrated according to the manufacturer procedure. For quantification of NH\textsubscript{3} decomposition yield, the following formula was used:

\[
\% \text{ d-NH}_3 = \frac{\text{vol} \% \text{ NH}_3 \text{ injected} - \text{vol} \% \text{ NH}_3 \text{ read by MS}}{\text{vol} \% \text{ NH}_3 \text{ injected}} \times 100
\]  

(6.1)

where d-NH\textsubscript{3} denotes decomposed-NH\textsubscript{3}. For detection of gaseous species the exhaust gas was monitored by MS in qualification mode. The experimental conditions of SWCNTs synthesis in presence of the NH\textsubscript{3} injection is summarized in Table 6.2.

Table 6.2  
Experimental conditions of high temperature NH\textsubscript{3} injection during the synthesis of SWCNT by induction thermal plasma

<table>
<thead>
<tr>
<th>Run</th>
<th>Nozzle type</th>
<th>Nozzle position (^a) (cm)</th>
<th>Heating wall (^b) (cm)</th>
<th>NH\textsubscript{3} (^c) (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>40.0</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>44.5</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>44.5</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>44.5</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>44.5</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>40.0</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>7*</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) From base of reactor  
\(^b\) The length of ammonia injection probe from the tip which is not water cooled  
\(^c\) SWCNT synthesis test without NH\textsubscript{3} injection

Prior to the SWCNTs synthesis experiment, preliminary NH\textsubscript{3} injection tests were performed to study the behaviour of NH\textsubscript{3} decomposition in the ITP reactor without feedstock injection. The experimental conditions and the obtained results are summarized in Table 6.5. It should be mentioned that for these series of tests, the NH\textsubscript{3} injection was performed counter-currently
using the water-cooled probe having an ID of 2 mm and with no nozzle at its tip (simple injection).

For the characterization purposes, the SWCNT samples were closely examined with elemental analyzer (TCH-600, LECO) for nitrogen (N) content measurement, Raman spectroscopy at 514.5 nm excitation wavelength for structural and quality assessment and Transmission electron microscopy (TEM, H750, Hitachi) for the morphological assessment. Online Mass spectroscopy using a Quadrupole mass spectrometer (ThermoStar, Balzers instruments) was performed in quantification (QC) and qualification (QL) modes during the process. Samples for Raman analysis were prepared from the solution by sonicating approximately 0.5–1 mg of SWCNTs material in ~1ml of acetone. Prior to the nitrogen elemental analysis, the samples were degassed under vacuum (P< 10⁻⁴ kPa) at 50 °C.

6.6 Computational fluid dynamic (CFD) model

The thermo-flow field of ITP system in the NH₃ injection zone was numerically modelled in 3-dimensional (3D) based on the following assumptions: i) steady-state; ii); negligible viscous dissipation and pressure work terms in the energy equation; iii) incompressible and temperature-dependent mass density; and v) turbulent flow. According to aforementioned assumptions, the fluid dynamic equations are described by steady-state conservation equations for the transport of mass, momentum, energy, and concentration of species as summarized in Table 6.3. The use of magneto-hydrodynamic equations in the model becomes useless since the electric and magnetic fields in this region of ITP system are deficient and can be neglected. The computational domains considered in the simulation work are illustrated in Figure 6.2, and consists of a tubular reactor and a water-cooled injection probe (with and without nozzle) placed at the centre. The boundary conditions applied for this 3D simulation are summarized in Table 6.4. The material properties such as density, viscosity, thermal conductivity, and specific heat were obtained from [Boulos et al., 1994; McBride et al., 1993]. To calculate the material mixture properties and specific heat, mass-weighted mixing and mixing laws were employed, respectively. The diffusion coefficients in the mixture were calculated for each species based on the kinetic theory considering the modified Chapman equations using Lenard-Jones (L-J) parameters. The 3D numerical simulations have been then performed using
academic ANSYS®FLUENT code. In the code, the governing equations are transformed into finite different equations and then solved by the SIMPLE-like pressure correction algorithm. The conservation equations for the thermo-fluid fields were solved by basic modules in ANSYS/FLUENT v.13.

Figure 6.2 Computational domains considered for CFD calculations (a) no nozzle, (b) 20 mm nozzle shown in Figure 6.1
### Table 6.3 Governing equations used in the 3D simulation

<table>
<thead>
<tr>
<th>Model</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass conservation</td>
<td>$\nabla \cdot (\rho \mathbf{u}) = 0$</td>
</tr>
<tr>
<td>Momentum conservation</td>
<td>$\nabla \cdot (\rho \mathbf{uu}) = -\nabla p + \nabla \cdot \mathbf{\tau}$</td>
</tr>
<tr>
<td>Energy conservation</td>
<td>$\nabla \cdot (\rho \mathbf{uh}) = \nabla \cdot \left( \frac{k_{\text{eff}}}{C_p} \nabla T \right)$</td>
</tr>
<tr>
<td>Turbulent Kinetic energy</td>
<td>$\nabla \cdot (\rho \mathbf{uK}) = \nabla \cdot \left( \mu + \frac{\mu_t}{Pr_e} \nabla K \right) + G_t - \rho \varepsilon.$</td>
</tr>
<tr>
<td>Dissipation rate</td>
<td>$\nabla \cdot (\rho \varepsilon) = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{Pr_e} \right) \varepsilon \right] + \frac{\varepsilon}{K} (C_t \varepsilon - C_\varepsilon \rho \varepsilon)$.</td>
</tr>
<tr>
<td>Effective viscosity/thermal conductivity</td>
<td>$\mu_{\text{eff}} = \mu + \mu_t$, $k_{\text{eff}} = k + k_t$.</td>
</tr>
<tr>
<td>Turbulent viscosity/thermal conductivity</td>
<td>$\mu_t = \rho C_p \frac{K^2}{\varepsilon}$, $k_t = \frac{\mu_t C_p}{Pr_e}$.</td>
</tr>
<tr>
<td>Species conservation</td>
<td>$\nabla \cdot (\rho \mathbf{uY}_i) = \nabla \cdot \left( \rho D_i + \frac{\mu_t}{Sc_t} \nabla Y_i \right)$</td>
</tr>
</tbody>
</table>

### Table 6.4 Boundary conditions applied in 3D simulation

<table>
<thead>
<tr>
<th>Boundary type</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet-Temperature, mass</td>
<td>$T = 2200 \text{ K}, 0.00125 \text{ kg/s}$</td>
</tr>
<tr>
<td>Inlet-gas composition</td>
<td>He : 135 slpm, Ar: 30 slpm</td>
</tr>
<tr>
<td>Wall-Temperature</td>
<td>$T = 1073 \text{ K}$</td>
</tr>
<tr>
<td>NH$_3$ -Temperature</td>
<td>$T = 300 \text{ K}$</td>
</tr>
<tr>
<td>NH$_3$ inlet-without Nozzle</td>
<td>2 mm ID</td>
</tr>
<tr>
<td>NH$_3$ inlet-with Nozzle</td>
<td>41(holes)x0.18 mm ID</td>
</tr>
<tr>
<td>NH$_3$ inlet -mass</td>
<td>0.0003887 kg/s</td>
</tr>
<tr>
<td>NH$_3$ inlet-gas composition</td>
<td>NH$_3$: 9 slpm, Ar: 10 slpm</td>
</tr>
<tr>
<td>Outlet</td>
<td>Pressure outlet</td>
</tr>
</tbody>
</table>

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6.7 Results and discussion

6.7.1 Thermodynamic calculation results

Figure 6.3 shows the equilibrium composition for the mixture system of C/Ni/Y2O3/S/NH3. From the equilibrium diagram, the two main products of NH3 decomposition in the reaction system are expected to be H2 and N2. Although increasing the temperature of reacting system results in increasing the yield of NH3 decomposition, the changes in decomposition yield seem to be greater at low temperature than high temperature regions, as shown in Figure 6.3, indicating less sensitivity of decomposition reaction to T > 1300 K at equilibrium state. By a close look at the equilibrium diagram, it is evident that introducing a reactive component (i.e., NH3) to the reaction system will result in formation of other intermediate reactive species containing N/H atoms such as H(g), NH2(g), NiH (g), NH (g), etc. According to Figure 6.3, many of these species are well below 10^{-10} mole in the reaction system and their effect on the SWCNT production seems to be thermodynamically negligible. As seen in Figure 6.3, the yield of NH3 decomposition at temperature over 900 K is close to 100% resulting in the stoichiometric formation of N2 and H2 via 2NH$_3$ $\rightarrow$ N$_2$+3H$_2$ reaction. Since the proposed kinetic mechanisms for thermal decomposition of NH3 suggest that it is highly dependent on the formation of amidogen (NH$_2$) in the reaction system [Fateev et al., 2005; Nishida et al., 2001; Rahinov et al., 2003], and the higher concentration has been reported from the experimental observation for amidogen [Rahinov et al., 2003], it is expected that the NH3 decomposition in the ITP reactor is more kinetically than thermodynamically controlled. Therefore, the thermodynamic calculation results are expected to explain the reaction system more qualitatively than quantitatively and any correlation between mole fraction of species in thermodynamic model and in actual reaction system is misleading. The thermodynamic calculation predicts the presence of CO, CO$_2$, CH$_4$ and HCN in the reaction system.
Further investigation was performed on thermodynamic calculation of the solid phase and the main results are brought into a diagram as illustrated in Figure 6.4a. For comparison purpose, XRD pattern of SWCNTs sample is presented in Figure 6.4b. The presence of Ni and Y$_2$O$_3$ in the final product has been perfectly predicted by thermodynamic calculation as XRD result indicates their presence in the SWCNTs final product. However, the prediction of the presence of YS, Ni$_3$S$_2$, Y$_2$S$_3$ in the final product is not in line with the XRD result implying that their formation is only thermodynamically favourable. According to the characteristic of ITP reactor, the cooling rate is so high that the equilibrium reaction condition of sulphur with catalysts is not satisfied. An interesting observation from both thermodynamic calculation and XRD analysis is the absence of metal-nitrogen compound such as nickel nitrate in the SWCNTs final product. This suggests that the NH$_3$ cannot interrupt the growth of SWCNT in the reactor by reacting with the catalysts. The peculiar observation in Figure 6.4a is the disappearance of graphite (C) at temperatures below 800 K which is not in line with the XRD results. By looking at Figure 6.3, at the same temperature as disappearance of C, the increase of CH$_4$ in the reaction system stops. Although the complete reaction of C with hydrogen containing species is thermodynamically favourable, because of the same reason as explained
for the reaction of sulphur with catalysts, the complete transformation of carbonaceous solid product containing SWCNTs to CH₄ is not experimentally favourable.

![Graph](image)

Figure 6.4 (a) Solid phase thermodynamic equilibrium compositions for a mixture system of C/Ni/Y₂O₃/S/NH₃ at 66.6 kPa (b) XRD pattern of SWCNT sample

6.7.2 Experimental results

To study the behaviour of NH₃ decomposition in the ITP system, without feedstock injection, the ITP system was run at different plate powers while NH₃ was injected at different flow rates. In these series of experiments, the injection of NH₃ into ITP system was performed without any nozzle through the water cooled cylindrical probe. While monitoring the temperature of gas stream at 2-3 cm above the injection point, the amount of NH₃ in the exhaust gas was quantified with MS and the results are summarized in Table 6.5.

Table 6.5 Decomposition history of NH₃ in ITP system at different plasma powers without feedstock injection

<table>
<thead>
<tr>
<th>Run</th>
<th>NH₃ (vol %)</th>
<th>Plasma net power (kW)</th>
<th>T_avg. (°C)</th>
<th>d-NH₃ a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1'</td>
<td>5</td>
<td>31.5</td>
<td>920</td>
<td>85</td>
</tr>
<tr>
<td>2'</td>
<td>10</td>
<td>31.5</td>
<td>895</td>
<td>74</td>
</tr>
<tr>
<td>3'</td>
<td>2.7</td>
<td>31.5</td>
<td>940</td>
<td>88</td>
</tr>
<tr>
<td>4'</td>
<td>5</td>
<td>28.0</td>
<td>884</td>
<td>78</td>
</tr>
<tr>
<td>5'</td>
<td>5</td>
<td>21.7</td>
<td>854</td>
<td>50</td>
</tr>
<tr>
<td>6'</td>
<td>2.7</td>
<td>21.7</td>
<td>820</td>
<td>41</td>
</tr>
<tr>
<td>7'</td>
<td>5</td>
<td>21.7</td>
<td>805</td>
<td>45</td>
</tr>
</tbody>
</table>

a d-NH₃ = decomposed- NH₃
From the results in Table 6.5, it is evident that the decomposition of NH₃ is tightly related to the plasma power, which is in good agreement with previous studies [Soucy et al., 1995], where the lower the plasma power is, the smaller yield of decomposition is achieved. Given that the main source of heat is the plasma, therefore lowering the plasma power results in a noticeable drop in the temperature profile of the reactor and especially in the region where NH₃ decomposition takes place. At constant plasma power (Run 1'-3'/Run 5'-7'), NH₃ decomposition yield seems to be dependent on the NH₃ flow rate with a higher dependency at higher flow rates. Since the injection is counter-current to the plasma stream, the initial velocity of injected NH₃ plays an important role in bulk delivery of NH₃ through the plasma reactor. Comparing the result of Run 5' and 7', it is also obvious that small decrease in the temperature (~50 °C) diminished the yield of decomposition by 5% which indicates the sensibility of NH₃ decomposition rate to the temperature profile. Comparing the data provided in Table 6.5 to those in Figure 6.3, one can see that even at temperatures much higher than 900 K, the 100% decomposition yield, predicted by thermodynamic calculation, cannot be achieved owing to system configuration and the non-equilibrium characteristic of ITP process. To quantify the decomposition of NH₃ during the SWCNT synthesis process and to identify the gaseous products, MS was performed in QC and QL modes and the results are depicted in Figure 6.5 and Figure 6.6, respectively. For identifying each peak in the spectra obtained in QL mode, the thermodynamic calculation results shown in Figure 6.3 was taken into account. Figure 6.5 shows a typical MS data obtained during the synthesis of SWCNT while NH₃ is injected. The fluctuation in the concentration of gas species and specially NH₃ is totally in accordance with the observed temperature fluctuation in the synthesis system. This fluctuation results from the variation in feed rate of the feedstock material. This observation implies that even low mass change of the feedstock in the plasma reactor affects directly the thermo-flow field of synthesis system. As shown in Figure 6.5, upon the introduction of feedstock material into the plasma, the decomposition yield of NH₃ decreases because of the change in the thermo-flow of the plasma subsequent to vaporization/nucleation process.
Figure 6.5 Concentration profile of Ar, He and NH$_3$ in the exhaust gas quantified by mass spectrometer during NH$_3$ injection process.

Figure 6.6 shows typical mass spectrums, in QL mode, obtained before and after injection of NH$_3$ into the SWCNT synthesis system. Upon NH$_3$ injection, the intensity of features at m= 4 (He) and 40 (Ar) is decreased because of the dilution effect. The appearance of a new species in the spectrum after NH$_3$ injection is detectable at m= 27. Taking into account the possible species in the reaction system from thermodynamic calculation, this feature can be assigned to the hydrogen cyanide (HCN). This observation suggests the possibility of unwanted side reaction between reactive species created during decomposition of NH$_3$ and carbonaceous materials during the synthesis of SWCNT. However, regarding the relatively weak signal of HCN, the reaction is considered to be less favourable. Multiple features at m=15–20 before and after NH$_3$ injection can be assigned to H$_2$O and H$_2$O/NH$_3$, respectively. Two features at m=16 and 17 become stronger after NH$_3$ injection; therefore they can be possibly assigned to CH$_4$ and the undecomposed NH$_3$ gas, respectively as also predicted by thermodynamic calculation. The presence of the feature at m=28 before injection of NH$_3$ can be readily assigned to carbon monoxide (CO) as predicted by thermodynamic calculation and also N$_2$ which is present in the whole experimental system because of the very low air leak. Two features at m=2 and 28 arise from H$_2$ and N$_2$, respectively which are both product of NH$_3$ decomposition. Weak features at m=32 and 44 are appointed to O$_2$ and CO$_2$, respectively. The
presence of these two oxygen-based gases without any external source of oxygen is attributed to \(^\text{Y}_2\text{O}_3\) which exists in the starting feedstock material. \(^\text{Y}_2\text{O}_3\) is decomposed in the very high temperature plasma region to its constituent elements. The intermediate species shown in the thermodynamic calculation results in Figure 6.3, cannot be observed experimentally because of their high reactivity nature and fast recombination. Therefore, they are expected to be in a non-equilibrium state and their existence in the reaction system is highly time-dependent. Therefore, it is not expected to observe them in the exhaust gas which is far from the \(\text{NH}_3\) injection point in the synthesis system.

![Mass spectra of the SWCNT synthesis exhaust gas before (solid) and after (dashed) injection of \(\text{NH}_3\) into the induction thermal plasma system](image)

Figure 6.6  Mass spectra of the SWCNT synthesis exhaust gas before (solid) and after (dashed) injection of \(\text{NH}_3\) into the induction thermal plasma system

Informative data obtained after each SWCNT synthesis experiment, previously mentioned in Table 6.2, are summarized in Table 6.6. In addition to the yield of decomposition, temperature at \(\text{NH}_3\) injection point (2-3 cm above the tip of nozzle) was also measured. The recovery yield of SWCNT product after each experiment was calculated to study the reactivity of \(\text{NH}_3\) with
carbonaceous products. The final product of each experiment was then analyzed with the nitrogen elemental analyzer and the results are presented in Table 6.6.

Table 6.6 Elemental nitrogen content in the SWCNT samples after exposed to ammonia during synthesis process

<table>
<thead>
<tr>
<th>Run</th>
<th>Recovery (%)</th>
<th>T_avg (°C)</th>
<th>d-NH$_3$ (°)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53</td>
<td>1071</td>
<td>74</td>
<td>0.3</td>
</tr>
<tr>
<td>2</td>
<td>72</td>
<td>955</td>
<td>49</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>62</td>
<td>1050</td>
<td>64</td>
<td>0.8</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
<td>1081</td>
<td>52</td>
<td>1.2</td>
</tr>
<tr>
<td>5</td>
<td>85</td>
<td>854</td>
<td>47</td>
<td>0.8</td>
</tr>
<tr>
<td>6</td>
<td>90</td>
<td>590</td>
<td>44</td>
<td>1.1</td>
</tr>
<tr>
<td>7*</td>
<td>100</td>
<td>750$^c$</td>
<td>N/A</td>
<td>0.1</td>
</tr>
</tbody>
</table>

$^a$ d-NH$_3$ = decomposed NH$_3$, $^b$ SD < 0.01, $^c$ T at 30 cm from the base of reactor, * without NH$_3$ injection

Figure 6.7 shows the normalized Raman spectra obtained from raw SWCNT containing soot and those exposed to high temperature NH$_3$ stream during their synthesis. Three main features of SWCNTs are clearly observed in Figure 6.7. The first feature at low frequency ranges (100–250 cm$^{-1}$) is because of the radial breathing mode (RBM) of SWCNTs which is the genuine proof for their presence in the synthesized soot. Disorder mode feature, so-called D-band, arising from sp$^3$ carbon atoms, is present in the range of 1250–1450 cm$^{-1}$. The most intense feature in the 1515–1590 cm$^{-1}$ region is assigned to the tangential mode, also known as G-band [Dresselhaus et al., 2005]. The increased ratio of D-band intensity to the G-band intensity is widely accepted as arising from the increased number of sp$^3$ hybridized carbon atoms in the hexagonal framework of the SWCNT [Bahr and Tour, 2001; Georgakilas et al., 2002]. As shown in Figure 6.7, D-band feature of all samples has been altered and increased after NH$_3$ injection compared to the reference sample at run 7. This observation suggests that NH$_3$ is enough reactive to attack the SWCNTs surface directly or indirectly via its decomposition intermediate species mainly such as NH$_2$, NH, H [Chellappa et al., 2002; Cooper and Ljungstrom, 1988; Rahinov et al., 2003; Varey et al., 1971]. In any cases, the electron-phonon coupling and electronic structure in SWCNT are changed which is reflected
in the intensity of D-band [Dresselhaus et al., 2002]. The increased content of N, shown in Table 6.6 can arise from the chemicals moieties in the SWCNT samples. For the samples with lower N content and higher D-band it is expected that the process introduced more vacancy defects (i.e., the absence of some carbon atoms in the SWCNT structure) than chemical moieties on the wall of SWCNTs. The Raman spectrum of the sample obtained with run 6 shows the lowest intensity D-band among other samples compared to the raw sample while it has the highest recovery yield and high N content. This suggests that the condition in run 6 is the most suitable condition for such high temperature treatment of SWCNTs by NH$_3$.

![Raman spectra for raw SWCNT (run=7) and that exposed to high temperature NH$_3$ (run=1–6). The spectra are normalized to the G-band and sorted in order of D-band intensity ($\lambda_{ext} = 514.5$ nm)](image)

Figure 6.7 Raman spectra for raw SWCNT (run=7) and that exposed to high temperature NH$_3$ (run=1–6). The spectra are normalized to the G-band and sorted in order of D-band intensity ($\lambda_{ext} = 514.5$ nm)

As seen in Table 6.6, the decomposition yield of NH$_3$ varies between each run: from the lowest in run 6 to the highest in run 1. Unlike d-NH$_3$ (%) in Table 6.5 which was directly related to the plasma power, d-NH$_3$ (%) in Table 6.6 is affected by other parameters as well. These parameters could be mainly the injection place, and also design of nozzles. Comparing the result of run 5 and run 3, one can see the effect of nozzle type (i.e. mixing) on the recovery yield of SWCNTs containing soot and also the structural quality of SWCNTs according to
Figure 7.7. Although in both runs (3 and 5), the nozzle tip position and heating wall are the same and in run 5 more NH$_3$ was injected into the reaction system, both the recovery yield and SWCNTs quality are much lower in run 3. Design (1) used in run 3, shown in Figure 7.1, is expected to provide more confined stream of NH$_3$ at the centre of the reactor and to disturb less the plasma flow pattern at injection point while design (2), is expected to disperse the stream of NH$_3$ more effectively. The better dispersion of NH$_3$ gas in the reaction system can be considered for the lower d-NH$_3$ (%) as NH$_3$ is brought to the lower temperature region of reactor. The lower recovery yield after NH$_3$ injection can be because of the formation of gaseous by product (e.g., CH$_4$ and HCN) in the synthesis system as predicted by thermodynamic calculation and also observed by MS data obtained during the synthesis process. Moreover, the formation of reactive species at higher temperature will result in a more severe destruction to happen on the SWCNTs. Therefore, the type of nozzle which directly affects the mixing process of NH$_3$ in the ITP reactor is an important parameter. Moreover, comparing the result of run 4 and run 6, the importance of injection place is clear. In both runs, the same type of nozzle was used however; the recovery yield of SWCNT containing soot, and the structural quality shown in Figure 6.7 are higher for run 6 in which a higher amount of NH$_3$ was injected. The reason could be the lower temperature at lower part of the reactor which lessens the destructive influence of NH$_3$ on the SWCNTs material.

Further study on the morphology of NH$_3$-treated SWCNTs sample obtained from run 6 was performed using TEM imaging and the results are depicted in Figure 6.8. Figure 6.8a represents the TEM image of raw SWCNT sample. In this figure, the presence of SWCNTs bundles along with other impurities is evident. The enlarged image on top-left clearly indicates that the bundles are indeed single-walled tubes having diameters of 1 to 2 nm, with respect to the scale bar in the inset. Figure 6.8b shows the morphological structure of the SWCNT sample after exposure to NH$_3$ in the synthesis system. Like the raw sample, SWCNTs are observed in bundles in this sample together with carbonaceous and catalysts impurities. Figure 6.8c-f indicates the spots in the NH$_3$-treated samples with different morphologies than the raw SWCNT sample. Thick tubular structures with the catalyst particles at the tip and a dense core at the centre are clearly observable from Figure 6.8d which is an enlarged area of Figure 6.8c. Small bundles of onion-like materials are also observable in the inset of Figure 6.8d with a
size ranging from few to tens of nanometre. Interesting morphology can be seen in Figure 6.8e and f where the planar structures are observable on the TEM grid and their thickness seems to be very thin, few nanometres, since the TEM grid beneath is clearly visible. The formation of graphene with chemical vapour deposition (CVD) method has been previously reported. In CVD method in the presence of Ni substrate and flowing H\textsubscript{2} and CH\textsubscript{4} gases the graphene is synthesized [Zhu et al., 2010]. The same phenomenon may occur as well in the ITP reactor where upon the high concentration injection of NH\textsubscript{3} followed by decomposition event which produces H\textsubscript{2} and CH\textsubscript{4} as seen in Figure 6.6, the formation of planar carbon nanostructure becomes possible. However, further experiments are necessary to better characterize these planar nanostructures.
To study the long-term dispersibility of SWCNTs material before and after exposure to NH₃, they were dispersed in Isopropanol and Dimethylformamide (DMF). The suspension of raw sample and sample containing 1.1% of N (from run 6) were stored for almost 2 months and the results are shown in Figure 6.9. The raw SWCNT sample started to precipitate while the NH₃-treated sample kept its dispersed form in both solvents. These results indicate that NH₃ injection into the ITP system during the synthesis process enhances the dispersibility of
SWCNT containing soot which is a demanding characteristic for their potential applications in many fields.

![Image](image.png)

Figure 6.9 Long-term dispersibility behaviour of (a) raw SWCNT, (b) NH$_3$-treated SWCNT

### 6.7.3 CFD simulation results

The thermo-flow field of the ITP system in the presence of counter-current NH$_3$ injection with and without nozzle was numerically modeled and the results are illustrated in Figure 6.10. For a better visualisation, the local values are illustrated for each plane with its distance from the injection point. As seen in Figure 6.10, the counter-current injection can evidently affect the thermo-flow field of the system up to at least 15 cm from the injection point. Comparing the mole fraction of NH$_3$ at y=0.1 cm in Figure 6.10a and b, it is observed that the use of the nozzle can significantly enhance the dispersion of NH$_3$ particularly at a region very close to the injection point. This is also reflected in the temperature and velocity profiles shown in Figure 6.10b. Therefore, one of the direct effects of the use of the nozzle in the counter-current injection of NH$_3$ can be a better dispersion of NH$_3$ at the injection point which is not observed without nozzle, as shown in figure 10 (a). At y=5 cm, a more uniform NH$_3$ concentration is obtained when the nozzle is used which is in line with its temperature profile. Since the
decomposition reaction of NH$_3$ should be tightly related to not only the temperature but also the velocity of the reacting flow, the velocity profiles are also depicted in Figure 6.10. At $y=5$ cm, the injection with nozzle shows lower flow velocity profile with a maximum of 22 m/s compared to 56 m/s for the injection process without nozzle. Moreover, one of the main effects of counter-current NH$_3$ injection on the velocity profile is attributed to the creation of a ring shaped low velocity region far from the reactor wall as seen at $y=5$ and 10 cm in Figure 6.10a and b. These low velocity regions can be expected to affect reaction system by enhancing the yield of slow reactions. At $y=15$ cm, the main thermo-flow field is still influenced by NH$_3$ injection without nozzle while the influence is reduced for the case of nozzle injection. Considering that the formation of reactive species related to the NH$_3$ decomposition is enhanced by temperature, the presence of NH$_3$ and its decomposition intermediate species at higher temperature region in the ITP reactor can result in destructive reaction with SWCNT products. In such reaction, reactive species can react with the SWCNT products in a way that gaseous species are produced. One of the main products can be CH$_4$ which is observed in both thermodynamic calculation and experiments. The result of simulation enables therefore to explain the variation observed in the recovery percentage summarized in Table 6.5. A nozzle which provides uniform NH$_3$ concentration profile along with a high enough uniform temperature profile can effectively decompose most of the injected NH$_3$ closer to the injection point while the non-uniform profiles will result in a partial decomposition of the injected NH$_3$ which in turn, allow more NH$_3$ to be delivered to the higher temperature region of the reactor as shown in Figure 6.10a. Therefore, the simulation results suggest that the NH$_3$ decomposition in the ITP reactor can be controlled by the type of nozzle where a better dispersion at injection point can cause the decomposition event to take place at lower temperature region of the reactor. This will consequently result in a less destructive effect of decomposition species on the SWCNTs in the ITP reactor.
Figure 6.10 Calculated NH$_3$ mole fraction, temperature and velocity profiles for two different types of injection, at 66.6 kPa (a) without nozzle and (b) with nozzle

6.8 Conclusion

The counter-current injection of ammonia during the synthesis of SWCNTs by ITP system was successfully developed and performed. The experimental results indicated a maximum of 10-fold increase in the quantity of nitrogen in the final SWCNTs product. With this, a long term dispersibility of SWCNTs material in Isopropanol and DMF was achieved. Raman
analysis indicated the structural alteration of SWCNTs upon ammonia injection. The injection place and nozzle type were found to be important parameters affecting the SWCNTs materials during NH₃ injection. TEM analysis revealed that high temperature ammonia injection could also alter the morphology of SWCNTs materials where the presence of onion like and planar carbon nanostructures, were observed. Thermodynamic calculation results of the gas phase system indicated the possibility of the formation of gaseous by products such as HCN and CH₄ during the synthesis process upon NH₃ injection in line with the experimental observation. NH₃ cannot alter the growth of SWCNTs by reacting with metal catalysts as confirmed by both thermodynamic calculation and XRD analysis. The results also indicated that some reactions which are thermodynamically favourable cannot completely happen in the ITP reactor because of the non-equilibrium characteristics of the system. The CFD simulations results clearly showed that the thermo-flow field of ITP system is influenced by the ammonia counter-current flow and, particularly, by the injection nozzle type. The injection without nozzle results in a longer NH₃ delivery into the ITP reactor in comparison to the nozzle. The high velocity injection without nozzle results in the channeling effect at the centre of main plasma flow close to the injection point while this phenomenon is much less pronounced at regions far from that point. The simulation results demonstrated that NH₃ decomposition process can be controlled through a proper design of the nozzle which in turn results in more effective chemical treatment of the final SWCNT product.

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CHAPTER 7. Effect of ammonia gas addition to the synthesis environment of single-walled carbon nanotubes on their surface chemistry

Avant-propos

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Contribution to the document: Ali Shahverdi performed the experimental works, interpretation and analysis of data, 2-dimentional numerical simulation using ANSYS/FLUENT/CHEMKIN codes, as well as drafting of the manuscript under supervision of Porf. G. Soucy and Dr B. Simard. This article contributes to the thesis by demonstrating that the ammonia addition to the SWCNTs synthesis environment can change their surface
chemistry. From the previous chapter, it was found that the addition of ammonia into the SWCNTs synthesis environment can enhance the dispersion of the final product in isopropanol and dimethylformamide. Therefore, to better understand the effect of ammonia on the chemistry of the SWCNTs final product, the obtained samples were characterized in greater detail. Moreover, the reaction system in the ITP reactor before and after ammonia addition was numerically modeled in order to better understand the \textit{in situ} chemistry process and investigate the possible mechanism by which the chemical modification of the SWCNTs final product proceeds.

Three different ammonia thermal decomposition mechanisms were initially considered in the model. The mechanism by which the model predicts the best fit to the experimental results is presented in this article while two other mechanisms are summarized in Appendix A and B. The fundamental of Raman spectroscopy which is used in this article to investigate the effect of \( \text{NH}_3 \) in the SWCNTs synthesis environment on their surface chemistry is explained in more details in Appendix C.

\textit{Titre français:}

Effet de l'addition de gaz ammoniac dans le milieu de synthèse de nanotubes de carbone mono-parois sur leur chimie de surface

\textbf{7.1 Résumé}

Cette étude évalue l'effet de l'addition d'ammoniac gazeux sur le milieu de synthèse et de la chimie de surface des nanotubes de carbone mono-parois (SWCNTs) produits par le système de plasma thermique inductif (PTI). L'influence de ce procédé \textit{in situ} sur le produit final a été examinée par spectroscopie Raman à trois longueurs d'onde, un système couplé par méthode thermogravimétrie et la spectroscopie infrarouge, et spectroscopie infrarouge en phase solide. Les résultats indiquent clairement la modification de surface de SWCNTs où les tubes métalliques avaient plus tendance que les tubes semi-conducteurs à réagir avec l'ammoniac. Pour mieux comprendre le système de réaction et prédire le profil de concentration des produits intermédiaires ainsi que les produits de décomposition thermique de l'ammoniac dans le réacteur ITP, une simulation numérique a été mise au point. Cette simulation est basée à la
This study evaluates the effect of ammonia gas addition on synthesis environment and surface chemistry of single-walled carbon nanotubes (SWCNTs) produced by induction thermal plasma system (ITP). The experiments were carried out based on the opposed-flow injection of ammonia into the ITP reactor used for mass production of SWCNTs containing soot. The influence of in situ ammonia injection on the SWCNT final products was closely examined by Raman spectroscopy at three wavelengths, coupled thermogravimetry-infrared spectroscopy (TG-FTIR) and solid-phase infrared spectroscopy. The results clearly indicated the surface modification of SWCNTs where the metallic tubes had a greater tendency than the semiconducting tubes to react with ammonia at high temperature. To better understand the reaction system and predict the concentration profile of the intermediates and the product species from thermal decomposition of ammonia in the ITP reactor, a numerical simulation was developed including both the detailed kinetic of ammonia decomposition and turbulent mixing in the reaction system. By comparing the experimental and simulation results, a two-step reaction mechanism is suggested for this in situ SWCNTs chemistry in which the reaction of atomic hydrogen and amidogen radicals with SWCNTs, is followed by the ammonia chemisorption.

7.3 Introduction

Among synthetic tubular nanostructured materials, carbon nanotubes (CNTs) and particularly single-walled carbon nanotubes (SWCNTs) have been of great interest since their discovery [Iijima, 1991; Iijima and Ichihashi, 1993], because of their unique one-dimensional structure and exceptional mechanical, thermal and electrical properties. The outstanding properties of CNTs have made them good candidates for many applications such as fillers in polymer
composite systems [Breuer and Sundararaj, 2004; Ci et al., 2008], gas storage, gas and pressure sensors [Darkrim et al., 2002; Genest et al., 2012; Lukaszewicz, 2006; Yun and Yeow, 2009], microelectronic devices, catalyst supports, energy [Candelaria et al., 2012; Dai et al., 2012; Lingyu et al., 2009], biotechnology and biosensors [Bekyarova et al., 2005].

Pristine SWCNTs constructed seamlessly of a perfect graphene sheet are chemically inert. However, they need to be processable and well-dispersible for most of their applications in order to achieve the optimum condition in which their extraordinary properties are leveraged. Up to now, several synthesis methods have been proposed for SWCNTs such as arc-discharge [Iijima and Ichihashi, 1993], laser ablation [Guo et al., 1995], chemical vapour deposition (CVD) [Dai et al., 1996], and induction thermal plasma [Kim et al., 2007]. But the SWCNTs end-products of these methods essentially need to be further modified through a post-treatment chemical process to enhance their functionality.

Recent studies have shown that the amide-functionalized SWCNTs can be used to produce low volume fraction polymer composite with dramatically improved thermal, electrical and mechanical properties [Ramanathan et al., 2005b]. Moreover, it has been shown that ammonia-adsorbed CNTs can present a much higher nitrate adsorption capacity from water than the pristine ones or other generally nitrate adsorbents used in water treatment industry [Ahmadzadeh Tofighy and Mohammadi, 2012]. In particular, the use of CNTs as carriers of biologically active molecules holds great promise [Chen et al., 2004; Richard et al., 2003]. For example, it has been shown that the ammonium functionalized CNTs are able to associate with the plasmid DNA through electrostatic interactions and to be used for plasmid DNA gene delivery [Pantarotto et al., 2004; Singh et al., 2005].

The surface chemistry modification of SWCNTs is a very important step towards their effective use in many applications. There have been several methods reported in the literature on the chemical modification of SWCNTs such as mechano-chemical [Kónya et al., 2002; Rubio et al., 2011], microwave-induced [Wang et al., 2005b; Wang et al., 2005c], gas phase [Mickelson et al., 1998; Xia et al., 2009] and solvent free methods [Dyke and Tour, 2003; Dyke and Tour, 2004b]. However, conventional approaches frequently used to modify the surface chemistry properties of pristine SWCNTs, are mainly based on wet chemistry.
Although, there are some advantages related to the wet chemistry-based methods such as a good control on the reaction parameters (e.g., temperature, and concentration), and the possibility of adding a wide range of functional groups on SWCNTs, these methods involve several additional steps including dissolution, sonication, mixing, filtering and drying, etc. Therefore, chemical modification of SWCNTs by these methods is a time consuming process. Furthermore, each of these steps adds a substantial cost to the integration process with a noticeable amount of chemical waste [Tseng et al., 2008; Hordy et al., 2013] which often limits the scalability of such processes. More importantly, these methods cannot be incorporated with the synthesis setup so that they are considered as post-treatment methods.

An alternative method to the wet chemistry is the cold plasma [Felten et al., 2005; Khare et al., 2002a] which is essentially a post-treatment process based on activation of reactive gas in relatively very low pressure by plasma process. Although the reaction time is relatively much faster than the wet chemistry, this method needs an extra unit of plasma system which has to be adapted for the treatment of SWCNT powders. Moreover, the treatment is limited mainly to the surface of the SWCNT samples which in turn results in a low yield and non-uniformity in the sample. Scaling up is also another challenge for the cold plasma process.

The limitations of the both wet chemistry and cold plasma methods suggest that a new method can be proposed by performing the chemical modification of SWCNTs during their synthesis process, i.e., *in situ* chemistry modification. Therefore, in this work the main objective is to experimentally and theoretically study the effects of the injection of reactive gas like ammonia into the synthesis environment of the ITP reactor on the SWCNTs final product. It is believed that this one-step chemistry approach excludes the disadvantages of the wet chemistry and cold plasma methods while it keeps the chemical modification process effective and uniform. Although post-treatment methods could be advantageous in some circumstances due to their better flexibility in the choice of reactive agents, and a good control on the reaction time and the chemistry, the *in situ* method is expected to be time and cost efficient since the process takes place during the synthesis and no additional unit is necessary. Moreover, the proposed method is expected to be cleaner than the wet chemistry-based methods and no further treatment on the SWCNTs samples is necessary after the process. This approach produces
chemically modified SWCNTs at the lowest cost in a scalable process. For this purpose ammonia (NH$_3$) was selected as a reactive gas to be injected into the ITP SWCNT synthesis system.

A theoretical study was performed by developing a two-dimensional numerical simulation of the reacting flow by incorporating the thermo-flow field and the kinetic of ammonia thermal decomposition in the ITP reactor. The ammonia thermal decomposition at high temperatures has been a subject of many experimental studies [Bradley et al., 1967; Davidson et al., 1990; Dove and Nip, 1979; Jacobs, 1963; Konnov and De Ruyck, 2000; Yumura and Asaba, 1981] from which the overall decomposition reaction has been found to be influenced by secondary reactions. The kinetic mechanisms proposed for such decomposition are mainly based on the formation of intermediate reactive species (i.e., radicals) which controls the overall rate of decomposition in a chain reaction. The formation of these radicals in the synthesis system can be an important source for the surface modification of SWCNTs.

In kinetic modeling, the choice of reaction mechanism is very important. In the literature, simplified mechanisms proposed for the ammonia thermal decomposition including 10 elementary reactions to more complex ones having up to 50 elementary reactions are found [Davidson et al., 1990; Dove and Nip, 1979; Konnov and De Ruyck, 2000; Yumura and Asaba, 1981]. Although a simplified mechanism is of interest because of lowering the computational cost of the simulation, it can underestimate the importance of some reactions which in some cases should not be neglected. As a result, two simplified mechanisms proposed by Dove and Nip [Dove and Nip, 1979], and Yumura and Asaba [Yumura and Asaba, 1981] were initially considered and coupled with the computational fluid dynamic (CFD) simulation of the ITP reactor. The simulation results were then compared to the overall decomposition of ammonia experimentally measured in the ITP reactor using mass spectroscopy. The mechanism proposed by Dove and Nip resulted in a very low decomposition yield while that proposed by Yumura and Asaba predicted a very high decomposition yield, based on the experimental measurements. In the mechanism proposed by Dove and Nip, they included an alternative initiation reaction of NH$_3$ + M → NH + H$_2$ + M (ℓ') to the well-known and well-established NH$_3$ + M → NH$_2$ + H + M (ℓ) initiation reaction.
[Baulch et al., 1972]. However, the route of alternative reaction (ℓ') has not been accepted because of its spin-inhibited resulting in a higher activation energy than the enthalpy difference associated to the reaction, and because of the shape of its activated complex that needs a much lower pre-exponential factor than reaction (ℓ) [Yumura and Asaba, 1981]. Considering these two reasons, this alternative initiation reaction should have a much lower rate than the reaction (ℓ) and can be neglected. This explanation was found to be in good agreement with our simulation results, not shown in this manuscript, where the mechanism proposed by Dove and Nip resulted in a very low and unrealistic decomposition yield for ammonia in the ITP reactor.

Another criticism to these two mechanisms comes from the overestimation of N₂H₃ role in the reaction. From sensitivity analysis performed by Davidson and co-workers [Davidson et al., 1990], it was found that the importance of N₂H₃ is not considerable in driving the NH₃ decomposition kinetic. Instead, the two-step formation-consumption reaction of N₂H₃ was replaced by a more complex mechanism in a way that the proposed kinetic model reproduced the experimental data. Therefore in this work, the numerical simulation was developed based on integrating the decomposition kinetic mechanism proposed by Davidson and co-workers [Davidson et al., 1990], and the turbulent mixing of ammonia gas stream in the ITP reactor with the aid of CHEMIKIN-CFD to essentially predict the concentration profile of the intermediates and the products which are expected to directly influence the surface chemistry of SWCNT soot during the synthesis process in the ITP reactor.

7.4 Experimental setup and procedure

To synthesize chemically-modified SWCNTs soot using the ITP system, ammonia gas was injected into the synthesis system at the base of the reactor, as shown in Figure 7.1. To closely monitor the decomposition of ammonia gas in the system, a Quadrupole mass spectrometer (ThermoStar, Balzers instruments) was connected to the exhaust gas of the synthesis system. This online mass spectroscopy allowed direct monitoring of the ammonia gas decomposition yield and the subsequent final products (i.e., N₂ and H₂) in the ITP system and enabled validation of 2D numerical modeling results. A mixture of carbon black (M280, Cabot Inc.) and metal catalysts including Ni: 1.2 at. % (Cerac Inc.) and Y₂O₃: 0.4 at. % (Herman C.Starck)
was chosen as a starting feedstock material. The plasma was generated from a mixture of \text{He}/\text{Ar} (135/30 slpm) using an ITP torch (PS50, TEKNA Inc.) at 45 kW plate power (i.e., the power provided by the generator to the torch). A summary of the operating conditions is given in Table 7.1. A mixture of \text{NH}_3/\text{Ar} (28/4 slpm) was counter-currently injected at the base of reactor into the ITP system used for the large-scale synthesis (i.e., 100 g/h) of SWCNTs-containing soot.

Table 7.1 Operating conditions used for the ITP torch

<table>
<thead>
<tr>
<th>Plasma power (kW)</th>
<th>Frequency (MHz)</th>
<th>Pressure (kPa)</th>
<th>Sheath gas (slpm)</th>
<th>Central gas (slpm)</th>
<th>Powder gas (slpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>3</td>
<td>67</td>
<td>135 (He)</td>
<td>25 (Ar)</td>
<td>5 (Ar)</td>
</tr>
</tbody>
</table>

The synthesized SWCNTs soot was characterized by Raman spectroscopy, coupled TG-FTIR and solid-phase FTIR spectroscopies. Raman spectroscopy equipped with a tunable laser with three different wavelengths: 514.5, 632.8, and 780 nm was performed on the SWCNT samples. TG analysis of SWCNT samples was performed by a Netzsch TG 209 F1 Iris® with simultaneous coupling of Bruker Tensor 27 Fourier Transform Infrared (FTIR) spectrometer via a TGA A588 TGA-IR module. The samples were characterized under inert desorption conditions. Upon loading the SWCNT samples, remaining air was removed and the sample was placed under the run gas conditions (Ar: 75 sccm). The thermal desorption measurements were consisted of a heating process in the following order: (i) from room temperature to 120 °C with 10 °C/min ramp, (ii) an isothermal soak at 120 °C for 20 min, (iii) heating from 120 °C to 950 °C with 10 °C/min ramp, and (iv) an isothermal soak at 950 °C for 30 min. Infrared (IR) data was simultaneously collected with the TGA data. An IR spectrometer (Perkinelmer, spectrum 100) was used to characterize the infrared absorption properties of SWCNT samples in form of transparent disk prepared from a well-mixed KBr-SWCNT fine powder. The IR data were then collected in the range of 450–4 000 cm\(^{-1}\), at a resolution of 4 cm\(^{-1}\). Prior to FTIR spectroscopy, as-received potassium bromide (KBr) powder and SWCNT samples were kept in oven at 110 °C.
Figure 7.1 Schematic diagram of the ITP synthesis system of chemically-modified SWCNT with its main components: 1) ITP torch, 2) ITP reactor, 3) filtration system, 4) powder feeder, 5) mass spectrometer and 6) product collection bucket

7.5 Numerical modeling

Due to the importance of ammonia decomposition on the proposed *in situ* SWCNTs chemical modification, 2D numerical simulation was developed to achieve a better understanding of the ammonia thermal decomposition chemistry under the ITP reactor conditions with the aid of a detailed kinetic model. Simulation is needed to better understand the reaction system because of the limitations associated with the ITP reactor geometry, very high temperature reacting environment, and very fast reactions hindering direct measurement of intermediate species. A 2D kinetic simulation was coupled with CFD to take into account the importance of mixing process on the NH$_3$ decomposition reaction. The simulation of reacting flows was carried out
in a two-step process. In the first step, the “cold-flow” (i.e., non-reacting flow) was obtained by solving only the energy, flow and species equations while no kinetic was considered. In the second step, when the basic thermo-flow field of the ITP reactor was established, the calculations continued with reaction enabled. The computational domain considered in the simulation work is depicted in Figure 7.2.

![Figure 7.2 Computational domain considered for numerical simulation](image)

As shown in Figure 7.2, the computational domain consists of two parts: (i) the ITP torch (PS50, TEKNA Inc.) and (ii) ITP reactor. The graphite insert inside the reactor was also taken into account [Arabzadeh Esfarjani et al., 2011].

The ITP torch was simulated separately based on the constant operating conditions and no reaction was considered to take place in this region during the NH$_3$ injection process about 80 cm from the exit of the torch. Once the thermo-flow field in the ITP torch was obtained, the corresponding data at the exit of the torch was used as the input of the ITP reactor. An opposed-flow ammonia gas stream was then considered at the base of the ITP reactor ($z = 0.95$ m). The operating and boundary conditions employed in this simulation work are summarized in Table 7.1 and Table 7.2, respectively. An efficiency of 70% was considered for the plate power of the ITP torch i.e. a net plasma power of 31.5 kW is used in the simulation. As mentioned earlier, three different mechanisms proposed for thermal decomposition of ammonia by Dove and Nip [Dove and Nip, 1979], 10 elementary reactions, Yumura and Asaba [Yumura and Asaba, 1981], 10 elementary reactions and Davidson et al.
[Davidson et al., 1990], 21 elementary reactions, were initially considered and coupled with the CFD simulation. Only the results of the mechanism proposed by Davidson et al., summarized in Table 7.3, are presented since it showed the best fit to the experimental observations by mass spectroscopy. CFD simulation was carried out on the computational domain shown in Figure 7.2, using academic ANSYS®FLUENT code v.13 which was further coupled with CHEMKIN-CFD code v.13 for detailed kinetic of ammonia decomposition. 

The following assumptions were considered in the simulation: (i) axisymmetric; (ii) steady-state; (iii) negligible viscous dissipation; and pressure work terms in the energy equation; (iv) incompressible and temperature-dependent mass density; and (v) turbulent flow. According to the aforementioned assumptions, the fluid dynamic equations are described by steady-state conservation equations for the transport of mass, momentum, energy, and species as summarized Table 7.4. External forces, in the ITP torch, presented in the magnetohydrodynamic equations were also taken into account [Mostaghimi and Boulos, 1989], while the use of these equations in the ITP reactor becomes useless since the electric and magnetic fields in this region of the synthesis system are deficient and can be neglected in the model.

The conservation equations for chemical species were solved by predicting the local mass fraction of each species through the solution of the convection-diffusion equation for that species in the following form,

$$\frac{\partial}{\partial t}(\rho Y_i) + \nabla \cdot (\rho \vec{v} Y_i) = -\nabla \cdot \vec{J}_i + R_i + S_i$$

where $R_i$ in Eq. (1) is the net production rate of species $i$ by a particular chemical reaction. The mass diffusion flux, $\vec{J}_i$, of the species $i$ was computed through solving the following equation:

$$\vec{J}_i = -\left(\rho D_{i,m} + \frac{\mu_i}{Sc_i}\right)\nabla Y_i$$

The rate of creation or destruction of species $i$ in reversible reaction $r$ was given by the following equation,
\[
\tilde{R}_{i,r} = \Gamma (\nu_{i,r} - \nu_{i,r}') \left( k_{i,r} \prod_{j=1}^{N} [C_{j,r}]^n_{j'} - k_{k,r} \prod_{j=1}^{N} [C_{j,r}]^m_{j'} \right)
\]

where \( \Gamma \) denotes the net effect of third-body on the reaction rate. To include the detailed chemical mechanism, the eddy-dissipation concept (EDC) model [Magnussen et al., 1979] in which the reaction is assumed to occur in the fine scales (i.e., small turbulent structures) was employed. Therefore, the source term in the conservation Eq. (1) for the mean species, \( i \), is modeled as the following,

\[
R_i = \frac{\rho (\xi^*)^2}{\tau^*} \left[ 1 - (\xi^*)^3 \right] (Y_i^* - Y_i)
\]

In Eq. (4), \( Y_i^* \) denotes the mass fraction of the fine-scale species after reacting over the time scale, \( \tau^* \). The species are assumed to react in the fine structures over a time scale. The length fraction of the fine scales, and the time scale are calculated via Eqs. (5) and (6):

\[
\xi^* = C_\xi \left( \frac{\nu \varepsilon}{K^2} \right)^{1/4}
\]

\[
\tau^* = C_\tau \left( \frac{\nu}{\varepsilon} \right)^{1/2}
\]

The reactions proceed over the time scale are governed by the Arrhenius rates of Eq. (3), and then are integrated numerically using In Situ Adaptive Tabulation (ISAT) method [Pope, 1997]. Using this storage-retrieval method, a chemistry table is in situ constructed. With EDC model, detailed kinetic mechanism of the ammonia thermal decomposition could be incorporated into the turbulent reacting flow in the ITP reactor. Furthermore, the solution-adaptive mesh refinement (AMR) was used to efficiently reduce the numerical error while minimizing the numerical cost. Assuming that maximum error occurs in high-gradient regions, the mesh adaption process was derived with the available physical features of the evolving...
reacting flow field. In this regard, an equi-distribution adaption technique, so-called the curvature approach was applied [Warren et al., 1991]. The material properties such as density, viscosity, thermal conductivity and specific heat for each species were obtained from [Boulos et al., 1994; McBride et al., 1993] and further used by mixing laws to calculate the mixture properties. A full multi-component diffusion was considered in the species transport model of the reacting flow. The diffusion coefficients in the mixture were calculated for each species based on the kinetic theory considering the modified Chapman equations using the Lenard-Jones (L-J) parameters.

Table 7.2 Boundary conditions of ITP reactor

<table>
<thead>
<tr>
<th>Inlet</th>
<th>NH$_3$ inlet</th>
<th>Pressure (kPa)</th>
<th>T$_{wall}$ (K)</th>
<th>Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITP torch exit</td>
<td>19 slpm</td>
<td>67</td>
<td>1073*</td>
<td>Pressure outlet</td>
</tr>
<tr>
<td>profile</td>
<td>(Ar:NH$_3$=1.1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* From experimental measurement
Table 7.3 Detailed reaction mechanism and rate parameters, $k=AT^n \ exp\ (-E/RT)$ (cm$^3$/mole.sec).

[Davidson et al., 1990]

<table>
<thead>
<tr>
<th>Elementary Reactions</th>
<th>Log A</th>
<th>n</th>
<th>Ea(KJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) NH$_3$+M$^*$ = NH$_2$+H+M</td>
<td>16.34</td>
<td>0.00</td>
<td>391.00</td>
</tr>
<tr>
<td>2) H+NH$_3$ = H$_2$+NH$_2$</td>
<td>5.80</td>
<td>2.39</td>
<td>42.50</td>
</tr>
<tr>
<td>3) H$_2$+M = H+H +M</td>
<td>14.34</td>
<td>0.00</td>
<td>401.54</td>
</tr>
<tr>
<td>4) NH+M = N+H+M</td>
<td>14.42</td>
<td>0.00</td>
<td>315.90</td>
</tr>
<tr>
<td>5) NH+H = H$_2$+N</td>
<td>13.55</td>
<td>0.00</td>
<td>1.36</td>
</tr>
<tr>
<td>6) NH+N = N$_2$+H</td>
<td>13.47</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>7) NH+N=NH = N$_2$+H+H</td>
<td>13.70</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>8) NH$_2$+M = NH+H+M</td>
<td>23.49</td>
<td>-2.00</td>
<td>382.42</td>
</tr>
<tr>
<td>9) NH$_2$+H = NH+H$_2$</td>
<td>13.60</td>
<td>0.00</td>
<td>15.27</td>
</tr>
<tr>
<td>10) NH$_2$+N = N$_2$+H+H</td>
<td>13.85</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>11) NH$_2$+NH= N$_2$H$_2$+H</td>
<td>15.17</td>
<td>-0.50</td>
<td>0.00</td>
</tr>
<tr>
<td>12) NH$_2$+NH$_2$=NH$_3$+NH</td>
<td>13.69</td>
<td>0.00</td>
<td>41.84</td>
</tr>
<tr>
<td>13) NH$_2$+NH$_2$=N$_2$H$_2$+H$_2$</td>
<td>11.69</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>14) N$_2$H$_2$+M=NNH+H+M</td>
<td>16.70</td>
<td>0.00</td>
<td>209.20</td>
</tr>
<tr>
<td>15) N$_2$H$_2$+H=NNH+H$_2$</td>
<td>13.69</td>
<td>0.00</td>
<td>4.20</td>
</tr>
<tr>
<td>16) N$_2$H$_2$+NH=NNH+NH$_2$</td>
<td>13.00</td>
<td>0.00</td>
<td>4.20</td>
</tr>
<tr>
<td>17) N$_2$H$_2$+NH$_2$=NNH+NH$_3$</td>
<td>13.00</td>
<td>0.00</td>
<td>4.20</td>
</tr>
<tr>
<td>18) NNH+M= N$_2$+H+M</td>
<td>14.30</td>
<td>0.00</td>
<td>83.68</td>
</tr>
<tr>
<td>19) NNH+H=N$_2$+H$_2$</td>
<td>13.60</td>
<td>0.00</td>
<td>12.55</td>
</tr>
<tr>
<td>20) NNH+NH=N$_2$+NH$_2$</td>
<td>13.69</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>21) NNH+NH$_2$=N$_2$+NH$_3$</td>
<td>13.69</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

* Third-body
<table>
<thead>
<tr>
<th>Model</th>
<th>Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mass conservation</strong></td>
<td>( \nabla \cdot (\rho u) = 0 )</td>
</tr>
<tr>
<td><strong>Momentum conservation</strong></td>
<td>( \nabla \cdot (\rho uu) = -\nabla p + \nabla \cdot \tau + F_L )</td>
</tr>
<tr>
<td><strong>Energy conservation</strong></td>
<td>( \nabla \cdot (\rho u h) = \nabla \cdot \left( \frac{k_{eff}}{C_p} \nabla h \right) + P_{ohm} - R_{rad} )</td>
</tr>
<tr>
<td><strong>Turbulent</strong></td>
<td><strong>Kinetic energy</strong> ( \nabla \cdot (\rho u K) = \nabla \cdot \left( \left[ \mu + \frac{\mu_t}{Pr_K} \right] \nabla K \right) + G_t - \rho \varepsilon. )</td>
</tr>
<tr>
<td><strong>Dissipation rate</strong></td>
<td>( \nabla \cdot (\rho u \varepsilon) = \nabla \cdot \left[ \left( \mu + \frac{\mu_t}{Pr_\varepsilon} \right] \nabla \varepsilon \right] + \frac{\varepsilon}{K} (C_i G_t - C_2 \rho \varepsilon). )</td>
</tr>
<tr>
<td><strong>Effective viscosity/thermal conductivity</strong></td>
<td>( \mu_{eff} = \mu + \mu_t ) ( \kappa_{eff} = \kappa + \kappa_t. )</td>
</tr>
<tr>
<td><strong>Turbulent viscosity/thermal conductivity</strong></td>
<td>( \mu_t = \rho C_p \frac{K^2}{\varepsilon} ) ( \kappa_t = \frac{\mu_t C_p}{Pr_t}. )</td>
</tr>
<tr>
<td><strong>Species conservation</strong></td>
<td>( \nabla \cdot (\rho u Y_i) = \nabla \cdot \left( (\rho D_i + \frac{\mu_t}{S_{Cl}}) \nabla Y_i \right) + R_i )</td>
</tr>
<tr>
<td><strong>Forces</strong></td>
<td><strong>Magnetic vector potential</strong> ( \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial A_\theta}{\partial r} \right) + \frac{\partial^2 A_\theta}{\partial z^2} - \frac{A_\theta}{r^2} = -\mu_0 (J_{coil} + J_{ind}). )</td>
</tr>
<tr>
<td><strong>Electric field/ Magnetic field</strong></td>
<td>( E_\theta = -i2\pi f A_\theta, \ \mu_0 H_z = \frac{1}{r} \frac{\partial (r A_\theta)}{\partial r}, \ \mu_0 H_r = -\frac{\partial A_\theta}{\partial z}. )</td>
</tr>
<tr>
<td><strong>Lorentz force/ Ohmic heating</strong></td>
<td>( F_r = \frac{1}{2} \mu_0 \sigma \text{Re}[E_\theta H^<em>], \ F_z = \frac{1}{2} \mu_0 \sigma \text{Re}[E_\theta H^</em>], \ P_{ohm} = \frac{1}{2} \sigma \text{Re}[E_\theta E^*]. )</td>
</tr>
</tbody>
</table>

* denotes the complex conjugate
7.6 Results and discussion

In our previous study, the influences of counter-current ammonia injection into the ITP reactor through different injection types and at different flow rates were experimentally investigated. The decomposition behaviour of ammonia was found an important parameter affecting the chemical composition of the SWCNT final product. Here, the focus is on studying the effect of such ammonia injection process on the surface chemistry of the SWCNT final product. In this section the experimental results obtained by various characterization techniques on the raw and NH$_3$-treated SWCNT samples are presented and discussed. The results of the cold and reacting flow simulation will be then presented, discussed and compared to the experimental observations.

7.6.1 Experimental

Figure 7.3 shows the TG-DTG graph of NH$_3$-treated SWCNT sample obtained in desorption mode along with its IR spectra.

![Graphs](image)

Figure 7.3 (a) TG-DTG graph of NH$_3$-treated SWCNT sample under desorption conditions. (b) 3D contour map of the FTIR spectra obtained from the evolved gas during TG desorption process

TG graph in desorption shows a maximum mass loss of 8% at T= 950°C with an intense peak at 130–250 °C. The main mass loss event happens where the sharp peak at 180°C is observed.
in Figure 7.3a which can be due to desorption of chemical moieties from SWCNTs sample. As shown in Figure 7.3b, the FTIR measurements of the evolved gases, during TG desorption event, show the presence of CO₂ through most of the temperature range as well as water vapor at lower temperatures. The primary source of oxygen for the generation of CO₂ in these measurements is interpreted to be adsorbed oxygen and water [Kingston et al., 2010]. By looking at temperature of ~ 200 °C, it is clear that there is a number of other IR features not seen at other temperatures. Two sharp features along with two other features close to the CO₂ features are evident from Figure 7.3b. Therefore, for more details, FTIR spectra were obtained on the evolved gas at 180 °C and the results are depicted in Figure 7.4.

![FTIR spectra](image)

Figure 7.4 FTIR spectra of extract gas @ 180 °C (a) low-frequency region (500-1 700 cm⁻¹), (b) mid-frequency region (2 000-2 500 cm⁻¹), (c) High-frequency region (2 500-4 000 cm⁻¹). §, ¥ and □ characters denote the presence of species other than CO₂ and H₂O.

For more details, the spectrum has been split in three regions: low-frequency, mid-frequency and high-frequency. According to [Kingston et al., 2010], signals at 668, 2 330, and 2 364 cm⁻¹ are due to CO₂. Some of multiple signals at 1 300–1 800 and 3 500–4 000 cm⁻¹ are because of water vapour. Signals at 931, 966, and 3 334 cm⁻¹ can be assigned to the presence of NH₃ gas in the evolved gas [Lubezky et al., 2000]. The presence of NH₃ in the evolved gas, noted by § in Figure 7.4, obtained from NH₃-treated SWCNT samples can be because of direct desorption of NH₃ molecules from the sample.

Feng and co-workers [Feng et al., 2005] showed NH₃ can only adsorb on HNO₃-purified SWCNT at low temperature (94 K) and desorption event maximizes at 140 K. However, controversy results were obtained by Ellison and co-workers [Ellison et al., 2004], where the
adsorption of NH$_3$ was achieved at room temperature on highly pure SWCNT sample and desorption was obtained at 430 K. Knowing that both groups used HiPCO-grown SWNCT samples from Carbon nanotechnologies Inc, the main reason for such controversy can be mainly because of different purification methods. The harsher is the purification method, the more defective sites (either with dangling bond or oxygenated-functional groups) on the SWCNT surface are expected which are energetically favorable to accept foreign molecules. Moreover Feng and co-workers showed that by using the same procedure, NH$_3$ could not adsorb on as-received unpurified SWCNT sample and purified SWCNT sample annealed at temperature over 773 K. They also observed the same results from as-received laser-grown SWCNT sample which has similar quality to ITP-grown SWCNT sample. Their finding was further corroborated with computational study indicating noticeably stronger interaction of NH$_3$ with defective or oxidized SWCNT compared to the pristine SWCNT. Therefore, from their observations it is suggested that not only NH$_3$ cannot chemisorb at room temperature but also cannot effectively physisorb at temperatures lower than 94 K on the pristine SWCNTs. Saying that, the observed results from TG-FTIR indicate that this in situ chemical process is enough effective that leads the generation of active sites on the nanotubes where NH$_3$ can bind.

The nature of bond between NH$_3$ and SWCNT sample can be explained by looking at high characteristic desorption temperature of NH$_3$-treated SWCNT sample (T > 180 °C). Since the weak physisorption bond are created at lower temperature than room temperature [Feng et al., 2005], adsorbed NH$_3$ on the SWCNT sample during the synthesis process is expected to be chemisorption in which NH$_3$ adsorbs on SWCNTs via both the lone pair on the N atom and H atoms [Ellison et al., 2004]. This is in good agreement with the result of nitrogen elemental analysis, data not shown, where prior to analysis, the samples were heated up to 323 K at very low pressure (<1.3×10$^{-4}$ kPa) to ensure the removal of weakly adsorbed gases. Therefore, if the NH$_3$ weakly adsorbed, the N content had to be lowered after this degassing process which did not happen.

The weak multiple signals at 3 200-3 300 cm$^{-1}$ are present at the same region as N-H stretching. The weak features at 1 500 and 3 220 cm$^{-1}$ can be assigned to the presence of NH$_2$.
species in the evolved gas as direct detection of NH₂ radical by infrared spectroscopy has been reported [Burkholder et al., 1988; Milligan and Jacox, 1965]. Two remaining features at 2 260 and 2 280 cm⁻¹ which do not match the IR database of stable gaseous species can be assigned to the HNCO which is the product of NH-CO reaction. The presence of this species with the same vibrational mode at what is observed in Figure 7.4, has been experimentally investigated in the IR spectroscopy during the photolysis study of CO:NH₃ for the NH₂ radical detection purposes [Jacox and Milligan, 1964; Milligan and Jacox, 1965].

The sensitivity of Raman to nanotubes enables to specifically probe the nanotubes in the sample and study any change in their surface chemistry. In this regard, a complete Raman analysis was performed on the SWCNT samples to firstly assess the effect of high temperature ammonia treatment on the SWCNT structure and secondly to investigate changes in the relative reactivity of different SWCNT types (metallic/semiconductive, [Saito et al., 1998]) and of different diameter distributions with ammonia. To probe a large portion of the SWCNTs with different chiralities and diameters in the sample, different laser excitation wavelengths are necessary to bring nanotubes of different types and diameters into resonance. To bring all SWCNTs to the resonance during Raman measurement, an expensive tunable laser instrument is necessary. However, since the diameter distribution of our SWCNT samples is smaller than 2 nm and bigger than 1 nm, according to the functional relationship of ωRBM on diameter of nanotube [Milner et al., 2000], it is expected that most of SWCNTs are effectively probed at three excitation wavelengths of 514.5, 632.8 and 780 nm according to Kataura plot [Kataura et al., 1999].

The use of Raman spectroscopy at aforementioned wavelengths, enabled to probe both metallic and semiconductive tubes of different diameters in the SWCNT samples. Regarding the diameter size distribution of ITP grown SWCNTs, the following conclusion was made based on the procedure explained in [Banerjee and Wong, 2004a]: (i) at λext = 514.5 nm, both metallic and semiconductive tubes are brought into resonance: larger diameter metallic and smaller diameter semiconductive. (ii) at λext = 632.8 nm, both metallic and semiconductive tubes are brought into resonance: smaller diameter metallic and larger diameter semiconductive. (iii) at λext = 780 nm, only metallic tubes are brought into resonance.
Normalization at so-called G-band feature \( \omega_{G+} \) allows for quality evaluation of SWCNT samples directly from D-band intensity where G-band \((1515-1590 \text{ cm}^{-1})\) and D-band \((1280-1350 \text{ cm}^{-1})\) are assigned to tangential mode of graphite \((\text{sp}^2)\) and disorder mode carbons \((\text{sp}^3)\), respectively [Dresselhaus et al., 2002; Dresselhaus et al., 2005]. Pristine SWCNT is expected to possess a higher G/D intensity ratio than chemically modified SWCNTs since the grafted moieties on the SWCNT wall can change the configuration of carbon atoms from \(\text{sp}^2\) to \(\text{sp}^3\) which consequently increase the intensity of dispersive D-band in Raman spectrum. Alongside G-band, the strong feature at lower frequencies \((100-500 \text{ cm}^{-1})\), due to the radial breathing mode (RBM) of tubular structure, is a unique mode which appears only in carbon nanotubes and its observation in Raman spectrum is considered as a direct verification for the presence of SWCNT in the sample. Since this mode strongly depends on the diameter of nanotube, the normalization allows the evaluation of the relative intensities of different carbon nanotubes existing in the raw and NH\(_3\)-treated samples.

Figure 7.5 shows the Raman spectra obtained at 632.8 nm excitation. Figure 7.5a shows an increase in the D-band intensity of NH\(_3\)-treated sample in comparison with that of raw sample which results from the disorder induced by \(\text{sp}^3\) hybridization of sidewall carbons upon NH\(_3\)-treatment. The chemical derivatization process effectively perturbs excitation between \(\pi\)-bands of bare \(\text{sp}^2\) hybridized SWCNTs. In Figure 7.5b, the higher frequency RBM features (i.e., smaller tubes) arise from metallic tubes with diameters ranging from \(~1.2\) to \(1.4 \text{ nm}\). For these smaller tubes, it is evident that RBM features are relatively reduced in intensity in NH\(_3\)-treated SWCNT. For further information, the tangential mode region of both samples is enlarged in Figure 7.5c. In Figure 7.5c, for the NH\(_3\)-treated nanotubes, the G-band appears to have a lower intensity at the low energy end \((G^-)\), indicating a substantially less contribution from the Fano shape. This is consistent with what would be expected from the RBM data illustrated in Figure 7.5b, since the smaller diameter tubes have been treated by ammonia are metallic nanotubes. Therefore, the remaining larger tubes have an increased semiconducting component which contributes to the decreased spectral weight of the Fano line. By looking at Figure 7.5 and c, a small shift in peak position is observed for both RBM and G-band: while the RBM has been upshifted to the right (blue shift); the G-band is downshifted to the left (red-shift). A change in the RBM feature upon functionalization has been reported by many authors. In most cases, a
upshift in the RBM frequency is reported [Chen et al., 1998; Chen et al., 2001a; Kukovecz et al., 2002; Martinez et al., 2003]. Also a downshift of G-band was reported upon functionalization, particularly in SWCNT samples treated by low pressure ammonia plasma [Chen et al., 1998; Khare et al., 2002b; Utegulov et al., 2005].

Figure 7.5 Raman spectra for raw (dotted-line) and NH$_3$-treated (solid-line) SWCNTs at $\lambda_{\text{ext}} = 632.8$ nm. (a) Complete Raman scattering region is normalized to the $\omega_{G^+}$, (b) RBM region: the spectra are normalized to the RBM feature at 180 cm$^{-1}$ (c) Tangential mode region, the low energy ends are identified with dashed circle.

Figure 7.6 shows Raman spectra of the same SWCNT samples but acquired at 514.5 nm excitation which is resonant with small diameter semiconducting and relatively large diameter metallic tubes. As seen in Figure 7.6a, the intensity of D-band increased for the sample treated with ammonia which is in line with the Raman data obtained at 632.8 nm excitation. By looking at Figure 7.6b, semiconducting nanotubes with diameters smaller than 1.51 nm, are greatly enhanced in the spectrum associated with ammonia-treated sample, while bigger diameter metallic nanotubes are slightly suppressed. The G-band profile in Figure 7.6c shows the same trend from what seen at 632.8 nm excitation. From the RBM data, the bigger diameter tubes chemically modified by ammonia chemistry appear to be metallic ones. As a result, the Raman enhancement loss of these nanotubes is reflected in a decreased intensity of
the Fano component in the G-band profile of NH$_3$-treated sample, as clearly seen in the dashed circle in Figure 7.6c. Figure 7.7 represents the Raman spectra at 780 nm excitation in which the laser wavelength brings primarily the metallic tubes into resonance. The main difference between Raman spectra obtained at this wavelength for NH$_3$-treated SWCNT sample and raw SWCNT sample is the large background of the spectrum. Since the nanotubes probed at this wavelength are metallic tubes, the spectrum background has been altered and become stronger than those obtained with two others wavelengths in which both metallic and semiconductive tubes are probed. The same observations have been reported for the chemically-modified nanotubes in other studies where the Raman spectra have been demonstrated with a large background [Dyke and Tour, 2004a; Peng et al., 2003a; Stevens et al., 2003; Wang et al., 2005b] implying the chemical moieties on the SWCNT to intensify the background spectrum upon functionalization process. Hence, from the Raman spectra acquired at 514.5, 632.8 and 780 nm, it is apparent that in this specific in situ gas phase NH$_3$ chemistry, not only the surface chemistry of SWCNTs has been modified but also there is a higher tendency for metallic nanotubes to react.

Figure 7.6 Raman spectra for raw (dotted-line) and NH$_3$-treated (solid-line) SWCNTs at $\lambda_{\text{ext}} = 514.5$ nm. (a) Complete Raman scattering region is normalized to the $\omega_{G^+}$ (b) RBM region: the spectra are normalized to the RBM feature at 168 cm$^{-1}$. (c) Tangential mode region, the low energy ends are identified with dashed circle
To further investigate, solid-phase FTIR measurement was performed on both raw and NH$_3$-treated SWCNT samples.
Figure 7.8 shows the obtained spectra from FTIR measurement on the SWCNT samples. The presence of two main peaks at 1 250 and 1 550 cm\(^{-1}\), attributed to C–C and C=C [Socrates G, 1980; Valentini et al., 2007], respectively, is observed in both samples shown in Figure 7.8a and b. The peak at \(\sim 3 400\) cm\(^{-1}\) followed by small peak at 3 250 cm\(^{-1}\) in Figure 7.8b which can be due to the stretch band and symmetric stretch of N-H bond, mainly from chemisorbed ammonia [Ellison et al., 2004], respectively. Moreover, the in-plane stretching mode of N-H bond featured at 1 570 cm\(^{-1}\) in the spectrum of NH\(_3\)-treaded SWCNT sample is seen in Figure 7.8b and small peaks at \(\sim 2 820\) and 2 900 cm\(^{-1}\) can be implicitly assigned to C–H stretching mode [Ramanathan et al., 2005a].

Through extensive characterization of the SWCNT sample treated by ammonia during their synthesis process, it was found that the presence of ammonia can alter the surface chemistry of SWCNTs so that the metallic tubes have shown a higher reaction tendency compared to semiconducting tubes. As mentioned earlier, performing experimental monitoring of the synthesis reacting flow, by e.g. spectroscopic techniques, is not feasible however, numerical simulation enables to further study the effect of ammonia injection into the synthesis reactor, to predict the concentration profile of reactive species in the SWCNT synthesis environment and to better explain the observed experimental results.

7.6.2 Simulation

In this section the results of the cold and reacting flow simulation are presented and discussed. The simulation results are also linked to the experimental observations to propose a mechanism for the ammonia \textit{in situ} chemistry on the SWCNTs.

Cold-flow

The results of cold-flow simulation of ITP system including ITP torch and reactor are depicted in Figure 7.9. In Figure 7.9, the temperature and stream-function (SF) contours in the ITP torch and reactor are shown. Due to the external forces from the coils, shown by circles in Figure 7.9a, the center of flowing gas reaches to very high temperatures transforming cold gas to thermal plasma. By making distance from the source term, the temperature of the plasma drops rapidly due to the very high cooling rate, in an order of \(10^7\) (K/s). In the SF profile,
recirculation area created by electromagnetic field is also seen at the coil level. The thermo-flow field at the exit line, shown by dashed-line in Figure 7.9a, of the ITP torch was then used for the simulation of the ITP reactor and the results are shown in Figure 7.9b. Still very high cooling rate, the characteristic of the ITP systems, causes a very steep temperature gradient along the ITP reactor. The temperature of the plasma drops from ~10 000 K at the top of the ITP reactor to the temperatures not lower than 1 400 K at the exit which agrees the experimental temperature measurement at the exit. As shown in Figure 7.9b, the SF contour indicates a recirculation area created at the top of ITP reactor due to the expansion after the exit of the ITP torch. Very small recirculation area in the middle of the ITP reactor is also evident where the volume of reactor is expanded.

![Temperature (top) and stream-function (bottom) contours in (a) the ITP torch, (b) the ITP reactor without NH₃ opposed-flow injection](image)

**Figure 7.9** Temperature (top) and stream-function (bottom) contours in (a) the ITP torch, (b) the ITP reactor without NH₃ opposed-flow injection

**Reacting-flow**

Upon opposed-flow injection of NH₃, the thermo-flow field of ITP reactor is influenced as shown in Figure 7.10. Comparing T profile of the ITP reactor, before and after NH₃ injection, shown in Figure 7.9 and Figure 7.10, respectively, the penetration depth of such injection is found to be about 20 cm from the injection point. Due to the high velocity cold injection of NH₃, the temperature drop in these areas is quite evident. The temperature drop of the bulk flow close to the injection point, as shown in Figure 7.11, is about the magnitude of that observed from the experimental measurement (i.e., ~300 K). As seen in Figure 7.11, except the first 5 mm from the center line, the bulk temperature profile is more uniform due to the
recirculation of the flow. The injection process not only affects the temperature profile of the ITP reactor but also it creates a very large recirculation area close to the base of reactor, as seen in SF profile in Figure 7.10, and the place where synthesized solids containing SWCNTs experience a longer residence time in the reactor. Therefore, apart from the kinetic effect of such injection, the direct effect of reactive NH$_3$ gas injection on the thermo-flow field of the ITP reactor is evident indicating the importance of coupled CFD-Kinetic model in simulation of reacting flow.

Figure 7.10 Temperature (top) and stream-function (bottom) contours of ITP reactor with opposed-flow NH$_3$ injection
The calculated mole fraction of intermediate species formed during decomposition of NH$_3$ in the ITP reactor is depicted in Figure 7.12. As shown in Figure 7.12, the simulation predicts the main decomposition event occurs not far than 30 cm from the base of reactor where the NH$_3$ was injected. The lowest mole fraction is predicted to belong to NNH species with a very narrow distribution. The formation of this species occurs in a region close to the NH$_3$ injection point and its concentration profile develops not far than 4 cm along the axis of the ITP reactor. Since the area close to the injection point experiences a very high turbulent intensity, because of very high velocity of injected gas, the formation of NNH seems to be strongly turbulent dependent. Compared to NNH, N$_2$H$_2$ experiences a more extended concentration profile in both radial and axial direction of the reactor. Although the highest concentration of this species exists in the same region as that of NNH, but its effective profile reaches to 8 cm from the injection point. Very low but broad concentration profile is predicted in 8–18 cm from the base of ITP reactor, as shown in Figure 7.12, for N$_2$H$_2$ intermediate species. The predicted concentration profile for NNH and N$_2$H$_2$ species suggests that they mainly play a role in NH$_3$ thermal decomposition rather than modifying the surface chemistry of SWCNTs.
Unlike NNH and N$_2$H$_2$ species, other intermediate species are mainly formed in the region of reactor far from the injection point, as illustrated in Figure 7.12. This suggests that the thermal decomposition of ammonia in the ITP reactor is both kinetic and mixing controlled otherwise the main reaction species would occur close to the injection point. NH$_2$ and NH species exhibit almost the same arc-shape concentration profile but NH$_2$ concentration is predicted to be at higher content than NH which is in good agreement with other experimental studies [Davidson et al., 1990; Konnov and De Ruyck, 2000]. Moreover, in comparison with NH the tail of arc has been extended for NH$_2$, as shown in Figure 7.12. The highest concentration of NH$_2$ and NH exists in a region more than 10 cm from the base of reactor (mainly in 15–20 cm) where the NH$_3$ was injected. The simulation predicts the highest concentration of intermediate species belongs to atomic hydrogen (H), with a very confined concentration profile which is formed about 20 cm from the base of the reactor. The model suggests that the main intermediate species driving the in situ chemistry of SWCNTs product are atomic hydrogen and NH$_2$ amidogen radicals compared to other intermediates.

Figure 7.13 shows the concentration profile of opposed-flow injected NH$_3$ gas and its final products (i.e., N$_2$ and H$_2$) in the ITP reactor. The highest penetration of NH$_3$ does not exceed 18 cm far than the base of reactor where its concentration is drastically diminished because of both the main flow field and its decomposition reaction. Considering the concentration profiles of NH$_3$, NH$_2$ and H, the model can explain the experimental observation discussed in experimental section 7.6.1. As seen in Figure 7.12, the main intermediate species, i.e., H and NH$_2$ are formed at the highest point from the injection point and above NH$_3$ profile. Therefore, the nanotubes interact firstly with these reactive species leading the formation of active sites on the nanotubes and then will be in contact with NH$_3$. Therefore, the pre-formed active sites allow the NH$_3$ molecules to chemisorb on the nanotubes more probably in the recirculation area shown in Figure 7.10. Since the concentration profile of NH$_2$ is much more extended in the ITP reactor compared to atomic hydrogen, H, and it is also present in the recirculation area, the nanotubes interaction with NH$_2$ is expected to be more effective than H atoms.

As model predicts, decomposition of NH$_3$ in the ITP reactor is not completed due to the fast flow compared to the rate of reaction. This prediction agrees very well with the experimental
measurement using mass spectrometer by which the maximum decomposition yield was found to be at a maximum of 85%. The model predicts a 70% yield for decomposition of ammonia. Besides the numerical errors caused mostly by the turbulent model, other phenomena that were not considered in the model can explain the difference between the experiment and the simulation results. For example, the presence of very small air leak (< 0.04 kPa/s) in the ITP reactor can slightly enhance the decomposition yield of ammonia since its oxidation has been experimentally found to be a fast exothermic reaction with relatively low activation energy [Baulch et al., 1972]. Therefore, very low concentration of oxygen in the system may help the decomposition process resulting in a higher yield than what the model predict.
Figure 7.12  Calculated mole fraction of intermediate species above the NH$_3$ injection point at the base of ITP reactor
7.7 Conclusion

The effect of ammonia gas addition to the synthesis environment of SWCNTs on their surface chemistry was studied. The study was based on the opposed-flow injection of ammonia into the ITP reactor used for the mass production of SWCNTs. The influence of this in situ process on the SWCNT final product was closely examined by Raman spectroscopy at three wavelengths, coupled thermogravimetry-infrared spectroscopy and solid-phase infrared spectroscopy. The results obtained with these techniques clearly indicated the surface modification of SWCNTs where the metallic tubes showed a greater tendency than semiconducting tubes to react with ammonia in the ITP reactor. To better understand the reaction system and predict the concentration profile of intermediates and product species of decomposed ammonia in the ITP reactor, a 2D numerical simulation was successfully developed including both the detailed kinetic and the mixing process. With the model, the
concentration profile of the intermediate species along with the products of ammonia thermal decomposition in the ITP reactor was successfully predicted. The proposed model predicted that the role of NNH and N₂H₂ intermediates is mainly to drive the ammonia thermal decomposition in the ITP reactor. It was found that the main intermediate species (i.e., H and NH₂) are formed 20 cm above the ammonia injection point with different concentration profiles. Unlike atomic hydrogen, NH₂ showed a much more extended concentration profile along the ITP reactor. The model suggested a two-step in situ chemistry upon the injection of ammonia in the SWCNT synthesis environment. In the first step the nanotubes interact mainly with NH₂ and H so that the active sites are created and in the second step ammonia chemisorbs on the nanotubes surface. Moreover, the simulation results indicated that thermal decomposition of ammonia in the ITP reactor is evidently influenced by the mixing process.

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8.1 Conclusions générales

Les SWCNTs ont été au centre de l’attention depuis leur découverte en 1993 en raison de leurs propriétés mécaniques, électroniques, thermiques exceptionnelles ainsi qu’à leur structure unidimensionnelle unique qui en font des candidats exceptionnels pour beaucoup d’applications. La plupart de leurs applications potentielles nécessitent cependant que les SWCNTs soient traitables et fonctionnels. Toutefois, les SWCNTs tels que produits se dispersent peu et montrent une faible solubilité dans beaucoup de solvants réduisant ainsi leur fonctionnalité et leur facilité à être utilisés. Les méthodes efficaces pour surmonter ce problème et pour modifier la chimie des SWCNTs sont essentiellement les procédés chimiques après-traitement. Aucun procédé in situ n’a été encore proposé pour la méthode de synthèse par PTI (plasma thermique inductif).

Dans ce travail, la modification chimique in situ des SWCNTs dans leur environnement de synthèse par l’addition de l’ammoniac par procédé d’injection à contre-courant a été étudiée et effectuée avec succès pour la première fois.

Avant la modification chimique in situ, le procédé de synthèse a été amélioré en réduisant les risques sanitaires liés à l’installation de synthèse et aux catalyseurs en métal contenant la matière première. À cet égard, l’installation du système de synthèse a été modifiée selon un système fermé qui a permis de réduire au minimum l’exposition de nanomatériaux en laboratoire. De plus, le remplacement des catalyseurs toxiques dans la matière première, l’effet de différents catalyseurs métalliques et leurs quantités dans la matière première sur la synthèse des SWCNTs ont été étudiés thermodynamiquement et expérimentalement. Les résultats ont clairement montré que ces SWCNTs de haute qualité pouvant être produits avec un mélange ternaire de catalyseur contenant du Ni, Y$_2$O$_3$, et du Co qui est fortement toxique, peuvent également être produits avec un mélange binaire de Ni et de Y$_2$O$_3$. Les calculs thermodynamiques ont indiqué que le type et la quantité de catalyseurs métal affecteraient plus la phase liquide de la solution formée dans le système de réaction de PTI pendant la
production de SWCNT et moins la phase gazeuse, alors que Y_2O_3 affecte plus la phase gazeuse avec moins d'impact sur la phase liquide de la solution. Contrairement aux résultats expérimentaux, les résultats des calculs thermodynamiques ont suggéré que le catalyseur de Mo a le potentiel de produire des SWCNTs de haute qualité en utilisant la méthode PTI. Compte tenu de la température eutectique du système de catalyseur-carbone, le temps de séjour efficace pour le Ni/Co s'est avéré à être 2,3 fois plus élevé que le Mo dans le réacteur de PTI ayant pour résultat un produit de SWCNT de haute qualité en utilisant le Ni/Co. Ainsi, le potentiel de Mo pour la synthèse de SWCNT peut être amélioré par l'optimisation du procédé de PTI en augmentant la longueur de la zone de température élevée (T > 2 000 K).

Concernant l'utilisation de la technique TG pour faire la caractérisation des SWCNTs tels que produits et chimiquement modifiés dans le travail actuel, la TG a été premièremenent normalisée en étudiant les effets de trois paramètres instrumentaux principaux (la rampe de température (RT), la masse initiale (MI) de l’échantillon, et le taux de débit de gaz (FR)) sur la T_onset (c.-à-d. la température de commencement) et sur la largeur à mi-hauteur (en anglais : FWHM) obtenues à partir de la TG et des graphiques dérivés de la TG du noir de carbone, respectivement. Par conséquent, un modèle statistique factoriel à deux niveaux a été effectué. L'analyse statistique a montré que l'effet de TR, IM et, dans une moindre mesure, FR est significatif sur le FWHM et non significatif sur la T_onset. L'effet de l'échantillonnage y compris la morphologie des échantillons de SWCNTs et leur teneur en humidité sur la TG a également été étudié. Les résultats ont toutefois indiqué que la TG de SWCNTs n'est pas affectée ce qui implique donc une sensibilité insuffisante de la TG pour les conditions d'échantillonnage ainsi que celles des conditions instrumentales. D'ailleurs, une perte de masse de 6% et un gain de masse de 23% ont été observés pour l’oxyde d’yttrium et le nickel pur nanométrique, respectivement. Le comportement de la TG du SWCNT tel que produit a été profondément étudié en exécutant l'analyse de la TG sur les échantillons de SWCNT à trois niveaux différents de pureté (c.-à-d. tel que produit, oxydé-thermique, et traité par HNO_3). Les résultats obtenus de la TG ont été alors comparés aux images associées de MEB à haute résolution de chaque échantillon. Par cette procédure, la déconvolution de la perte de masse à plusieurs étapes obtenue par la TG des échantillons tel que produits de SWCNT a été réalisée permettant l'évaluation de la pureté des SWCNTs tels que produits synthétisés par la méthode PTI.
L'injection à contre-courant de l'ammoniac pendant la synthèse des SWCNTs par le système PTI a alors été développée et effectuée avec succès. Les résultats expérimentaux ont indiqué une augmentation de 10 fois la quantité d'azote dans le produit fini de SWCNT par l'ajout de 15 vol% d'ammoniac dans le réacteur PTI. De plus, une dispersion stable de SWCNT dans l'isopropanol et le DMF a été réalisée. L'analyse Raman a indiqué la modification de la structure des SWCNTs par l'injection d'ammoniac. L'endroit d'injection et le type de buse se sont avérés être des paramètres qui peuvent affecter le matériau des SWCNTs pendant le procédé à contre-courant de l'injection NH₃. L'analyse par MET a indiqué que les injections d'ammoniac pourraient également changer la morphologie du matériau des SWCNTs synthétisés en présence de la solution d'ammoniac de 15 vol% dans le réacteur PTI, dans laquelle la présence des nanostructures de carbone en forme d'oignon et plane, a été observée. Les résultats des calculs thermodynamiques du système de phase gazeuse ont indiqué la possibilité de former des sous-produits gazeux tels que le HCN et le CH₄ pendant le procédé de synthèse dès l'injection de NH₃. Cette conclusion est en accord avec les observations expérimentales. Le NH₃ ne peut pas influencer la croissance des SWCNTs en réagissant avec les catalyseurs métal tel que confirmé par les deux calculs thermodynamiques et l'analyse DRX. Les résultats ont indiqué que quelques réactions, thermodynamiquement favorables, ne peuvent pas complètement se produire dans le réacteur PTI due à la caractéristique de non-équilibre du système. Les résultats des simulations CFD ont clairement prouvé que le champ de thermo-écoulement du système PTI est influencé par l'écoulement à contre-courant d'ammoniac et particulièrement, par le type de buse d'injection. L'injection sans buse entraîne une absence prolongée du NH₃ dans le réacteur PTI par rapport à la présence d'une buse. L'injection à vitesse élevée sans une buse entraîne un effet d'acheminement au centre de l'écoulement principal de plasma près du point d'injection tandis que ce phénomène est beaucoup moins prononcé aux régions loin de ce point. Les résultats de simulation ont démontré que le procédé de la décomposition du NH₃ peut être contrôlé par une conception appropriée de la buse ce qui a ainsi permis un traitement chimique plus efficace du produit fini des SWCNTs.

En outre, l'influence de cette addition d'ammoniac dans l'environnement de synthèse des SWCNTs sur le produit fini des SWCNTs synthétisés par le système PTI en présence de...
15 vol % de NH₃ a été examinée de manière approfondie par la spectroscopie Raman à trois longueur d'onde, la TG-FTIR, et la spectroscopie infrarouge en phase solide. Les résultats obtenus avec ces techniques ont clairement indiqué la modification de la surface des SWCNTs où les tubes métalliques ont eu une plus grande tendance que les tubes semi-conducteurs à réagir avec l'ammoniac dans le réacteur PTI. La présence de NH₃ et de HNCO dans le spectre de FTIR du gaz évolué de l'échantillon de SWCNT traité par NH₃ a été observée pendant la TG en mode désorption à 200 °C. En raison de la désorption à haute température, et du fait que l'ammoniac peut seulement s'adsorber physiquement à basse température sur l'échantillon de SWCNTs tel que produit, on a conclu que le NH₃ s'adsorbe chimiquement sur les échantillons des SWCNTs. Pour mieux comprendre le système de réaction et prévoir le profil de concentration des produits de l'ammoniac décomposé dans le réacteur PTI et des espèces intermédiaires, une simulation numérique en 2D a été développée comprenant la cinétique détaillée et l'effet du mélange turbulent. Le modèle a prévu une grande zone de recirculation près du secteur d'injection à contre-courant qui affecte le temps de séjour du produit solide contenant les SWCNTs dans le réacteur PTI. Avec le modèle, le profil de concentration des espèces intermédiaires avec les produits de la décomposition thermique d'ammoniac (N₂ et H₂) dans le réacteur PTI a été prévu. Par conséquent, le rôle du NNH et du N₂H₂ a été jugé essentiel sur la conduite de la décomposition de l'ammoniac plutôt que la modification chimique des SWCNTs dans le réacteur PTI. Les espèces intermédiaires principales prédites montrant les profils de concentration les plus élevés, H et NH₂, sont formés à approximativement 20 cm du point d'injection d'ammoniac au-dessus du profil de concentration du NH₃. Contrairement à l'hydrogène actif, le NH₂ a montré un profil de concentration beaucoup plus prolongé le long du réacteur PTI atteignant le secteur de recirculation près de la base du réacteur. Considérant les résultats expérimentaux, le modèle a corrobore l'idée d'un mécanisme en deux étapes pour le procédé de modification chimique in situ dès l'injection d'ammoniac dans l'environnement de synthèse des SWCNTs. Dans la première étape, les nanotubes interagissent principalement avec le NH₂ et le H de sorte que des sites actifs sont créés. Dans la deuxième étape, l'ammoniac s'adsorbe chimiquement à la surface des nanotubes.
8.2 Overall conclusions

SWCNTs have been at the center of attention since their discovery in 1993 due to their outstanding mechanical, electronic, and thermal properties, and their unique one-dimensional structure that make them exceptional candidates for many applications. Most of their potential applications however need SWCNTs to be processable and functional. As-produced SWCNTs, on the other hands, have shown a poor dispersibility and insolubility in most solvents reducing their functionality and processability. The effective methods to overcome this problem and modify the SWCNTs surface chemistry are essentially post-treatment chemical processes, and no in situ process for the induction thermal plasma (ITP) synthesis method had yet been proposed.

In this work, the in situ chemical modification of SWCNTs in their synthesis environment (i.e., the ITP synthesis system) by addition of ammonia gas through a counter-current injection process was studied and successfully performed for the first time.

Prior to the in situ chemical modification, the synthesis process was enhanced regarding the health risks associated with the synthesis setup and the metal catalysts containing feedstock. In this regard, the synthesis setup was modified to an enclosed system which enabled to minimize the nanomaterials exposure to the laboratory. Moreover, towards the replacement of toxic catalysts in the SWCNT feedstock, the effect of different metallic catalysts and their quantity in the feedstock on the SWCNTs synthesis were thermodynamically and experimentally studied. The results clearly showed that high quality SWCNTs which could be produced with a ternary catalyst mixture containing Ni, Y$_2$O$_3$, and highly toxic Co can also be produced with a binary mixture of Ni and Y$_2$O$_3$. Thermodynamic calculations indicated that type and quantity of metal catalysts would affect more the liquid solution phase formed in the ITP reaction system during SWCNT production and less the gas phase, while Y$_2$O$_3$ affects more the gas phase with less impact on the liquid solution phase. Unlike the experimental results, the results of the thermodynamic calculations suggested that the Mo catalyst has the potential for the production of high quality SWCNTs using the ITP method. Considering the eutectic temperature of the catalyst-carbon system, the effective residence time for Ni/Co was found to be 2.3 times more than Mo in the ITP reactor resulting in a higher quality Ni/Co-grown
SWCNT. Thus, Mo potential for the synthesis of SWCNT can be improved through the ITP process optimization by increasing the length of the high temperature zone (T > 2 000 K).

Towards the use of TG technique in characterizing as-produced and chemically modified SWCNTs in the present work, TG was firstly standardized by studying the effects of three main instrumental parameters (temperature ramp, TR, initial mass of the sample, IM, and gas flow rate, FR) on the T_{onset} and FWHM obtained from TG and derivative TG graphs of carbon black, respectively. Accordingly, a two-level factorial statistical design was performed. The statistical analysis showed that the effect of TR, IM, and to a lower extent FR is significant on FWHM and insignificant on T_{onset}. The effect of sampling including SWCNTs sample morphology and moisture content on the TG was also studied. The results indicated that TG of SWCNTs is not affected by the sampling conditions. Moreover, a complementary TG analysis on the nano-sized Ni and Y_{2}O_{3} which are present in the SWCNTs samples indicated a mass gain of 23 wt % and a mass loss of 6 wt % in flowing Ar-O_{2}(80%-20%), respectively. The TG behavior of the as-produced SWCNT was studied in detail by performing the TG analysis on the SWCNT samples at three different levels of purity (i.e. as-produced, thermally-oxidized, and HNO_{3}-treated). The obtained TG results were then compared to the associated HRSEM images of each sample. Through this procedure, the multi-step mass loss obtained by TG of the as-produced SWCNT samples was fully de-convoluted enabling the purity evaluation of the as-produced SWCNTs synthesized by the ITP method.

The counter-current injection of ammonia during the synthesis of SWCNTs by the ITP system was then successfully developed and performed. The experimental results indicated a 10-fold increase in the quantity of nitrogen in the final SWCNT product by adding 15 vol % of ammonia in the ITP reactor. With this, a long term dispersibility of SWCNT material in the isopropanol and DMF was achieved. Raman analysis indicated the structural alteration of SWCNTs upon ammonia injections. The injection place and nozzle type were found to be the parameters that can affect the SWCNTs materials during the counter-current NH_{3} injection process. TEM analysis revealed that ammonia injections could also alter the morphology of SWCNTs material in which the presence of onion-like and planar carbon nanostructures were observed in the sample synthesized in the presence of 15 vol % ammonia in the ITP reactor.
Thermodynamic calculation results of the gas phase system indicated the possibility of the formation of gaseous by-products such as HCN and CH₄ during the synthesis process upon NH₃ injections. This was in line with the experimental observation. NH₃ cannot alter the growth of SWCNTs by reacting with metal catalysts as confirmed with both thermodynamic calculations and XRD analysis. The results indicated that some reactions which are thermodynamically favorable cannot completely happen in the ITP reactor due to the non-equilibrium characteristics of the system. The CFD simulations results clearly showed that the thermo-flow field of the ITP system is influenced by the ammonia counter-current flow and, particularly, by the injection nozzle type. The injection without nozzle results in a deeper NH₃ delivery into the ITP reactor in comparison to the nozzle. The high velocity injection without nozzle results in the channelling effect at the center of the main plasma flow close to the injection point while this phenomenon is much less pronounced at regions far from this point. The simulation results demonstrated that NH₃ decomposition process can be controlled through a proper design of the nozzle which in turn results in a more effective chemical treatment of the final SWCNT product.

Furthermore, the influence of this ammonia addition into the SWCNTs synthesis environment on the SWCNTs final product synthesized by the ITP system in the presence of 15 vol% NH₃ was closely examined by Raman spectroscopy at three-wavelength, coupled TG-FTIR spectroscopy, and solid-phase infrared spectroscopy. The results obtained with these techniques clearly indicated the surface modification of SWCNTs where the metallic tubes showed a greater tendency than semiconducting tubes to react with ammonia in the ITP reactor. The presence of NH₃ and HNCO in the FTIR spectrum of evolved gas from the NH₃-treated SWCNT sample were observed during desorption TG at ~ 200 °C. Due to the high temperature desorption, and the fact that ammonia can only physisorb at low temperatures on as-produced SWCNTs sample, it was concluded that NH₃ chemisorbed on the SWCNTs samples. To better understand the reaction system and predict the concentration profile of intermediates and product species of decomposed ammonia in the ITP reactor, a 2D numerical simulation was developed including both the detailed kinetics and turbulent mixing effect. The model predicted a large recirculation area close to the opposed-flow injection area that affects the residence time of solid product containing SWCNTs in the ITP reactor. With the model,
the concentration profile of intermediate species along with the products of ammonia thermal decomposition (N\textsubscript{2} and H\textsubscript{2}) in the ITP reactor was successfully predicted. Accordingly, the role of NNH and N\textsubscript{2}H\textsubscript{2} intermediates was found to be mainly on driving the ammonia thermal decomposition rather than chemical modification of SWCNTs in the ITP reactor. The main intermediate species showing the highest concentration profiles were predicted to be H and NH\textsubscript{2} which are formed approximately 20 cm from the ammonia injection point and above the NH\textsubscript{3} concentration profile. Unlike atomic hydrogen, NH\textsubscript{2} showed a much more extended concentration profile along the ITP reactor reaching the recirculation area close to the base of the reactor. Considering the experimental results, the model corroborated the idea of a two-step mechanism for the \textit{in situ} chemical modification upon the ammonia injection into the SWCNTs synthesis environment. In the first step the nanotubes interact mainly with NH\textsubscript{2} and H so that the active sites are created. In the second step, ammonia chemisorbs on the nanotubes surface.

8.3 Future work

The present study provides a sound basis for the \textit{in situ} chemical modification of SWCNTs material using the ITP method for the first time. Future investigations are suggested for further development of the proposed SWCNT synthesis method:

- To produce high quality SWCNTs using an Mo catalyst by increasing its effective residence time in the ITP reactor. Changing the operating conditions such as plate power and plasma gas composition of the ITP system is suggested.
- To expand the proposed model by including the ammonia decomposition kinetics in the 3D simulation of the nozzle injection using the developed CHEMKIN code used in 2D model. It helps to create a more realistic model of the reacting flow and the injection process in the ITP reactor. This improvement in the model is important for further optimization of this process.
- To incorporate this chemically modified SWCNTs material into a proper polymer matrix and to investigate its applicability in enhancing the final mechanical and electrical properties of the composite.
- To employ this chemically modified SWCNTs material in biological applications e.g., bone tissue engineering.
Table A.1  Detailed reaction mechanism and rate parameters proposed by Dove and Nip (1979) for the ammonia thermal decomposition, \( k=AT^n \exp\left(-E/RT\right) \) (cm\(^3\)/mole.sec).

<table>
<thead>
<tr>
<th>Elementary Reactions</th>
<th>Log A</th>
<th>n</th>
<th>Ea(kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) ( \text{NH}_3+\text{M} = \text{NH}_2+\text{H}+\text{M} )</td>
<td>15.93</td>
<td>0.00</td>
<td>387.18</td>
</tr>
<tr>
<td>2) ( \text{NH}_3+\text{M} = \text{NH}+\text{H}_2+\text{M} )</td>
<td>15.74</td>
<td>0.00</td>
<td>380.90</td>
</tr>
<tr>
<td>3) ( \text{NH}_2 + \text{NH} = \text{N}_2\text{H}_3 + \text{H}_2 )</td>
<td>11.90</td>
<td>0.50</td>
<td>90.27</td>
</tr>
<tr>
<td>4) ( \text{N}_2\text{H}_3 + \text{M} = \text{NH} + \text{NH}_2 + \text{M} )</td>
<td>12.80</td>
<td>0.00</td>
<td>41.86</td>
</tr>
<tr>
<td>5) ( \text{H} + \text{NH}_3 = \text{H}_2 + \text{NH}_2 )</td>
<td>13.39</td>
<td>0.00</td>
<td>71.57</td>
</tr>
<tr>
<td>6) ( \text{H} + \text{NH}_2 = \text{H}_2 + \text{NH} )</td>
<td>13.79</td>
<td>0.00</td>
<td>21.87</td>
</tr>
<tr>
<td>7) ( \text{NH}_2 + \text{NH}_2 = \text{NH} + \text{NH}_3 )</td>
<td>12.80</td>
<td>0.00</td>
<td>41.86</td>
</tr>
<tr>
<td>8) ( \text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M} )</td>
<td>17.95</td>
<td>-1.00</td>
<td>0</td>
</tr>
<tr>
<td>9) ( \text{NH} + \text{NH} = \text{N}_2 + \text{H}_2 )</td>
<td>11.55</td>
<td>0.55</td>
<td>7.95</td>
</tr>
<tr>
<td>10) ( \text{NH}_2 + \text{NH}_2 = \text{N}_2 + \text{H}_2 + \text{H}_2 )</td>
<td>13.60</td>
<td>0.00</td>
<td>50.22</td>
</tr>
</tbody>
</table>

\( \text{M} = \text{Third-body} \)
APPENDIX B

Table B.1 Detailed reaction mechanism and rate parameters proposed by Yumura and Asaba (1981) for the ammonia thermal decomposition, \( k=AT^n \exp (-E/RT) \) (cm³/mole.sec).

<table>
<thead>
<tr>
<th>Elementary Reactions</th>
<th>Log A</th>
<th>n</th>
<th>Ea(kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) ( \text{NH}_3 + \text{M} = \text{NH}_2 + \text{H} + \text{M} )</td>
<td>16.25</td>
<td>0.00</td>
<td>385.34</td>
</tr>
<tr>
<td>2) ( \text{H} + \text{NH}_3 = \text{H}_2 + \text{NH}_2 )</td>
<td>14.10</td>
<td>0.00</td>
<td>92.21</td>
</tr>
<tr>
<td>3) ( \text{H} + \text{NH}_2 = \text{H}_2 + \text{NH} )</td>
<td>13.48</td>
<td>0.00</td>
<td>35.81</td>
</tr>
<tr>
<td>4) ( \text{NH} + \text{NH} = \text{N}_2 + \text{H} + \text{H} )</td>
<td>13.39</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>5) ( \text{NH}_2 + \text{M} = \text{NH} + \text{H} + \text{M} )</td>
<td>14.31</td>
<td>0.00</td>
<td>289.16</td>
</tr>
<tr>
<td>6) ( \text{NH} + \text{M} = \text{N} + \text{H} + \text{M} )</td>
<td>12.51</td>
<td>0.50</td>
<td>289.82</td>
</tr>
<tr>
<td>7) ( \text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M} )</td>
<td>14.37</td>
<td>0.00</td>
<td>401.66</td>
</tr>
<tr>
<td>8) ( \text{NH}_3 + \text{NH}_2 = \text{N}_2 \text{H}_3 + \text{H}_2 )</td>
<td>11.90</td>
<td>0.50</td>
<td>90.25</td>
</tr>
<tr>
<td>9) ( \text{NH}_2 + \text{NH}_2 = \text{NH} + \text{NH}_3 )</td>
<td>12.80</td>
<td>0.00</td>
<td>48.41</td>
</tr>
<tr>
<td>10) ( \text{N}_2 \text{H}_3 + \text{M} = \text{NH}_2 + \text{NH} + \text{M} )</td>
<td>12.80</td>
<td>0.00</td>
<td>48.41</td>
</tr>
</tbody>
</table>

M=Third-body
APPENDIX C Raman spectroscopy of SWCNTs

Figure C.1 Schematic diagram of Raman scattering process.

Background

Raman effect was firstly discovered by Sir Chandrasekhara Venkata Raman in 1928 [Raman and Krishnan, 1928]. Raman spectroscopy has been widely used in characterization of carbon materials mostly with $sp^2$ configuration. It can give useful information about CNTs e.g. the presence of $sp^3$ hybridization, chemical impurities, defects by crystal disorder, optical energy gap, carbon nanotube diameter and chirality, and metallic vs. semiconducting behavior of carbon nanotubes [Saito et al., 2011].

Raman scattering

In general, Raman scattering is the inelastic scattering of light by a matter (the elastic scattering is called Rayleigh scattering). In this scattering process, an electron is firstly excited by absorbing a photon so which results in displacement of the electron from the valance band to the conductive band. The excited electron is then scattered by absorbing or emitting
phonons (the quantized mode of vibration in lattice). The process terminates when the electron relaxes back to the valance energy band by emitting a photon [Dresselhaus et al., 2005]. To obtain the Raman spectra of materials, the intensity of the scattered light is measured as a function of the frequency downshift (i.e., Raman shift) caused by the loss of energy of the scattered light. In fact, Raman scattering measures the shift between the incident and scattered light frequencies \( \Delta \omega = \omega_{\text{phonon}} - \omega_{\text{scat}} \) when the \( \omega_{\text{phonon}} \) is an optical phonon mode vibration [Poole and Owens, 2003]. The scattering process is called Stokes process when the Raman scattering occurs for phonon emission and it is called anti-Stokes when the Raman scattering occurs by phonon absorption. Raman spectroscopy is an important tool for an accurate measurement of the phonon frequency of materials [Dresselhaus et al., 2005].

**First-order Raman scattering of SWCNTs: RBM, \( G^+ \), \( G^- \)**

In Raman scattering process, the number of phonons which are emitted prior to the lattice relaxation can be one, two, three or more. The first-order process (i.e. one-phonon) is the lowest Raman scattering process which occurs in \( sp^2 \) carbon [Dresselhaus et al., 2005]. In SWCNTs, two first-order Raman modes are the tangential mode, so-called G band around 1580 cm\(^{-1}\), and low frequency radial breathing mode, so-called RBM, as shown in Figure C.2.

![Figure C.2](image)

Figure C.2 Two first-order modes of SWCNTs: tangential G band and RBM

Unlike in graphite, in SWCNTs G band splits into two main components so-called \( G^+ \) and \( G^- \) bands. Interestingly, the \( G^- \) band line-shape, line-width and frequency of metallic nanotubes differ from those of semiconducting tubes [Saito et al., 2011]. Although the G band feature is also observed in Raman spectra of graphitic carbon, RBM mode is a unique one which only
appears in carbon nanotubes. Therefore, the presence of RBM features in the Raman spectrum is a reliable proof implying that the sample contains SWCNTs [Dresselhaus et al., 2005]. Since RBM arises from the fact that all the carbon atoms in SWCNT move coherently in the radial direction as shown in Figure C.2, there is a relation between the RBM frequency and the nanotube diameter. For a SWCNT in the bundle this relation can be expressed as follows,

\[ \omega_{\text{RBM}} \frac{(\text{cm}^{-1})}{d_n(\text{nm})} = \frac{234(cm^{-1}nm)}{10(cm^{-1})}, \text{[Milnera et al., 2000]} \]  

\[ \text{(C1)} \]

**Breit-Wigner-Fano line shape**

Raman spectra of metallic SWCNTs do not show a symmetric \( G^\text{-band} \) line-shape and can be fitted to a so-called Breit-Winger-Fano (BWF) line-shape function as follow:

\[ I(\omega) = I_0 \frac{1 + (\omega - \omega_{\text{BWF}} / q\Gamma)^2}{1 + (\omega - \omega_{\text{BWF}} / \Gamma)^2} \]

\( I_0, \omega_{\text{BWF}}, \) and \( \Gamma \) are fitting parameters which represents the intensity, central frequency and the broadening factor, respectively in the above function. \( 1/q \) represents the asymmetry of the line-shape. It is worth mentioning that the BWF line-shape appears only for metallic SWCNTs but not for the semiconducting SWCNTs [Dresselhaus et al., 2005].

**Second-order Raman scattering of SWCNTs:** D

D band (disorder-induced) is associated to the breakage of the symmetry in the graphitic plan of the SWCNT which is normally caused by defects. D band is also associated to the presence of sp\(^3\) bonds [Saito et al., 2011]. In SWCNTs, D band appears in the Raman spectrum at around 1 350 cm\(^{-1}\). A typical Raman spectrum of SWCNTs with its main features is depicted in Figure C.3.
Resonance Raman scattering

The intrinsic geometry of SWCNT induces a quantum confinement that creates many van Hove singularities (vHS) in the density of states (DOS). Therefore, the optical transition is allowed among different pair of vHS of the valence and conduction bands. Once the energy of the incident photons matches a vHS in the electronic joint DOS (JDOS), the corresponding photo-physical process in Raman scattering is expected to be resonant enhanced. There are two resonance conditions in which the Raman signal is greatly enhanced: i) incidence resonance which is caused by the incident laser photon and ii) scattered resonance which is cause by scattered photon [Dresselhaus et al., 2005]. In fact, when either the energy of the incident or scattered light matches a vHS energy in JDOS, due to the resonance effect the Raman intensity becomes very strong for certain SWCNTs satisfying the resonance condition.

Kataura plot

The electronic transition energy between the electronic valence and conduction bands (i.e., \( E_{\text{ii}} \)) approximately matches the energy of the excitation laser in resonance condition (i.e. \( E_L \)) [Dresselhaus et al., 2005]. The Kataura plot which is calculated theoretically is a set of \( E_{\text{ii}} \) for each \((n,m)\) SWCNT versus the SWCNT diameter. Kataura plot provides a useful tool in
determining different (n,m) SWCNTs, i.e. chirality, regarding the Raman excitation wavelength used during the experimental measurement [Saito et al., 2011]. As mentioned, the diameter of nanotubes in sample can be calculated from the equation C1. The RBM features can provide the corresponding $\omega_{\text{RBM}}$ to be used in C1. Therefore, the frequency region in which the RBM features are observed gives the diameter distribution of SWCNTs in a sample. As shown in Figure C4, a region is highlighted according to the calculated diameter distribution of SWCNTs samples synthesized by ITP method in this work (i.e., ~ 1.2-2.0 nm). By doing this, the possible (n,m) SWCNTs which are present in the ITP grown samples can be identified on the Kataura plot according to the laser excitation wavelength used during the Raman measurements. Three different laser excitation wavelengths were used in this work: 514.5, 632.8 and 780 nm. As indicated in Figure C4, at $\lambda_{\text{ext}}=780$ nm, only metallic tubes are probed, at $\lambda_{\text{ext}}=632.8$ nm, larger diameter semiconducting and smaller diameter metallic tubes are probed, and at $\lambda_{\text{ext}}=514.5$, larger diameter metallic tubes and smaller diameter semiconducting tubes are probed in ITP-grown SWCNTs samples.
Figure C.4  Calculated energy transition of various (n,m) SWCNTs versus the SWCNTs diameter. Filled circle in black shows semiconducting SWCNTs while the open circle in red shows the metallic SWCNTs. The horizontal lines indicate the laser energies used in the present work. Probed SWCNTs at each wavelength are identified with solid and dashed closed-lines, for metallic and semiconducting tubes, respectively.
References


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