C$_{60}$ Encapsulation inside Nitrogen-Doped and Pristine Multi-Walled Carbon Nanotubes (MWCNTs) and Investigation of the Dynamics of Encapsulated C$_{60}$s inside Thin-Walled MWCNTs

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Encapsulation inside Nitrogen-Doped and Pristine Multi-Walled Carbon Nanotubes (MWCNTs) and Investigation of the Dynamics of Encapsulated \( \text{C}_6\text{O}_0 \)s inside Thin-Walled MWCNTs

ABSTRACT

Filling the hollow cavity of carbon nanotubes (CNTs) opens new possibilities of producing nearly one-dimensional nanostructures, whereas the molecular dynamics of the confined material can be dramatically affected. The main focus of this project was to fill nitrogen-doped and pristine multi-walled carbon nanotubes (MWCNTs) with fullerene \( \text{C}_6\text{O}_0 \) to investigate the \( \text{C}_6\text{O}_0 \) rotational behavior after encapsulation. Nitrogen-doped CNTs (N-CNTs) were synthesized by chemical vapor deposition (CVD) and purified by both physical and chemical based methods. Highly pure commercial thin-walled pristine MWCNTs were also used without any further purification. Two main filling approaches were fulfilled in the project including; vacuum-based and solution-based. In the vacuum-based method a mixture of the CNTs and \( \text{C}_6\text{O}_0 \) was vacuum sealed and heated above the sublimation temperature of \( \text{C}_6\text{O}_0 \) for several hours. High resolution transmission electron microscopy (HRTEM) images revealed partially filled CNTs especially in the entry ports of the tubes. In the second approach the CNTs were immersed in a \( \text{C}_6\text{O}_0 \) solution and capillary force contributed to the filling process. Different solvents (poor and good solvents) and methods were examined to reach an optimum filling rate. Based on the HRTEM images a significant improvement was achieved using the solution based method compare to the vacuum-based process. All the filled samples were characterized by Raman spectroscopy as well to verify the filling success.

Nuclear magnetic resonance (NMR) spectroscopy was performed at Larmor frequencies of 500 MHz at room temperature to investigate encapsulation influence on \( \text{C}_6\text{O}_0 \) molecules behavior. The recorded spectrum of \( \text{C}_6\text{O}_0 \)-filled MWCNTs indicated presence of three groups of encapsulated \( \text{C}_6\text{O}_0 \)s regarding to their dynamics behavior. First, \( \text{C}_6\text{O}_0 \)s in the central area of the tube which are not in the vicinity of side walls and behave as well as pristine \( \text{C}_6\text{O}_0 \)s in solid. Second, a small portion of \( \text{C}_6\text{O}_0 \)s located in side walls vicinity which are diamagnetically shielded from ring current. And the last group is assigned to the static \( \text{C}_6\text{O}_0 \)s located beside the side walls defects or holes which cancel the ring current and stop the rotation of \( \text{C}_6\text{O}_0 \). The nuclear spin-lattice relaxation time (T\( \text{i} \)) measurement, by considering the recovery of C nuclear magnetization with time M(t) after the saturation pulses, revealed faster rotation of encapsulated \( \text{C}_6\text{O}_0 \)s compared to that in bulk \( \text{C}_6\text{O}_0 \).
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Part I

Introduction
Chapter 1

Carbon Nanotubes (CNTs)

1.1 Carbon nanotubes (CNTs)

During the last decades carbon nanotubes have attracted great attention due to their promising properties and applications. Many methods have been used to modify the structure of CNTs in order to expand their applications in various fields. Electronic and field emission devices [1-4], super capacitors and batteries [5-7], nanosensors [8], electromechanical actuators [9, 10], separation membranes [11, 12], filled polymer composites [13], and drug-delivery systems [14, 15] are some of the potential applications of CNTs. In addition, great improvements in synthesis and purification techniques have been achieved and CNTs can be synthesized in bulk with high purity.

1.2 Structure of CNTs

A typical CNT can be visualized as a wrapped graphene layer into a cylinder. In a graphene layer each carbon atom, incorporated in a 6-membered ring, has three strong covalent bonds (σ-bond with \(sp^2\) hybridization) with its neighboring atoms in a plane which cause extraordinary mechanical strength in CNTs [16]. The extra valence electron of carbon induces a relatively weak out-of-plane bond (the \(\pi\)-bond) which contributes to the interaction between the layers in MWCNTs and between SWCNTs in a SWCNT bundle [17]. In general, CNTs are classified in two main categories according to their structures; single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs).
CHAPTER 1. CARBON NANOTUBES (CNTS)

1.2.1 Single-walled CNTs

Single-walled CNTs constitute as 1D molecules due to their high length to diameter ratio. SWCNTs structure, except their length, can be completely described by a vector called chiral vector \( C_h \) and its corresponding angle \( \theta \) [18]. The chiral vector is defined by a linear combination of the lattice basis, \( a_1 \) and \( a_2 \), in a planar graphite sheet [17, 18] given by Eq. 1.1.

\[
C_h = n a_1 + m a_2 \tag{1.1}
\]

where \( n \) and \( m \) are integers. Value of \( (n, m) \) can affect the optical, mechanical and electronic properties of SWCNTs. For instance, SWCNTs with \( |n - m| = 3q \) are metallic while those with \( |n - m| = 3q \pm 1 \) are semiconducting \( (q \) is an integer) [18]. Based on the chirality, three types of SWCNTs can be specified; zigzag \( (m = 0 \) and \( \theta = 0^\circ \)), armchair \( (m = n \) and \( \theta = 30^\circ \)) and chiral \( (m \neq n \) and \( 0^\circ < \theta < 30^\circ \)) [17] (Fig. 1.1).

1.2.2 Multi-walled CNTs

Multi-walled Carbon Nanotubes (MWCNTs) consist of two or more coaxial rolled graphene layers. The interlayer spacing, \( d \), is a function of curvature and number of layers [17] and has been reported to be 0.34 nm [20, 21], 0.36 nm [22], and 0.37 nm [23] for CNTs with different structural properties. Eq. 1.2 has given to fit TEM experimental data [24]

\[
d = 0.344 + 0.1 exp(-c/4\pi) \tag{1.2}
\]
where $c/4\pi$ is the radius of the tube. According to this equation, the interlayer distance $d$ gets closer to 0.344 by increasing CNT diameter.

1.3 Synthesis of CNTs

Iijima discovered CNTs in 1991, synthesized by arc discharge in He atmosphere [21]. Due to impressive properties of CNTs, many research groups tried to find appropriate methods to produce bulk amount of high quality CNTs. In general, CNTs can be synthesized by three common methods; arc discharge, laser ablation and chemical vapour deposition (CVD). Laser ablation is technically similar to arc discharge method, however they are different in the sense of the product purity. CVD is the most utilized technique to synthesize bulk amount of CNTs with low levels of impurity. Indeed, CVD is the process of catalytic decomposition of hydrocarbons over a transition metal catalyst. The most commonly used metallic catalysts are Fe [25, 26], Co [27] and Ni [28] (individually or in mixture). As shown in Fig. 1.2, the hydrocarbon and carrier gas(es) are passed over the catalyst at a temperature between 500°C to 1100°C. The hydrocarbon is then catalytically decomposes into carbon and hydrogen at high temperature. Diffusion of carbon atoms into or over the catalyst particles, saturation of catalyst particles, and precipitation of graphitic layers occur respectively and result in the formation of CNTs (Fig. 1.3). Variation of experimental parameters such as catalyst materials, carbon precursor, growth time and temperature can affect morphology and chemical composition of CNTs.

1.4 Nitrogen-doped CNTs (N-CNTs)

Introducing hetero atoms (nitrogen, boron, . . . ) to the graphitic structure of CNTs have been the subject of many recent researches in order to expand the applications era of CNTs. Incorporation of nitrogen atom into CNTs structure leads to n-type
CHAPTER 1. CARBON NANOTUBES (CNTs)

Figure 1.3: Growth mechanism of CNTs including; decomposition of hydrocarbon, diffusion of carbon into or over the catalyst, and precipitation of carbon [29]

material due to the presence of one extra valence electron in nitrogen electronic structure [30, 31]. Therefore, nitrogen-doped CNTs are chemically more active and less stable compared to the undoped CNTs. Scanning tunneling electron microscopy (STEM) studies also found only metallic behavior for nitrogen-doped CNTs with a strong donor peak just above the Fermi level [32, 33], while a single layer undoped CNT can show either metallic or semiconducting behavior depending on its chirality [18]. Because of their modified conductivity, it is suggested to employ nitrogen-doped CNTs in field emission devices, biosensors and to improve the catalytic performance. Vertically aligned nitrogen-doped CNTs have been successfully employed as a metal-free electrode for oxygen reduction in alkaline fuel cells as they have much better electrocatalytic activity, long-term operation stability, and tolerance to crossover effect compared to platinum [34, 35]. In addition, Saha et al. [36] has reported preparation of 3D composite electrodes consist of Pt nanoparticles supported on nitrogen-doped CNTs. Highly dispersed Pt nanoparticles with smaller size (2-3 nm) and higher electrochemical Pt surface area were obtained for oxygen reduction reaction compared to when undoped CNTs support were used.

1.4.1 Synthesis of Nitrogen-doped CNTs

Nitrogen-doped CNTs can be synthesized by two main routs; post-synthesis modification of CNTs with nitrogen containing organic molecules [37, 38], and nitrogen incorporation during the growth of CNTs [32, 39]. The complexity of the post synthesis modification including oxidation of the grown CNTs followed by amination to obtain nitrogen functional groups is the main drawback of the method. The
1.4. NITROGEN-DOPED CNTS (N-CNTS)

second method is the incorporation of nitrogen atoms into graphitic structure by introducing nitrogen containing precursor during CNTs synthesis process. The same methods as the synthesis of CNTs such as laser ablation [39, 40] and arc discharge [41] are employed but in the presence of nitrogen source. Although a high content of nitrogen concentration (up to 33%) [39, 42] is achieved by these methods, but high growth temperature about 1000°C is needed. Low temperature synthesis (600°C-800°C) can be done by pyrolysis [32, 43, 44] or chemical vapor deposition of nitrogen containing organic compounds over supported transition metal catalyst in the presence of carbon source [32, 45, 46]. The nitrogen concentration by this method reaches up to 20% [47].

1.4.2 Nitrogen-doped CNTs Morphology

Transition electron microscopy (TEM) is an effective imaging technique to investigate the morphology of synthesized CNTs. Doped and undoped SWCNTs have almost similar morphology, while nitrogen-doped MWCNTs are usually morphologically different from undoped MWCNTs. The central cavity of doped MWCNTs is usually bridged by capping one or more inner tubes which form bamboo-like compartment layers inside the tube as shown in Fig.1.4 [48].
Part II

Theory
Chapter 2

Filling of Carbon Nanotubes

As synthesized CNTs usually contain various types of impurities such as amorphous carbon, carbon nano particles and metal catalyst particles [49]. It is important to purify CNTs to promote their potential applications and properties; as for filling with different materials they need to be opened and uncapped initially.

2.1 Purification of CNTs

In general, purification methods can be classified into chemical and physical methods [49].

Chemical-based purification methods

Purification of CNTs by chemical methods is based on the fact that the carbon impurities oxidize at a faster rate compared to CNTs due to their higher density of defects and solubility of metallic particles in acids. Chemical oxidation of impurities can take place in gas phase [50-53], liquid phase [50-56] and by electrochemical oxidation [57]. Oxidant agents such as air [50-53], HNO₃ [50, 52, 55, 56], HF [53], mixture of H₂O₂ and HCl [54], mixture of H₂SO₄ and H₂O₂ [55], mixture of KMnO₄ and H₂SO₄ [53], Br (aq) [51, 52], mixture of NH₃ (aq) and H₂O₂ [55] are used for purification of CNTs. The reaction of Oxidant material and impurities is more effective by refluxing, boiling, heating or stirring of the mixture.

Although chemical oxidation method is effective in most cases, but since oxidation is involved, it has destructive effects on surface structure of CNTs. Shortening of CNTs [49, 55] and introducing oxygenate functional groups on CNTs [49] are some other major drawbacks of this method. However, basic oxidant agents are less destructive compared to acidic agents [55].

The other chemical reaction in purification of CNTs is dissolution of catalytic
metal particles. Depending on the catalyst material, an appropriate solvent is to be used in order to remove them. As catalyst materials in CVD synthesis usually contain transition metals, the best solvents are HCl for iron [51, 52, 54, 55] and HF for Co [53].

**Physical-based purification methods**

Physical methods purify CNTs based on the difference between the physical properties of CNTs and impurities such as; size, aspect ratio, mass, magnetic properties, and etc. [49]. Commonly used physical methods are filtration [58], chromatography [59, 60], centrifugation [61], electrophoresis [62] and high temperature annealing [63, 64]. Physical-based purification methods have less destructive effects on CNTs surface structure compared to chemical oxidation.

The most common physical method used in many experimental works is high temperature annealing in high vacuum or an inert atmosphere. This method can effectively remove metallic particles from the surface of CNTs as well as those particles covered by carbon layers or enclosed inside the CNTs [49, 63, 64]; while they cannot be removed by acid treatment. However, high temperature annealing can influence CNTs structure by removal of structural defects [65] or diameter enlarging [66]. This method is not appropriate for samples with high density of carbon impurities since it can enhance the impurities structure by graphitization [49].

### 2.1.1 Nitrogen-doped CNTs purification

In the case of nitrogen-doped CNTs, the purification methods are similar to those used for undoped CNTs. However, due to the presence of more structural defects, a milder and less destructive oxidant material is to be used to remove amorphous carbons. The other specific aspect of nitrogen-doped CNTs purification, regarding to the filling aim, is elimination of carbon compartment layers inside the tubes. To the best of our knowledge, no effort has been done on opening the central cavity of nitrogen-doped CNTs.

### 2.2 Filling of carbon nanotubes

The inner cavity of CNTs provides a suitable space to confine nano scale compounds and molecules. It can be considered either as a kind of doping which may modify the electronic properties of CNTs or a way to control the size and shape of confined material [67]. Many research groups have been working on encapsulation of different particles and molecules such as fullerenes [68-72], polymers [73], metals [74, 75] and other organic and inorganic materials [76] inside CNTs. For instance, many investigations have been carried out on CNTs filled with fer-
romagnetic metals like Fe, Ni and Co called ferromagnetic nanowires, which have significant potential in data storage technology [74]. These types of nanowires are protected against oxidation and other chemical reactions and show new magnetic properties due to their low dimension and large geometric aspect ratio [75].

2.2.1 Synthesis of filled CNTs

Depending on the physical properties of filling material and the cavity diameter of CNTs, different methods have been used to synthesize filled CNTs. Arc discharge [77, 78], high temperature heat treatment [79], ion beam sputtering [80] and chemical vapor deposition (CVD) [74, 75] are a number of reported methods. Filling of CNTs can occur either during or after the synthesis process. In-situ filling of CNTs is a single-step procedure which is carried out by electric arc discharge [81] and CCVD [82]. For instance, Leonhardt et al. [74] employed CVD method to in-situ synthesize of filled CNTs with transition metals (encapsulated transition metal nanowires) by a simple pyrolysis of a metallocenes in the carrier gas.

In post-synthesis filling of CNTs, purified and uncapped CNTs are required. In chemical approach, an element-salt solvent bath is provided for already opened CNTs [83] or an element-salt is refluxed with an oxidant simultaneously to fulfill both opening and filling process [84]. In the gas phase filling process, opened CNTs and chosen compound are mixed directly, vacuum sealed in a capsule and then heated above the vaporization (in some cases sublimation) temperature of the compound for up to several days [85, 86]. When filling is performed in liquid phase, the CNTs are immersed in the molten material or solution and capillary force contributes to the filling process.

2.2.2 Mechanism of capillarity-driven filling of CNTs

When in filling process liquids are involved, either a molten material or a solution, it is necessary to consider the wetability of the interior surface of the nanotube [87] and the surface tension properties of the introduced liquid or solution. It is well accepted from experiment that capillarity-driven mechanisms for filling of CNTs with liquids follow the Young-Laplace equation (Eq. 2.1) which describes wetting of a solid by a liquid.

\[ \Delta p = 2\gamma \cos \theta / r \]  

(2.1)

Where \( \Delta p \) is the pressure difference across the liquid-surface interface, \( \gamma \) is surface tension of the liquid, \( \theta \) is the liquid-solid contact angle and \( r \) is the radius of curvature. According to the equation, two different situations can be considered;
CHAPTER 2. FILLING OF CARBON NANOTUBES

Figure 2.1: Schematic picture of wetting a solid by liquid showing two different situations
i) $\theta < 90^\circ$ spontaneously wetting by capillary force
ii) $\theta \geq 90^\circ$ an applied pressure is needed to wet the solid

when $\Delta p$ is negative (or $\theta < 90^\circ$) capillary force spontaneously drives the liquid into the tubes, while when $\Delta p$ is positive (or $\theta \geq 90^\circ$) some pressure must be applied to drive the liquid into the CNTs (Fig. 2.1). It can be also expressed that fluids with surface tension $\gamma$ below 200 mN m$^{-1}$ can spontaneously enter the hollow cavity of CNTs at atmospheric pressure [88, 89], while those with higher surface tension can enter the tube only by performing a so-called Laplace pressure on liquid surface [90]. In addition, the viscosity of the liquid and nanotube inner diameter can be considered as significant parameters in the capillary-driven filling process [67].

2.3 $\text{C}_{60}$-filled CNTs (peapods)

Filled SWCNTs with $\text{C}_{60}$ molecules, the so-called peapods, were first discovered by Smith et al. [69] during pulsed laser vaporization of graphite in the presence of metallic catalyst. Many research groups have reported synthesis of small diameter peapods ($\approx 2$ nm) [72, 91], while wider peapods ($\approx 5$ nm) have been rarely observed [92]. Insertion of $\text{C}_{60}$ in CNTs with diameters matching the van der Waals size of $\text{C}_{60}$ is a highly exothermic process with an energy of about 3 eV per $\text{C}_{60}$ which is therefore a spontaneous and irreversible reaction [93]. Filling SWCNTs with diameters of less than 1.25 nm is strongly endothermic [94] because it needs a distortion of the CNT and the spontaneous formation of peapods is prohibited [93]. However, double-walled CNTs (DWCNTs) with narrower average diameter around 1.13 nm have been effectively filled due to the presence of the second
graphene layer and its contribution to the attractive part of van der waals interaction between C$_{60}$ and tube [93]. The second graphene layer has the greatest stabilizing effect, but increasing the number of nanotube walls beyond two has little effect on the C$_{60}$-nanotube interaction [91].

2.3.1 Formation mechanism of peapods

Gas phase C$_{60}$ encapsulation inside CNTs is usually carried out by sublimation of fullerene molecules in a reaction chamber containing both opened CNTs and C$_{60}$ under high vacuum. It shows high electronic affinity with the graphene lattice which was proven to be a surface diffusion-driven mechanism. Once the sublimation temperature is reached, it is expected that C$_{60}$ molecules interact more strongly with a SWCNT than with each other due to the greater number of carbon-carbon Van der Waals interactions in the SWCNTs. Therefore when a sublimated fullerene molecule gets close enough to the nanotube, surface diffusion through an open end or sidewall defect could take place [95].

The filling rate is highly dependent on the reaction temperature and time, but weakly on the partial pressure of the filling material vapour. Facilitating an appropriate temperature for filling prevent temperature-induced stochastic movements of the filling molecules and give them a sufficient residence time on the CNTs surface to find the entry ports. In addition, a long processing time in the range of several hours to a few days is necessary to achieve high filling rate. When the C$_{60}$ molecules is inserted into the tubes, the stabilizing Van der Waals coordination with the surrounding tube causes them to remain inside and self-assembly of the molecules into chains subsequently take place [95].

In the other approach, filling process is performed by simply immersing the opened CNTs in a C$_{60}$ solution [96-98]. Stirring, sonication, and refluxing can also be used to promote the interaction process. Regarding to the experimental achievement described earlier, the surface tension of the used C$_{60}$ solvent has to be below 200 mN\text{m}^{-1} to have a spontaneous wetting of the CNTs by solvent molecules. Typically C$_{60}$ solvents satisfy this condition, however the solubility value and the solution concentration have significant effect on the filling rate.

2.3.2 Configuration of encapsulated C$_{60}$s inside SWCNTs

Several research groups have reported different configurations of confined C$_{60}$s inside CNTs. These configurations can be affected by the CNT inner diameter as well as both C$_{60}$-C$_{60}$ and C$_{60}$-CNT interactions. Hodak et al. [91] calculated ten different phases of fullerene molecules inside SWCNTS with different diameters ranging from 1.245 nm to 2.714 nm. According to their calculations the type of the phase is strictly defined by the size of the tube cavity and has a transition of the
CHAPTER 2. FILLING OF CARBON NANOTUBES

Figure 2.2: Experimentally proven configurations of encapsulated C$_{60}$s inside SWCNTs with different diameters [93]

Figure 2.3: Bonding between C$_{60}$s by [2+2] cyclo-addition reaction causes different phases of C$_{60}$ inside SWCNTs including; a) monomer C$_{60}$s b) dimer C$_{60}$s c) polymer C$_{60}$s chain [68]

straight chain to zigzag phase when the inner diameter reaches 1.45 nm. The experimentally reported phases of encapsulated C$_{60}$ molecules are in agreement with Hodak’s theoretical predication and include linear one-dimensional chains, achiral zigzags, chiral double helices, and achiral two-molecule layers [93, 99, 100]. The other theoretical simulation suggest two different orientations with low potential energy for C$_{60}$s confined in SWCNTs including; pentagonal and hexagonal orientation with pentagons and hexagons perpendicular to the tube axis [101]. Bonding between two or more encapsulated C$_{60}$ molecules by a [2+2] cyclo-addition reaction (Fig. 2.3) results in the formation of dimers and polymers [102] shown in Fig. 2.3. These different configurations and phases of C$_{60}$s affect the intermolecular interactions which cause different structures and properties for filled CNTs.
2.3. Rotational dynamic behavior of encapsulated C$_{60}$s inside CNTs

C$_{60}$ molecule has high symmetry and relatively weak intermolecular interaction. Confined C$_{60}$s in SWCNTs are unique due to their one dimensional confinement and the reduced number of nearest neighbors [95] compared to its crystalline bulk structure (2 to 12). Near-infrared Raman spectroscopy (NIR) has been employed to study rotational state of C$_{60}$, polymer bond and type of the polymeric C$_{60}$ phase. Yonggang et al. [67] analyzed the intermediate frequency modes of peapods at high pressure. They found a ratcheted rotation of encapsulated C$_{60}$ with preferred hexagonal orientation due to C$_{60}$-C$_{60}$ and C$_{60}$-SWCNT interactions. However, C$_{60}$-C$_{60}$ interaction strength in SWCNT peapods depend on filling rate and by increasing that the intermolecular interaction strength increases. The nearest distance between inserted C$_{60}$ and tube wall is around van der Waals distance (0.3 nm), while the intermolecular distance between inserted pristine C$_{60}$s is around 0.98 nm [99]. In general, C$_{60}$-CNT interaction is stronger than C$_{60}$-C$_{60}$ interaction. These two different interactions influence the vibrational properties of confined molecule[97].

Hamada et al. [100] investigated temperature dependent rotational dynamic and phase transition in one-dimensional crystal of C$_{60}$ encapsulated inside SWCNT by CNMR spectroscopy. They found encapsulated fullerenes have a phase transition at 100 K from continuous rotational diffusion to uniaxial rotations and finally freeze out at 25 K. Whereas the phase transition temperature for pristine C$_{60}$ molecules from simple cubic (SC) into face-centered cubic (FCC) is higher and around 260 K. From 300 K to 260 K the fcc-C$_{60}$ rotate freely while from 260 K to 100 K rotations are hindered and stop below 85 K. The significant changes in the dynamical properties of encapsulated C$_{60}$ result from the reduction of the number of nearest neighbors and its interaction with the SWNT side walls.

2.3.4 The effect of nitrogen doping on the rotational behavior of encapsulated C$_{60}$s

Tunable rotational dynamic of confined C$_{60}$ molecules inside the nitrogen-doped CNTs is expected due to the presence of stronger C$_{60}$-CNT interaction compared to undoped CNTs. An extra valence electron in the electronic structure of incorporated nitrogen is an efficient factor to control the rotation of confined C$_{60}$, which gives enough motivation to the current project.
Chapter 3

Characterization of C$_{60}$-filled CNTs

3.1 Electron Microscopy [EM]

Electron microscopy (EM) is a field of science which uses a beam of electrons and electromagnetic lenses to form an image of a specimen [103]. Operating EM under high vacuum enables the electron beam to travel in a straight line. The significant short wavelength of electron beam causes higher magnification and greater resolving power in electron microscopes compared to optical microscopes which use visible light instead. There are two types of electron microcopies including; transmission electron microscopy (TEM) and scanning electron microscopy (SEM) which give 2D and 3D images respectively. In high resolution TEM increasing the electron beam accelerating voltage causes shorter wavelength and greater resolving power.

3.1.1 Image modes in TEM

Electromagnetic lenses including; condenser lenses, an objective lens, Intermediate lenses and a projector lens [103, 104] are employed in a transmission electron microscope. An electron beam generating by an electron gun is first focused on the sample by condenser lenses and then travels through the specimen. Depending on the density of the material some of the electrons are scattered and some are transmitted. The direction of the transmitted electrons is changed relative to the optical axis and then they are gathered by an objective lens to form a diffraction pattern and image in the back focal plane and on image plane. Finally, intermediate and projector lenses are used to magnify and display the image on a fluorescent screen. The ultimate information is provided based on either the variation of elec-
tron beam direction or by measuring the energy loss of the electrons (the initial energy of the electron beam is known). For an optimum resolution, an ultra-thin specimen is required to minimize multiple scattering of the electrons which decreases the number of detected electrons. In high resolution TEM (HRTEM) both transmitted and scattered electrons are used to create image, while conventional TEM only uses transmitted electrons.

### 3.1.2 Morphological analysis of CNTs

TEM imaging is a powerful technique to investigate the morphology of CNTs. In the case of filled CNTs, HRTEM is more effective to observe the filling materials which are in atomic size.

### 3.2 X-Ray Photoelectron Spectroscopy (XPS)

XPS is a surface analysis technique based on the photoelectric effect. Photoelectrons are ejected from the surface of element by absorbing energy from the incident X-ray beam. The kinetic energies of emitted photoelectrons are then measured by an energy analyzer. Binding energy, \( B_e \), a characteristic and unique property of elements which gives information about the elemental identity of the sample can be calculated using Eq. 3.1.

\[
K_e = h\nu - B_e - \varphi
\] (3.1)
3.2. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Where \( K_e \) is the kinetic energy, \( B_e \) is binding energy of atomic orbital which the electron has been emitted from, \( h\nu \) is the energy of incident X-ray and \( \phi \) is the work function (the minimum energy of the electron to be able to escape from the surface). By measuring the number of emitted electron as a function of binding energy, XPS spectrum can be obtained.

3.2.1 XPS analysis of nitrogen-doped CNTs

A typical spectrum of nitrogen-doped CNTs and high resolution N1s peak are shown in Fig. 3.3. The presence of nitrogen signal (N1s) implies the incorporation of nitrogen atoms in CNTs structure. N1s signal can be deconvoluted to several peaks which reveal the different types of nitrogen functionalities incorporated into the CNT structure. Types of nitrogen incorporation can be identified from the binding energies; pyridinic (398.6 eV), pyrrolic (400.3 eV), quaternary (N-Q\text{center} 401 eV, N-Q\text{valley} 402.3-402.6 eV) and nitrogen-oxide groups (402.6-405 eV) [81]
Figure 3.4: Different types of nitrogen incorporation in CNTs structure

Figure 3.5: Schematic pictures of Raman instrumentation and Raman Effect process

shown in Fig. 3.4.

3.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light usually from a laser source in the visible, near infrared, or near ultraviolet range. Photons of the incident laser light excite the molecules of sample and transform them to oscillating dipoles. These dipoles then re-emit the light with up-shifted (anti-stokes) or down-shifted (stokes) frequencies due to the interaction with sample, called the Raman Effect (Fig. 3.5). The resulting light is then converted to electrical signal by signal processing devices and finally displayed in computer screen (Fig. 3.5). The Raman shifts provide information about vibrational, rotational and other low frequency transitions in molecules.

3.3.1 Raman spectrum of CNTs

Raman spectroscopy is a powerful technique which provides information about the structure and properties of CNTs. Fig. 3.6 shows a typical Raman spectrum of SWCNTs. First order Raman scattering process involves one-phonon emission
3.3. RAMAN SPECTROSCOPY

Figure 3.6: Typical Raman spectrum of SWCNTs

spectrum and it includes the so-called $G$ band at around 1580 cm$^{-1}$ and radial breathing mode (RBM) in the range between 100-500 cm$^{-1}$ [106]. $G$ band appears in Raman spectra of CNTs due to the tangential vibration of the carbon atoms which is a characteristic feature of the graphitic structure. The $G$ band for graphite shows only one single Lorentzian peak at 1582 cm$^{-1}$ but in SWCNT upon rolling a graphite sheet into a nanotube, an axial and circumferential tangential vibration will be activated which results in a $G$ mode with two peaks. While for large diameter CNTs, the $G$ band is similar to that observed in graphite [106]. The other first order Raman scattering, radial breathing mode (RBM), is assigned to the motion of all carbon atoms in-phase in the radial direction creating breathing-like vibration of the entire tube [107]. Eq. 3.2 shows the inverse relation between CNTs diameter, $d_t$, and RBM frequency.

$$\omega_{RBM} = \frac{A}{d_t} + B$$

Where $\omega$ is vibration frequency, and $A$ and $B$ are experimentally determined constants. This feature can be only observed in SWCNT Raman spectrum and it is so weak to be observed in MWCNTs Raman spectra. $D$ band at around 1350 cm$^{-1}$ and $\tilde{G}$ band at 2700 cm$^{-1}$ are second order Raman scattering features. The defect induced peak, the $D$ band, in a typical Raman spectrum of CNT is formed due to the presence of asymmetry in the rolled graphene layer and its intensity increases by increasing the defects concentration in the structure. The first overtone of $D$ band is called $\tilde{G}$ mode [18]. Investigation of intensity changes and frequency
shifts of $D$ and $G$ bands can give useful information about the characterization of defective CNTs. In high quality CNTs the $G$ band is free from defect contributions and its intensity can be comparable to the $G$ band [106]. The other evaluation route of the purity and defect concentration in CNTs is investigation of the $D$ to $G$ band integrated area ratio [106]; the more the ratio reveals the lower crystallinity of the tubes.

### 3.3.2 $C_{60}$ Raman modes

$C_{60}$ Raman active modes have been investigated both theoretically and experimentally [108, 109]. The measured values are different due to the effect of perturbation fields from the chemical potentials of neighboring molecules, ambient molecules and temperature. Raman spectrum of a $C_{60}$ single crystal and the corresponding calculated frequencies are shown in Fig. 3.7. $C_{60}$ molecule has 46 vibrational modes distributed over the 174 vibrational degrees of freedom. Out of 174 normal vibration modes of $C_{60}$ only ten of them are Raman active; two nondegenerate gerade modes of symmetry $A_g$ and eight fivefold degenerate gerade modes of symmetry $H_g$. All ungerade modes are either silent or IR active [108]. Three of the Raman active modes, $H_g(7)$, $A_g(2)$, and $H_g(8)$ are surface modes and correspond to pentagon shear, pentagon pinch and hexagon shear modes respectively [110]. The most prominent mode is pentagonal pinch mode (PPM) or $A_g(2)$ mode at 1469 cm$^{-1}$ at room temperature [108]. The $A_g(1)$ is a radial breathing mode (RBM) where all atoms are radially displaced at same quantity and in phase. Other vibration modes are known as the intermolecular vibration modes.

#### Figure 3.7: Raman spectrum of $C_{60}$ single crystal and its Raman active modes frequencies [108]
Chadli et al. [102] have calculated the Raman active modes of three different phases of C\textsubscript{60} including monomer, dimer, and polymer C\textsubscript{60} (Fig. 3.8). At low frequencies below 200 cm\textsuperscript{-1} no mode is expected for pristine C\textsubscript{60} molecules, while in the C\textsubscript{60} dimer three intermolecular modes with the most Raman active mode at 82 cm\textsuperscript{-1}, and in the C\textsubscript{60} polymer chain five modes with the most Raman active mode at 122 cm\textsuperscript{-1} are observed. In addition, the PPM, A\textsubscript{g}(2) mode, shifts from 146 cm\textsuperscript{-1} (C\textsubscript{60} monomer) to 1458 cm\textsuperscript{-1} and 1439 cm\textsuperscript{-1} for C\textsubscript{60} dimer and infinite polymer chain, respectively. No shift of A\textsubscript{g}(1) mode was calculated in the C\textsubscript{60} dimer, while a 5 cm\textsuperscript{-1} downshift predicted in the C\textsubscript{60} polymer.

The H\textsubscript{g}(1), H\textsubscript{g}(2), and H\textsubscript{g}(4) modes split to several new peaks in the C\textsubscript{60} dimer and polymer, but H\textsubscript{g}(3) is not affected by dimerization, however it splits after polymerization. High frequency H\textsubscript{g}(5), H\textsubscript{g}(6), H\textsubscript{g}(7) and H\textsubscript{g}(8) modes downshift in C\textsubscript{60} dimer and polymer, while they split after polymerization.

### 3.3.3 SWCNT peapods Raman analysis

In the case of SWCNT peapods, Raman spectroscopy is effective enough to investigate the presence of encapsulated C\textsubscript{60}s. For encapsulated C\textsubscript{60}s, all Raman modes except H\textsubscript{g}(8) which is covered by G band of the CNT are detectable [108]. The prominent C\textsubscript{60} mode, A\textsubscript{g}(2), in peapods has a shift around 6 cm\textsuperscript{-1} and its position...
is at 1463 cm$^{-1}$ with a satellite peak at 1472 cm$^{-1}$ [108]. RBM upshifts due to the C$_{60}$-tube interactions, however the position of $G$ band is slightly depends on filling of the tube [102]. In addition, another feature around 90 cm$^{-1}$, can be assigned to the stretching mode of bonded fullerenes in C$_{60}$ dimer and polymer. The presence of this feature indicates the presence of polymerized C$_{60}$s inside CNT, while it is not predicted for confined pristine C$_{60}$ molecules [102].

The presence of C$_{60}$ dimers and polymers inside CNTs has been investigated and several new peaks due to the splitting of C$_{60}$ modes have been observed. For instance, $H_g(1)$ and $A_g(1)$ splitting and also $H_g(2)$ shift due to lower symmetry of the environment cause a multipeak in the Raman spectrum Fig. 3.9 [102].

### 3.3.4 Raman characterization of C$_{60}$-filled double-walled CNTs (DWCNTs)

Qiu et al. [99] performed Raman scattering measurement to characterize C$_{60}$ encapsulation inside DWCNTs. They observed two C$_{60}$ modes at the room temperature (Fig. 3.10); the strong $A_g(2)$ mode at about 1464 cm$^{-1}$ which is downshifted about 5 cm$^{-1}$ compared to that of bulk C$_{60}$, and weak $H_g(7)$ peak at 1422 cm$^{-1}$.
3.4. NMR SPECTROSCOPY

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique to probe the structure and dynamical behavior of chemical compounds. The technique is based on the ability of atomic nuclei to act as a small magnet and align with an
A superconducting electromagnet is used to generate a very strong magnetic field to align all the nuclei in a molecule in the same direction. In addition, radio frequency coils are used to realign the nuclei in a molecule opposite to the magnetic field. The energy frequency at which this happens can be measured and display as an NMR spectrum. To cool the system the coil of the magnet is surrounded by liquid helium (-269°C) and liquid nitrogen (-77°C) which are isolated by a layer of vacuum. Sample tube and radio frequency coils are located in a narrow hole existing in the middle of the magnet.

### 3.4.1 Relaxation process

When external magnetic field is applied, an energy transfer happens between the base energy to a higher energy level (generally a single energy gap). The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency. At radio frequencies, re-emission is negligible and only non-radiative relaxation processes (thermodynamics) is important. There are two main relaxation processes: Spin-lattice (longitudinal) relaxation and spin-spin (transverse) relaxation.

**Spin-lattice relaxation**

Nuclei held in a lattice (the sample) have vibrational and rotational motion which creates a complex magnetic field called the lattice field. This lattice field has many components and these components can interact with nuclei in the higher energy state, and cause them to lose energy and return to the lower state. The energy that a nucleus loses increases the amount of vibration and rotation within the lattice resulting in a small rise in the temperature of the sample. The relaxation time,
3.4. NMR SPECTROSCOPY

T₁, is the average lifetime of nuclei in the higher energy state and depends on the magnetogyric ratio of the nucleus and the mobility of the lattice.

**Spin-spin relaxation**
Spin-spin relaxation refers to the interaction between adjacent nuclei with identical precessional frequencies but varying magnetic quantum states. These nuclei can exchange quantum states; while a nucleus in the lower energy level will be excited, the excited nucleus can relax to the lower energy state.

3.4.2 Molecular Dynamic of Encapsulated C₆₀ inside SWCNT

Rotational dynamic of C₆₀ molecules can be probed by NMR spectroscopy. Solid-state ¹³C NMR studies at room temperature revealed a narrow resonance line located at around 143 ppm which indicates rapid isotropic molecular reorientation of C₆₀ in solid. However it changes dramatically as a function of temperature as shown in Fig. 3.12. Variation in the magnetic shielding of a nucleus with molecular orientation known as chemical shift anisotropy (CSA) causes a broad characteristic powder pattern. This broad pattern develops as the sample is cooled which implies hindered molecular rotation in lower temperatures [113].

Encapsulation inside CNTs can significantly affect the dynamics of C₆₀ due to the interaction with CNT side walls and reduction of the number of nearest neighbors [114]. In recorded NMR spectra of peapods at room temperature three resonance lines are observed at around 111.3 ppm, 111.8 ppm, and 148.2 ppm (Fig. 3.13). The first line at 111.3 ppm is assigned to the C₆₀s encapsulated inside...
the tube and the sharpness of the signal indicates that they are still rotating. However it has diamagnetically shifted from the line position of pristine C$_{60}$ at 143.6 ppm due to the local magnetic field originating from the ring currents on the tube surface. The line at 111.8 ppm is referred to the carbons inside the CNT structure. The last signal at 148.2 ppm represents encapsulated C$_{60}$s inside SWCNT which are located in the vicinity of sidewalls defects, leading to a paramagnetic shift of the line from its normal position for pristine C$_{60}$. The broadening of this signal indicates that these C$_{60}$s are static and no longer rotating [115].

3.4.3 The Effect of Nitrogen Doping On the Rotational Behavior of Encapsulated C$_{60}$s

Tunable rotational dynamic of confined C$_{60}$ molecules inside the nitrogen-doped CNTs is expected due to the presence of stronger C$_{60}$ - CNT interaction compared to undoped CNTs. An extra valence electron in the electronic structure of incorporated nitrogen is an efficient factor to control the rotation of confined C$_{60}$, which gives enough motivation to the current project.
Part III

Experimental work
Chapter 4

Experiment

4.1 Synthesis of nitrogen-doped MWCNTs

4.1.1 Experimental setup

The CVD system shown in Fig. 4.1 consist of; an ETF 30/12 H-V single hot zone tube furnace from Entech with the ability to heat up to 1200°C, a quartz tube with the outer diameter of 2.8 cm and about 1 m in length passing through the furnace horizontally, four gas lines (varigon, argon, acetylene and ammonia) with flow meters and a wash bottle containing KOH, was used to synthesize nitrogen-doped MWCNTs. The chamber (quartz tube) inlet was connected to a junction where various gases were combined before entering the reaction chamber and the outlet was connected to wash bottle.

4.1.2 Pre-experiments

A series of pre-experiments were planned in order to synthesize N-CNTs with acceptable wall structure and nitrogen content. Pyridine was the first choice of C/N precursor due to its ability to grow N-CNTs with high nitrogen content and low impurity level. 10 mg of catalyst material (ferrocene 98.8% from Sigma-Aldrich) in a small crucible was placed into the quartz tube, far enough from the furnace hot zone. After purging with argon for about 15 minutes, furnace was heated up to 800°C and then pyridine vapour was introduced to the reaction chamber by turning the hot plate on and setting it at the desired temperature. Varigon (91.6 ml/min) and argon (123 ml/min) were used as carrier gases during the growth. After cooling the system in the presence of argon, CNTs in the form of a black deposit was collected from the quartz tube inner wall. In order to find the optimum growth condition, different growth times (45 and 30 min) and pyridine flow rates were investigated. The latter was achieved by changing the pyridine bath temperatures.
(70, 80 and 90°C). Based on the results which will be discussed later, pyridine turned out to be not the best precursor due to the growth of thick walled, bamboo-structured CNTs. Pyridine was therefore replaced with ammonia and acetylene as nitrogen and carbon sources. A number of pre-experiments were done to find the best acetylene to ammonia ratio to achieve the optimum growth.

4.1.3 Growth process

10 mg of ferrocene was used as catalyst material; ferrocene was loaded into a small crucible and placed into the quartz tube, at the entrance of the oven and far enough from the furnace hot zone. After assembling and sealing, the system was purged by argon and then furnace was heated up to 800°C; while the temperature at the entrance of the oven, where ferrocene was placed, was estimated to be around 200°C. When the desired temperature was reached, argon was replaced by varigon (91.6 ml/min), acetylene (3.80 ml/min) and ammonia (20.5 ml/min). After 20 min of growth, system was cooled and then carbon nanotubes (in the form of a black deposit) were collected from the inner wall of the quartz tube.

4.2 Purification and opening of nitrogen-doped MWCNTs

For filling purpose, the synthesized CNTs needed to be purified and opened first. In this work a combination of both chemical and physical methods was done to optimize the result. Amorphous carbons were first oxidized chemically using dif-
4.2. PURIFICATION AND OPENING OF NITROGEN-DOPED MWCNTS

Table 4.1: Temperatures and times of synthesized N-CNTs oxidation in air

<table>
<thead>
<tr>
<th>Oxidation temp. (°C)</th>
<th>250</th>
<th>300</th>
<th>350</th>
<th>400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation time (hours)</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
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<tr>
<td></td>
<td>3.5</td>
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<td></td>
<td>5.0</td>
<td>4.5</td>
<td>4.5</td>
<td></td>
</tr>
</tbody>
</table>

Different oxidant agents and then iron catalyst particles at the base of the tubes were dissolved in HCl. In addition, it was essential to remove the compartment layers inside the central cavity of CNTs, to minimize their influence on filling process of nitrogen-doped MWCNTs.

**Oxidation of impurities by nitric acid**

As-synthesized nitrogen-doped MWCNTs were refluxed in concentrated nitric acid (65% from Scharlau, 0.13 g/l) at 130°C for 6 hours to remove amorphous carbons on the side walls and carbon layers covering the catalyst particles. The mixture was then filtered, washed with distilled water several times to reach the normal PH, then dried in air. The resulting powder was collected from filter paper and then immersed in 10 ml concentrated HCl (37% from VWR) and stirred at 70°C overnight, followed by filtration, washing and drying.

**Carbon impurities oxidation in air**

To determine the best combination of oxidation temperature and time, many pre-experiments were done as summarized in table 4.1. The most effective and less destructive combination was then selected.

2 mg of nitrogen-doped MWCNTs were oxidized in air, using a high temperature oven from Elite, at 350°C for 3 hours to remove amorphous carbons and carbon layers covering the catalyst particles. In order to dissolve the iron catalyst particles the oxidized CNTs were mixed with 10 ml of concentrated HCl and stirred overnight at 70°C. After filtration, washing with distilled water and drying in air, the resulting black powder was treated once again in air at 200°C for 90 min to oxidize carbon compartment layers inside the central cavity of tubes.

**Purification of CNTs via Bromination**

3 mg of produced nitrogen-doped MWCNTs was sonicated in ethanol for about 5 min to disperse CNTs in order to increase the interaction surface between tubes and bromine water. After filtration, washing with distilled water and drying in air,
the resulting powder was immersed in 10 ml bromine water and stirred for 3 hours at 90°C. After filtration, washing and drying, the collected powder was loaded in a quartz crucible and placed into a furnace for 1 hour at 350°C to oxidize the amorphous carbons in air. The CNTs were then mixed with concentrated HCl and kept at 70°C under stirring overnight to remove iron particles. The mixture was finally filtered, washed with distilled water and dried in air for several hours.

Mild oxidation of impurities by \( \text{H}_2\text{O}_2 \)
As-synthesized nitrogen-doped CNTs were added to a mixture of concentrated HCl and \( \text{H}_2\text{O}_2 \) (30% from VWR) (1:1 volume ratio, 0.1 g/l). The mixture containing flask was placed on a hot plate and kept at 80°C under stirring for 4 hours. Since the influence of \( \text{H}_2\text{O}_2 \) was diminished during time, every one hour 10 ml of \( \text{H}_2\text{O}_2 \) and 10 ml of HCl were added to the mixture. After 4 hours the mixture was filtered and washed with distilled water several times to reach normal pH, and dried in air. The black powder was then collected from the filter paper.

High temperature annealing in argon atmosphere
1 mg of produced nitrogen-doped MWCNTs was loaded into an aluminum oxide crucible and placed in the middle of CVD reaction chamber (quartz tube). After sealing, system was purged with argon and then in the same flow of argon heated up to 800°C. After 4 hours of treatment, chamber was cooled down to room temperature and then treated CNTs were collected from the crucible.

4.3 Encapsulation of \( \text{C}_{60} \) inside Nitrogen-doped and Pristine MWCNTs

After opening and purification of nitrogen-doped CNTs, filling process was performed. In the current project, two major filling methods including vacuum-based and solution-based were investigated. Both nitrogen-doped and pristine MWCNTs were used to be filled with \( \text{C}_{60} \)s.

4.3.1 Filling of CNTs under High Vacuum

Nitrogen-doped MWCNTs
A mixture of purified nitrogen-doped MWCNTs and high purity \( \text{C}_{60} \) (99.9% from MER, 1:3 weight ratio) was loaded into a NMR tube and the tube was connected to the vacuum pump. A combination of membrane and turbo pumps was employed to provide high vacuum. When the pressure inside the tube was reached to \( \approx 10^{-3} \) mbar, NMR tube was melted from the middle using a torch while it was still connected to the vacuum pump. After a short while, the molten wall of the tube was
4.3. ENCAPSULATION OF C\textsubscript{60} INSIDE NITROGEN-DOPED AND PRISTINE MWCNTS

Table 4.2: Examined conditions for filling of CNTs under high vacuum.

<table>
<thead>
<tr>
<th></th>
<th>N-MWCNTs vacumm of (\approx 10^{-3}) mbar</th>
<th>Temp.(°C)</th>
<th>400</th>
<th>500</th>
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<td></td>
<td>Time (hours)</td>
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<tr>
<td>b</td>
<td>Pristine MWCNTs vacumm of (\approx 10^{-3}) mbar</td>
<td>Temp.(°C)</td>
<td>400</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td></td>
<td>Time (hours)</td>
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<tr>
<td>c</td>
<td>Pristine MWCNTs vacumm of (\approx 10^{-5}) mbar</td>
<td>Temp.(°C)</td>
<td>650</td>
<td>750</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Time (hours)</td>
<td></td>
<td>24,12</td>
<td>24,12</td>
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</table>

closed and the mixture was sealed inside the tube under high vacuum (Fig. 4.2). The obtained NMR tube was then placed in the furnace and kept at the desired temperature for specific time. Then, the tube was cut and the grayish powder was sonicated in toluene for 15 min to solve extra C\textsubscript{60}s which had not contributed to the filling process. Then the mixture was filtered and dried in air. The examined reaction times and temperatures are summarized in table 4.2.a.

**Pristine MWCNTs**

High purity thin-walled MWCNTs from Nanocyl (95.0% purity with average diameter of 9.5 nm) were first heat treated in a vacuum oven (with a pressure \(\approx 10^{-1}\) bar) for 24 hours at 200°C in order to remove possible attached functional groups and humidity. A mixture of treated MWCNTs and C\textsubscript{60} (1:3 weight ratio) was then loaded into a NMR tube and vacuum sealed as described earlier. The tube was then heated at a desired temperature for a specific time interval summarized in table 4.2.b. After filling process the sample was washed with toluene, filtered and dried.

Since the optimum result was not achieved, higher degree of vacuum was performed by using a quartz glass tube instead. A mixture of heat treated MWCNTs and C\textsubscript{60} (1:3 weight ratio) was loaded into the tube and vacuum sealed while the pressure inside the tube reached to around \(\approx 10^{-5}\) mbar. The sealed tube was then placed in a furnace and kept at desired temperatures for specific times summarized in table 4.2.c. As no improvement was observed by increasing the reaction time, therefore, shorter time intervals considered for these experiments.

4.3.2 Solution-based Filling of CNTs

**Nitrogen-doped MWCNTs**

*Refluxing in n-hexane*

A mixture of purified nitrogen-doped MWCNT and high purity C\textsubscript{60} (1:1 weight ratio) was first sonicated in n-hexane (95.0% from Scharlau- 0.6 g/l) for about 5
min to disperse the C$_{60}$s. The suspension was then refluxed for 2 hours at 70°C. After filtration the extra C$_{60}$s were removed from outside of tubes by oxidation in air at 450°C for 30 min.

**Pristine thin-walled MWCNTs**

**Sonication in methanol**

A mixture of MWCNT and C$_{60}$ (1:1 weight ratio) was ultra sonicated in methanol (0.5 g/l) at room temperature for 2 hours. The same process was performed for a longer time (4 hours) as well to observe the reaction time effect on filling rate. After filtration the resulting powder was oxidized in air at 450°C for 45 min to remove the extra C$_{60}$s from the tubes surface.

**Refluxing in n-hexane**

A mixture of MWCNT and C$_{60}$s (1:1 weight ratio) was sonicated in n-hexane (0.6 g/l) for 5 min and then refluxed for 2 hours at 70°C. The longer reflux (6 hours) was also examined to investigate the reaction time effect on filling rate. The mixture was filtered and oxidized in air at 450°C for 45 min to remove extra C$_{60}$s.

**Bulk diffusion of C$_{60}$s through the defects on CNTs walls**

In order to have bulk diffusion through the CNTs walls, holes were introduced on their surface by first oxidizing at 450°C for 1 hour and then reducing under varigon flow at 900°C for 1 hour to remove attached oxygenate groups.

Two methods were then examined for the reduced CNTs as described below.

a) a mixture of reduced MWCNT and C$_{60}$ (1:1 weight ratio) was sonicated in n-hexane (0.6 g/l) and then refluxed at 70°C for 2 hours. After filtration, the resulting powder was oxidized in air at 450°C for 45 min to remove extra C$_{60}$s.

b) a mixture of reduced MWCNTs and C$_{60}$ (weight ratio 5:1) was sonicated in toluene (from VWR, 0.21 g/l) for 5 min. The suspension was then kept under nitrogen flow for about 24 h to evaporate the toluene completely. The gained powder was then collected and oxidized in air at 450°C for 45 min to remove extra C$_{60}$s.
4.4 Characterization systems

Transmission Electron Microscopy (TEM)
The morphology of produced CNTs before and after purification was characterized by a JEOL 1230 transmission electron microscope. A little amount of produced CNTs was sonicated and dispersed in ethanol. Then TEM copper grid was dipped in the mixture dried and loaded in the microscope.

High Resolution TEM (HRTEM)
The high resolution images of the filled CNTs were obtained by a JOEL 2100 with accelerating voltage of 200 KV. The sample preparation was the same as low resolution TEM described above.

X-ray photoelectron spectroscopy (XPS)
Elemental analysis of produced nitrogen-doped MWCNTs before and after purification was done using an XPS axis ultra DLD. Measurements were done at chemistry department.

Raman Spectroscopy
In order to confirm the success of filling process Raman spectra of different samples were recorded by a Renishaw InVia spectrometer with CCD chip. A little amount of grounded CNTs was placed on a glass slide and flattened by a silicon wafer to have a homogeneous surface. Measurements were done with a He-Ne laser with the excitation wavelength of 514 nm and a focusing 50 mm objective.

Nuclear Magnetic Resonance (NMR) Spectroscopy
$C_{60}$-filled reduced MWCNTs synthesized by refluxing in n-hexane, as described earlier, was first grinded with $Al_2O_3$ powder to get a homogenous sample. The resulting powder was then loaded in a rotor and placed in NMR sample holder. $^{13}C$ NMR experiment was carried out using a Bruker Avance III spectrometer operating at Larmor frequencies of 500 MHz at room temperature. The nuclear spin-lattice relaxation time ($T_1$) was also measured by considering the recovery of C nuclear magnetization with time $M(t)$ after the saturation pulses.
Part IV

Results, Discussion and Conclusion
Chapter 5

Results and discussion

5.1 Synthesis of Nitrogen-doped MWCNTs (N-CNTs)

Nitrogen-doped MWCNTs was synthesized with CVD using different C/N sources. The experimental conditions of the growth process and respective nitrogen content of the samples are summarized in table 5.1.

TEM images of both samples (Fig. 5.1) revealed the growth of highly pure N-CNTs with relatively uniform diameters of around 50 nm and 15 nm for sample 1 and 2. The rough CNT walls of sample 1 as can be seen from TEM images is related to the incorporation of nitrogen in the graphitic structure [116]. In addition, it is found that most of the tubes have bamboo-like morphology with transverse carbon bridges forming compartments, in agreement with other reports about N-CNTs [105, 117, 118]. Presence of nitrogen in the structure is likely to form defects in basal hexagonal planes which leads to curvature of graphite sheets and the formation of bamboo-like structure [116]. A mixture of acetylene and ammonia as C/N source was chosen for further experiments due to the growth of thin walled N-CNTs with large cavity and few number of compartment layers inside (Fig. 5.1.b). Three different ratios of carbon to nitrogen including 1:2, 1:2.5, and

| Table 5.1: growth conditions and nitrogen content of synthesized N-CNTs |
|---|---|---|---|---|
| Sample | C/N source | Flow rate (ml/min) | Growth temp. (°C) | Growth time (min) | Nitrogen concentration |
| 1 | Pyridine | 8.37 | 800 | 45 | 2.14% |
| 2 | Acetylene/ammonia | 3.8/20.5 | 800 | 20 | 1.13 % |
CHAPTER 5. RESULTS AND DISCUSSION

Figure 5.1: TEM images of nitrogen-doped MWCNTs synthesized by different C/N source; a) pyridine and b) acetylene/ammonia

1:4.2 were examined whereas the other growth conditions kept the same as those used for sample 2. As shown in Fig. 5.2, all samples were relatively free of side products with the outer diameters ranging from 5 nm to 25 nm. It was also found that the length of compartments decreases by increasing the ammonia flow rate (Fig. 5.2.c) in a well agreement with previous report [117]. The C/N ratio of 1:2 was finally chosen for further experiments due to the acceptable morphology of CNTs regarding to the filling aim.

XPS spectra of synthesized N-CNTs (Fig. 5.3) confirmed presence of nitrogen in the structure. Carbon and nitrogen signals appeared at 285 eV (C1s) and 401 eV (N1s) respectively. High resolution N1s signal can be deconvoluted to four peaks centered at 398.6 eV, 401.3 eV, 402.2 eV, and 405.0 eV which are assigned to pyridinic, N-Q_center, N-Q_valley, and nitrogen-oxide groups nitrogen functionalities, respectively, as described earlier. The incorporated nitrogen content in the structure is estimated to be 1.13%, 1.21%, and 1.60% for mentioned C/N ratios. An increase in nitrogen content is recorded by increasing the ammonia flow rate.

5.2 Purification process

Two major types of impurities were observed in TEM images of grown N-CNTs including; iron particles (denoted by circles in Fig. 5.4.a and Fig. 5.4.b) and non-CNT microstructures such as amorphous carbon (Fig. 5.4.c). The iron catalyst particles in the base of the tubes are usually covered by carbon layer(s), which hinder the metal particles removal by treatment in acid solution. Prior oxidation
5.2. PURIFICATION PROCESS

Figure 5.2: TEM images of grown N-CNTs with a mixture of acetylene and ammonia as precursor with different C/N ratios; a) 1:2, b) 1:2.5, and c) 1:4.2

Figure 5.3: XPS spectrum of as-synthesized N-CNTs at 800°C with acetylene/ammonia precursor.
CHAPTER 5. RESULTS AND DISCUSSION

Figure 5.4: TEM images of grown N-CNTs indicating a) iron particle covered by carbon layer in the base of the tube, b) iron particle enclosed inside the tube, and c) amorphous carbon on the tube surface

of amorphous carbons is therefore an important step of the purification process. Bamboo-like compartments cannot be considered as impurity, whereas a hollow cavity is needed for CNTs filling. The enlarged HRTEM image of synthesized N-CNTs (Fig. 5.5) clearly indicates the internal capping of the tube by five inner walls which can stop the motion of filling material along the tube cavity. Therefore, removing these obstacles is an important approach to achieve an acceptable filling rate.

Figure 5.5: HRTEM image of N-CNT with bamboo-like compartments inside the central cavity
5.2. Elimination of amorphous carbon

Several methods were employed to oxidize and remove amorphous carbons. Nitrogen doping causes high defect density in the graphitic structure of CNTs which can result in faster rate of oxidation in N-CNTs [117]. Therefore, moderate oxidation condition should be performed in order to remove amorphous carbons without destructive effects on the tubes surfaces. In this work both acidic and basic oxidants were employed and the results were analyzed by TEM.

Oxidation by nitric acid
As described previously, synthesized N-CNTs were oxidized by refluxing in nitric acid for 6 hours at 130°C. TEM images revealed severe etching of graphitic structure, leading to fragmented and curled tubes as shown in Fig. 5.6. It suggests that the strong acidic oxidative purification causes major damages on CNTs structure in agreement with other reported work [55].

Oxidation in air at 350°C
Among the examined calcination temperatures, described in experiment part, 350°C was chosen as the best condition to oxidize the amorphous carbons without serious damages on the CNTs surface. Fig. 5.7 shows TEM images of N-CNTs after calcinations at 350°C for 2.5 h, 3 h, and 4.5 h. Amorphous carbons on the walls start to oxidize after 2.5 h and are almost removed after 3 h, whereas longer treatment for up to 4.5 h severely damages the walls structure. In general, moderate oxidation in air can be used as a convenient, low cost, and safe method to eliminate amorphous carbon with low destructive effect on CNTs morphology.

Bromination effect on oxidation process
The influence of performing a prior step of bromination on oxidation rate of amorphous carbons was investigated. The N-CNTs were initially stirred in bromine water at 90°C for 3 hours and then calcinated at 350°C for 1 h. TEM images revealed faster rate of oxidation of amorphous carbons due to the bromination. The brominated sample is relatively free of carbon impurities after calcinations for 1 h (Fig. 5.8.a), whereas non-brominated N-CNTs still contains impurities after calcinations at the same temperature for 2 h (Fig. 5.8.b). It suggests that the prior bromination step increases the reactivity of carbon impurities toward oxygen and a shorter oxidation time which has less destructive effects on CNTs structure can be performed [51, 52]. The major drawback of this method was the several steps of purification, filtration and washing which resulted in a significantly low yield.

Oxidation by hydrogen peroxide (H\textsubscript{2}O\textsubscript{2})
N-CNTs were stirred in a mixture of H\textsubscript{2}O\textsubscript{2} and concentrated HCl for 4 hours at
CHAPTER 5. RESULTS AND DISCUSSION

**Figure 5.6:** TEM images of oxidized N-CNT by nitric acid indicating severe damages and fragmentation of the tubes

**Figure 5.7:** TEM images of oxidized N-CNTs in air at 350°C after a) 2.5 h b) 3 h and c) 4.5 h
5.2. PURIFICATION PROCESS

Figure 5.8: TEM images of oxidized N-CNTs in air at 350°C a) for 1 h with a prior bromination step and b) for 2 h without prior bromination step

Figure 5.9: TEM images of N-CNTs a) before annealing in argon and b) after annealing in argon at 800°C for 4 h
80°C to eliminate amorphous carbons and iron particles simultaneously. Regarding to the reported works, this method can be effective to purify CNTs in high scale without severe damages on CNTs structure [54], however the optimum result was not achieved in the current work. The iron content decreases only by 20% after purification process; whereas an increase of 49% in nitrogen concentration was observed in XPS measurement indicating shrinkage in carbon content.

**High temperature annealing in argon**

as mentioned earlier, high temperature annealing is one of the most effective methods for metallic particles removal (either on the base or enclosed inside the tubes) [119] and structural enhancement [64]. TEM images of N-CNTs before and after thermal annealing in argon are shown in Fig. 5.9 which reveals a significant decrease in iron particles density (confirmed by XPS measurement from 0.25% to the under detection limit). However, in some cases big catalyst particles could not be removed, denoted by circle in Fig. 5.9.b. Structural transformation from a disordered CNTs to straight ordered CNTs can be relatively observed in agreement with previous work [64].

### 5.2.2 Catalyst particles removal by treatment in HCl

Conventional treatment by hydrochloric acid (HCl) has been used for removal of iron particles previously [51, 52]. As described before, after oxidation process N-CNTs were treated in concentrated HCl in order to dissolve iron particles. TEM images showed the efficiency of the iron particles removal without destructive effect on the morphology of CNTs. Fig. 5.10.a and Fig. 5.10.b compare N-CNTs before and after treatment with HCl.

XPS measurement also verify a 60% decrease in iron content after one step HCl treatment, whereas a two steps purification consist of oxidation in air followed by HCl treatment resulted in 87% decrease in the iron content. It suggests that covered metallic particles with carbon layer could not be dissolved completely by one step acid treatment (as denoted by circle in Fig. 5.10.b).

### 5.2.3 Effect of purification process on the removal of compartment layers

No obvious elimination of internal compartments layers could be observed in the TEM images of purified samples. Compartment layers removal seems more challenging than the removal of other impurities, due to the protection by graphitic structure side walls. In addition, they have more stable structure consist of either pentagonal or hexagonal rings compared to amorphous carbons.
5.3 \textit{C}_{60} ENCAPSULATION INSIDE NITROGEN-DOPED AND PRISTINE MWCNTS

5.3.1 Filling Process under High Vacuum

Nitrogen-doped MWCNTs

As it was described in experiment part, a mixture of purified N-CNTs and \textit{C}_{60} was vacuum sealed and kept at different temperatures (400°C, 500°C, and 600°C) for different times. After washing with toluene, the resulted samples were investigated by high resolution TEM and the images revealed partially filled N-CNTs (Fig. 5.11).

Major portion of encapsulated \textit{C}_{60} were observed in the entry ports of CNTs (Fig. 5.12.a and Fig. 5.12.b) which suggests that the performed vacuum ($\approx 10^{-3}$ mbar) has been efficient enough to drive the sublimated \textit{C}_{60}s into the CNTs. However, the presence of compartments layers inside the central cavity has blocked the motion of \textit{C}_{60}s along the tubes cavity (denoted by circles in Fig. 5.12.c and Fig. 5.12.d). In addition, confined \textit{C}_{60}s in the middle of the tubes length can be rarely found. The reaction temperatures and times have been effective enough as well. The synthesized filled CNTs at 600°C had a lot of remained \textit{C}_{60}s outside compared to those synthesized at lower temperatures. It is in agreement with the report of Smith et al [95] describing that sublimated \textit{C}_{60}s would not have enough residence time on the tube surface to find the entry ports, if the reaction temperature during filling process is too high. The relatively large inner diameter of the N-CNTs has been resulted in high residence of agglomerated \textit{C}_{60}s inside the tubes.
CHAPTER 5. RESULTS AND DISCUSSION

Figure 5.11: HRTEM images of N-CNTs filled with $C_{60}$ under high vacuum at a) 400$^\circ$C, b) 500$^\circ$C, and c) 600$^\circ$C for 24 hours

Figure 5.12: HRTEM images of $C_{60}$-filled N-CNTs under high vacuum a,b) in the tube entry port c,d) blockage of $C_{60}$ motion along the tube by internal layers
5.3. $C_{60}$ ENCAPSULATION INSIDE NITROGEN-DOPED AND PRISTINE MWCNTS

Figure 5.13: Enlarged image of $C_{60}$s encapsulated in N-MWCNT. The arrangement of $C_{60}$s is not clear.

in the filled areas shown in an enlarged image with modified contrast in Fig. 5.13.

**Pristine thin-walled MWCNTs**

For pristine MWCNTs, initially, the filling conditions including temperature and time were repeated the same as those done for N-CNTs; however TEM images did not show any traces of filling. Two filling conditions including temperature and the pressure inside the sealed tubes were investigated as the effective factors to maximize the filling rate. Pristine MWCNTs have smaller diameter (average of $\approx 9.5$ nm) compared to that of N-CNTs which suggests the necessity of performing higher vacuum to provide stronger driving force. NMR tubes were therefore replaced with quartz glass tubes which could fix better on vacuum line and provide a lower pressure inside. Higher temperature was also provided to see the temperature effect on filling process. High resolution TEM images revealed the low filling rate of MWCNTs for the samples synthesized at $650^\circ$C for both 12 and 6 hours at pressure around $10^{-5}$ mbar. In the initial experiments, despite of sonication in toluene a lot of $C_{60}$s had still remained outside the tubes and walls was damaged by sonication as they were rough and wrinkled. Thereafter the samples were oxidized in air instead to remove the extra $C_{60}$s.

5.3.2 Solution-based Filling Process

**Nitrogen-doped MWCNTs**

As it was described in chapter 4, Nitrogen-doped MWCNTs were refluxed in a dispersion of $C_{60}$ and n-hexane for 2 hours at $70^\circ$C. TEM images revealed noticeable
improvement in the filling rate of N-CNTs filled by this method compared to the vacuum-based method. In addition, filled areas between two internal caps were occasionally found in the sample (Fig. 5.14) which can suggest the bulk diffusion of C\(_{60}\) molecules through the defects or holes on the walls.

**Thin-walled Pristine MWCNTs**

Different C\(_{60}\) solvents were examined in the solution-based filling process described in details earlier. HRTEM images of the samples prepared by ultra-sonication of pristine CNTs in a mixture of C\(_{60}\) and methanol for 2 hours is shown in Fig. 5.15. The filling rate is higher compared to vacuum driven method, however it is not significant and the long sonication has caused severe damages to the CNT walls. A lot of C\(_{60}\)s also seem to be trapped on the surface defects and remained outside the tubes despite of post filling purification.

In other experiment, pristine MWCNTs were refluxed in a mixture of C\(_{60}\) and n-hexane for 2 hours at 70° C. The recorded TEM images (Fig. 5.14) revealed efficiency of using n-hexane, as a lot of filled CNTs with continues packed C\(_{60}\)s were observed. In addition a narrow empty space can be seen between the encapsulated C\(_{60}\)s and the sidewalls (denoted in Fig. 5.14 by arrow) which may be caused by the C\(_{60}\)-CNT interface.

**Bulk diffusion of C\(_{60}\)s through the defects on MWCNTs walls**

In order to improve the filling rate, introduction of holes into the CNTs walls was considered as an effective approach to the bulk diffusion of C\(_{60}\)s through the tube walls. The pristine CNTs were therefore oxidized in air and reduced in varigon before performing the filling process as described in chapter 4. Brocken walls
5.3. \( \text{C}_6\text{O} \) ENCAPSULATION INSIDE NITROGEN-DOPED AND PRISTINE MWCNTS

Figure 5.15: HRTEM images of holes introduced MWCNTs by oxidation in air at 450° C for 1 hour and then reducing in varigon atmosphere at 900° C for 1 hour.

denoted by circles in Fig. 5.15 were obtained after reduction process. This can be compared with the presence of defective sites on nitrogen-doped CNTs surface which caused inserting \( \text{C}_6\text{O} \) through the walls and filling the areas between two internal caps as shown in Fig.5.14.

The reduced CNTs were refluxed in a mixture of \( \text{C}_6\text{O}s \) and n-hexane as described earlier. TEM images (Fig. 5.18.a) shows improved filling rate for the filled reduced CNTs compared to the non-reduced sample filled by the same method. It can therefore verify that the presence of holes on the CNT walls can contribute to the filling rate through the bulk diffusion mechanism.

A relatively good solvent of \( \text{C}_6\text{O} \), toluene, was also used to synthesis filled MWCNT. Reduced CNTs was immersed in a solution of \( \text{C}_6\text{O} \) in toluene and the filling process performed under the nitrogen flow to evaporate all the toluene. HRTEM images revealed \( \text{C}_6\text{O} \) filled CNTs with large gaps between two groups of encapsulated \( \text{C}_6\text{O}s \) in a numbers of areas which indicates a non-continuous filling rate as shown in Fig.5.18.b.

In a comparison between the two employed solvents, n-hexane with poor solubility of \( \text{C}_6\text{O} \) (0.046 mg/ml) and toluene with high \( \text{C}_6\text{O} \) solubility (3 mg/ml), it can be concluded that using n-hexane is resulted in a good and continuous filing rate in contrary to the filled CNTs synthesized in toluene. This obtained result can be in agreements with a previous reported work [120] which investigates the effect of solubility on SWCNTs filling rate by employing two \( \text{C}_6\text{O} \) solvents with different solubility values. Accordingly, formation of \( \text{C}_6\text{O} \) clusters in a poorer solvent lead to a continuous filling rate as \( \text{C}_6\text{O}s \) can enter into the tube one by one immediately. In contrast, any trace of \( \text{C}_6\text{O} \) encapsulation was not observed by using a good \( \text{C}_6\text{O} \) solvent. Presence of single isolated \( \text{C}_6\text{O}s \) prohibits the continuous insertion of \( \text{C}_6\text{O} \).
Figure 5.16: HRTEM images of C$_{60}$-filled reduced MWCNTs by a) refluxing in n-hexane, and b) immersing in toluene under nitrogen flow.

molecules into the tubes (Fig. 5.17).

5.4 **Vibrational and Dynamical Analysis of Encapsulated C$_{60}$s**

5.4.1 **Raman spectroscopy**

Raman technique was employed to confirm the success of filling and investigate the vibrational states of the encapsulated C$_{60}$s. Different points of the samples were characterized by Raman mapping. Fig. 5.18.a shows the recorded spectrum of bulk pristine C$_{60}$ and its corresponding Raman active modes which are in agreement with the described work in chapter 3 [108].

Raman spectrum of C$_{60}$-filled N-MWCNT shown in Fig. 5.18.b revealed the presence of encapsulated C$_{60}$s. The PPM, $A_g(2)$ mode, is observed at 1467 cm$^{-1}$ which has a downshift by 3 cm$^{-1}$ compared to that of pristine C$_{60}$. It suggests a partial charge transfer and interaction between C$_{60}$s and CNT side walls due to encapsulation [112]. The G band and D bands of MWCNTs are located at 1596 cm$^{-1}$ and 1350 cm$^{-1}$ respectively. The other C$_{60}$ modes which could be observed were $H_g(3)$ at 706 cm$^{-1}$, $A_g(1)$ at 495 cm$^{-1}$, and $H_g(1)$ at 272 cm$^{-1}$. In general, polymerization effects are not observed in the Spectrum. No significant downshift of $A_g(2)$ peak and the absence of low frequencies peaks below 200 cm$^{-1}$ specially at 90 cm$^{-1}$ confirm the presence of unpolymerized encapsulated C$_{60}$s inside the
5.4. VIBRATIONAL AND DYNAMICAL ANALYSIS OF ENCAPSULATED C$_{60}$S$_{57}$

Figure 5.17: C$_{60}$ encapsulation inside SWCNT using a) a poor solvent of C$_{60}$ which leads to the formation of C$_{60}$ clusters and subsequent dense filling rate, and b) a good solvent of C$_{60}$ which results in a low filling rate with large physical gaps [120].

Figure 5.18: Recorded Raman spectra of a) pristine C$_{60}$ and the experimentally obtained frequencies, and b) C$_{60}$-filled N-MWCNT after washing with toluene.
5.4.2 NMR Studies of Encapsulated C_{60}s inside MWCNTs

Fig. 5.19 shows recorded MAS $^{13}$C NMR spectrum of the C$_{60}$-filled reduced MWCNTs (synthesized by refluxing in n-hexane) performed at 500 MHz magnetic field at room temperature. The spectrum revealed a strong resonance line at 143.6 ppm and a weak line at 200.3 ppm. In addition, a broad signal can be recognized at around 111.2 ppm. The peak at 143.6 ppm with FWHM (full width half maximum) of 1.01 ppm indicates rapid reorientation of the major numbers of encapsulated C$_{60}$s which is consistent with NMR resonance line of the bulk C$_{60}$ at room temperature. However from HRTEM images of the sample ignorable portion of C$_{60}$s are remained outside the tubes after purification. This strong line can be assigned to the fullerenes located in the center of the tube cavity (shown by green color in schematic picture 5.21). These fullerenes are not in the vicinity of the tube side walls and therefore not affected by magnetic shielding originating from $\pi$ electrons of the carbon atoms of the CNT. It suggests that these C$_{60}$ molecules behave similarly to those bulks unencapsulated fullerenes as they are not affected by the interaction force of the CNT side walls.

On the other hand a relatively small portion of encapsulated C$_{60}$ are in the vicinity of side walls. These C$_{60}$s depending on where they are located, either beside to the wall defects or not can behave dynamically different. The broad weak resonance
5.4. VIBRATIONAL AND DYNAMICAL ANALYSIS OF ENCAPSULATED C$_{60}$S

Figure 5.20: The nuclear spin-lattice relaxation time ($T_1$) curve measured by considering the recovery of C nuclear magnetization with time $M(t)$.

The line at 111.2 ppm suggests presence of a few percentage of C$_{60}$s in the vicinity of side walls which are diamagnetically shielded from ring current circulating on the cylindrical surface of the tube and shifted by 32 ppm from its normal position at 143.6 ppm in agreement with previous reports [114, 115]. The other resonance line at 200.3 ppm also shows presence of static C$_{60}$s located in the vicinity of side walls defects or holes. Presence of these defects or holes induces a paramagnetic shielding from the tube and cancels the circulating ring current originating from the paired $\pi$ electrons. In addition, coulombic interaction can freeze out the rotational diffusion of these C$_{60}$s with the energy barrier becoming too high [114].

As described in chapter 4, the $^{13}$C spin-lattice relaxation process was performed at room temperature. After fitting the recorded data to the time dependent magnetization Eq. 5.1 the curve shown in Fig. 5.20 was obtained.

$$M_z(t) = M_0(1 - 2e^{-t/T_1}) \quad (5.1)$$

Where $M_z(t)$ is magnetization, $M_0$ is the magnetization at the initial time and $T_1$ is spin-lattice relaxation time. Considerable change in the relaxation time was observed compared to that of bulk C$_{60}$ from around 70 s to 4.4 s which may refer to the faster rotation of the encapsulated C$_{60}$s compared to the bulk C$_{60}$s.
CHAPTER 5. RESULTS AND DISCUSSION
Chapter 6

Summary and Conclusion

Nitrogen-doped MWCNTs (N-MWCNTs) were synthesized by chemical vapor deposition (CVD), using iron particles as catalyst material and a mixture of acetylene and ammonia as carbon/nitrogen precursor. Transition electron microscopy (TEM) revealed successful growth of thin-walled N-CNTs with relatively large internal cavity of around 12 nm in diameter. The synthesized CNTs were purified and uncapped, regarding to the filling aim, using both physical and chemical based methods. In chemical based method, acidic and basic oxidants including nitric acid, air, and $\text{H}_2\text{O}_2$ were used to eliminate carbonous impurities. Oxidation in air at different temperatures and times was found to be an effective method to remove impurities physically. Finally, heat treatment at 350°C for 3 hours was chosen as a convenient rout to remove amorphous carbons with low destructive effects on CNTs structure. The oxidized sample was then treated in HCl to dissolve iron particles. TEM and X-ray photoelectric spectroscopy (XPS) confirmed effective removal of impurities and opening of high percentage of tubes entry ports. For filling, the purified N-MWCNTs were used along with the commercial highly pure pristine thin-walled MWCNTs.

Two main filling approaches were performed including; vacuum-based and solution-based methods. In vacuum-based method the CNTs and highly pure $\text{C}_{60}$s were mixed (1:3) and vacuum sealed inside a tube. The sealed tube was then kept at specific temperature for a predefined time. High resolution TEM images showed partial filling of N-CNTs especially in their entry ports, while the motion of $\text{C}_{60}$ thorough the cavity of the tubes had been blocked by internal carbon layers. The same filling method was repeated to fill the thin-walled pristine MWCNTs, however no trace of filling was observed in the recorded TEM images. It was concluded that since the used pristine MWCNTs have smaller inner diameter (around 5.5 nm), compared to that of N-CNTs, higher degree of vacuum is needed to drive the $\text{C}_{60}$s into the nanotubes. Thereafter, a 1:3 mixture of pristine MWCNTs and
C\textsubscript{60} was vacuum sealed in lower pressure around 10\textsuperscript{−5} mbar and kept at 350°C for 24 hours. TEM images showed filled MWCNTs however the filling rate was low. In solution-based approach, different C\textsubscript{60} solvents including n-hexane, methanol, and toluene were employed. Uncapped nitrogen-doped MWCNTs and C\textsubscript{60} (ratio of 1:1) were refluxed in n-hexane at 70°C for 2 hours. Considerable improvement in filling rate was obtained compared to N-CNTs filled under high vacuum. In addition, filled areas between two internal carbon compartments were occasionally observed which can suggest bulk diffusion of C\textsubscript{60} through walls defects. A similar method also performed for pristine MWCNTs and more acceptable results was achieved compared to vacuum-based method. Methanol was the other examined C\textsubscript{60} solvent, where a mixture of pristine MWCNTs and C\textsubscript{60} was sonicated in methanol for 2 hours. Filled tubes were observed however they were seriously damaged due to long sonication.

In order to achieve a better filling rate through the bulk diffusion, holes were introduced on pristine MWCNTs walls by calcination at 450°C for 1 hour. The defect introduced tubes were then reduced in varigon atmosphere at 900°C. The reduced MWCNTs were refluxed in n-hexane and C\textsubscript{60} mixture at 70°C for 2 hours. HRTEM images indicated an improved and continuous filling rate which can suggest bulk diffusion of C\textsubscript{60}s through the introduced holes on the tubes walls. Toluene also was used as a good solvent of C\textsubscript{60}, and reduced MWCNTs were immersed in the C\textsubscript{60} solution and kept under nitrogen flow overnight. The filled CNTs by this method had non-continuous filling with large gaps between two groups of encapsulated C\textsubscript{60}s.

In general, it can be concluded that n-hexane as a poor solvent of C\textsubscript{60}, can be a good candidate in order to fill the CNTs with C\textsubscript{60}s which results in acceptable and continuous filling rate. In addition, introduction of holes can contribute to have more filled areas. Raman spectroscopy of the filled CNTs indicated four main C\textsubscript{60} raman modes including A\textsubscript{g}(2), H\textsubscript{g}(3), H\textsubscript{g}(1), and A\textsubscript{g}(1) with a small down shift compared to that of pristine C\textsubscript{60}. It suggests encapsulation of C\textsubscript{60}s inside CNTs and possible charge transfer between C\textsubscript{60} and CNT side walls. The polymerization effect was not observed in the Raman spectra due to the insignificant downshift of A\textsubscript{g}(2) and absence of peaks at low frequencies under 200 cm\textsuperscript{−1}. Rotational behaviour of encapsulated C\textsubscript{60}s inside pristine MWCNTs was also investigated by \textsuperscript{13}C nuclear magnetic resonance (\textsuperscript{13}C NMR) spectroscopy. The recorded spectrum revealed a strong resonance line at 143.6 ppm, a weak line at 200.3 ppm, and a broad signal at around 111.2 ppm. These resonance lines represents presence of three groups of encapsulated C\textsubscript{60}s regarding to their dynamics behavior. The line at 143.6 ppm is assigned to C\textsubscript{60}s in the central area of the tube which are not in the vicinity of side walls and behave similar to pristine C\textsubscript{60}s in solid. The weak line at 200.3 ppm shows small portion of C\textsubscript{60}s located in side walls
vicinity which are diamagnetically shielded from ring current. And the broad signal at 111.2 ppm is assigned to the static C$_{60}$s located beside the side walls defects or holes which cancel the ring current and stop the rotation of C$_{60}$s. The nuclear spin-lattice relaxation time (T$_1$) measurement was performed as well by considering the recovery of C nuclear magnetization with time M(t) after the saturation pulses. The obtained recovery curve revealed faster rotation of encapsulated C$_{60}$s compared to that in bulk C$_{60}$s.
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