Chemical Vapor Deposition of Carbon Nanostructures and Carbon Nanotubes-Reinforced Composites

by

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CURRICULUM VITAE

The author was born in Taipei, Taiwan on June 14, 1976. He attended Tunghai University from 1994 to 1998, and graduated with a Bachelor of Science degree in 1998. He came to the University of Rochester in the Fall of 2000 and began graduate studies in Chemical Engineering. He received a Frank J. Horton Research Fellowship from 2001 to 2006. He pursued his research in polymeric composite materials with nanostructures reinforcement under the direction of Professor David R. Harding and received the Master of Science degree from the University of Rochester in 2004.

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ABSTRACT

The vapor deposition of open-networked carbon nanostructures and carbon nanotubes (CNTs)-reinforced composites have been developed and studied parametrically. Carbon nanostructures, including nano-tubes, nano-foams, nano-particles, and nano-walls, have been deposited on catalyst-assisted substrates using microwave plasma electron cyclotron resonance-chemical vapor deposition (ECR-CVD) system at temperature as low as 300 °C. Processing parameters determining the morphologies and properties of the nanostructures were identified to optimize the productions.

Carbon nanotubes-reinforced polymer composite films were synthesized at low temperature by a two-step process using: (1) ECR-CVD system to vapor deposit a nanotube film substrate at 480 °C with gas mixture of methane and hydrogen, and (2) chemical vapor infiltration (CVI) of hydrocarbon (CH) polymers into the nanotube substrate. In this study, parylene and glow-discharge polymerization (GDP) polymers were utilized to infiltrate the nanotube substrate at temperature below 70 °C. A strong interfacial adhesion between the carbon nanotubes and the polymer matrix is a major factor that determines the reinforcement performance of such nanocomposites. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies showed that nanotubes embedded within the

polymer matrix not only provide a chemically compatible interface with the polymer but also enhance interfacial adhesion by mechanical interlocking or entangling.

The feasibility of making carbon nanotubes-reinforced composite depends on the processing parameters, including the effect of polymer vapor infiltration and the volume density of the nanotube substrate. Characterizations of these composite films have been conducted and it was found that vapor-deposited parylene/CNTs composite possessed better interfacial bonding and an infiltration distance ~200% greater than the GDP/CNTs one, while using a 39 vol.% nanotube substrate. In addition, analyses via nano-indentation measurement revealed that the effect of nanotubes reinforcement within the composite resulted in 14% increase in elastic modulus.

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SYMBOLS

$\mathbf{a_1}$	unit vector of the hexagonal lattice (dimensionless)
$\mathbf{a_2}$	unit vector of the hexagonal lattice (dimensionless)
$\mathbf{C_h}$	chiral vectors in the graphene plane (dimensionless)
$\mathbf{D_{CNT}}$	outer diameter of carbon nanotube (L)
$\mathbf{d_{CNT}}$	inner diameter of carbon nanotube (L)
$\mathbf{L_c}$	critical length of carbon nanotubes (L)
$\mathbf{n_{PA}}$	refractive index of parylene (dimensionless)
$\mathbf{t_{PA}}$	parylene thickness per fringe (L)
$\mathbf{vol_{inner}}$	volume of inner (hollow) tube (L^3)
$\mathbf{vol_{outer}}$	volume of outer (tubular) tube (L^3)
$\rho_{graphite}$	density of graphite (ML^{-3})
ρ_{CNT}	density of individual multi-walled carbon nanotube (ML^{-3})
σ_{CNT}	tensile strength of a nanotube segment ($ML^{-1}t^{-2}$)
τ_{CNT}	nanotube-polymer interfacial shear strength ($ML^{-1}t^{-2}$)
λ	IR laser wavelength (L)

ABBREVIATIONS

AFM	atomic force microscope
CH	hydrocarbon
CNTs	carbon nanotubes
CSM	continuous stiffness measurement
CVI	chemical vapor infiltration

CVD	chemical vapor deposition
ECR-CVD	electron cyclotron resonance chemical vapor deposition
FEDs	field emission displays
GDP	glow discharge polymerization
ICF	inertial confinement fusion
LLE	Laboratory for Laser Energetics
MWNTs	multi-walled carbon nanotubes
NIF	National Ignition Facility
PAMS	poly-α-methylstyrene
PHAE	polyhydroxyaminoether
PMMA	polymethylmethacrylate
PS	polystyrene
SEM	scanning electron microscopy
SWNTs	single-walled carbon nanotubes
TEM	transmission electron microscopy
VDP	vapor deposition polymerization
VGCF	vapor grow carbon fiber

Chapter 1. Introduction

1.1 Carbon Nanotubes

Since discovered in 1991 [1] as elongated fullerenes, carbon nanotubes (CNTs) have introduced an important opportunity to the fields of scientific and engineering worlds with their superior properties and outstanding geometrical dimensions. Carbon nanotubes can be described as a hexagonal sheet of carbon atoms rolled into a seamless cylindrical shape, as shown in Figure 1.1. A nanotube is composed entirely of sp^2 bonds structure, which is similar to those of graphite and provides the molecules with its unique strength. A typical nanotube has outer diameters varying between 1-2 and few tens of nanometers when it was first discovered, while the inner hollow diameter is typically of the order of only 1 to 5 nm [2,3]. There are two types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs), as shown in Figure 1.2 (a) and (b), respectively. The detailed structures and properties will be described in the next section.

Besides their extremely small size, it has been suggested that carbon nanotubes possess tensile strengths at least 100 times stronger than high strength steel alloys [4], have current capacities 1000 times higher than copper [4,5], and transmit heat twice as well as pure diamond [6]. To take advantage of this unique combination of

size and properties, researchers have been exploring the potential of CNTs in a wide variety of applications. For example, CNTs have been experimentally demonstrated as an atomic force microscope (AFM) tip for imaging and lithography [7,8]. With extremely small sizes and good conductivity of CNTs, this tip now can be made as small as few nm offering reasonable resolution. In addition, the remarkable electronic properties of nanotubes enable them for use as quantum wires to bridge a junction device, as shown in Figure 1.3, for the nanoelectronics applications [9,10]. Also, the geometric properties of CNTs, such as the high aspect ratio, mechanical strength and chemical stability, qualify them an ideal candidate for the electron field emission displays (FEDs) [11-13]. Other than these thermal and electrical applications, second major application will be based on nanotube strength, elasticity and mechanical properties including mechanical memory, supersensitive sensors, hydrogen and ion storages, and nano-structural materials. While the outstanding properties of carbon nanotubes have led to a wide range of applications, in this study here we limit our analysis to the use of carbon nanotubes as a filler for structural reinforcement in a host polymer matrix, a material referred to as a *carbon nanotube-reinforced polymer composites*, which is one of the main subject of this study and will be discussed in detail in Chapter 4.

1.2 Structures and Properties of Carbon Nanotubes

Carbon nanotubes are fullerene-related structures, which is aforementioned as a piece of graphene sheet to form a cylinder with end caps containing pentagonal rings. The role of a pentagonal ring defect is to produce a convex structure, which helps to form the curved structures and close the tube at two ends [14]. In the mapping of a graphene plane into a cylinder, chiral vector C_h = n a_1+ m a_2 is defined in terms of the lattice translation indices (n, m) and the unit vectors a_1 and a_2 of the hexagonal lattice, as shown in Figure 1.1(a), to identify and determine the directions along which the graphene sheets are rolled to form tubular structures. The nanotubes of type (n, n) in Figure 1-1(b) are commonly called armchair nanotubes with a symmetry _/‾_/ shape. Another type of nanotubes (n, 0) is known as zigzag nanotubes because of the \/\/ shape along the axis. All other types of nanotubes could be defined as a pair of indices (n, m), where n ≠m [14]. The electronic conductivity of nanotube is highly sensitive to a change of these parameters, which determines a carbon nanotube being either metallic or semiconducting [14,15].

Interest in nanotubes for nano-scale material applications exists due to a number of extraordinary properties:

(1) Single and multi-walled carbon nanotubes have very good mechanical properties. The tensile modulus and strength of the nanotubes ranging

from about 270 GPa to 1 TPa and 11-200 GPa, respectively, have been reported [16, 17], making nanotubes perhaps the ultimate high stiffness reinforcement material. Table 1.1 shows the mechanical properties of CNTs with other materials [2,4-6,16,17]. It indicates that CNTs possess most superior mechanical characteristic.

(2) Nanotubes possess hollow and closed topology that produce a distinct mechanical response compared to other graphitic structures. Nanotubes can sustain extreme strains (40%) in tension without showing signs of brittle, behavior, plastic deformation, or bond rupture [18].

(3) Nanotubes are lightweight, high aspect-ratio structures and could be the ideal packing materials for gas-storage and hydrocarbon fuel storage devices [14].

It is also worth noting that the carbon nanotubes are chemically and molecularly defined structures with reproducible dimensions that make them stiffer and stronger than any potentially known material with applications for the design of polymer composites. Early evaluations of carbon nanotubes indicated they possess outstanding mechanical properties – greater than those of vapor grow carbon fiber (VGCF), a reinforcement fiber usually employed in materials and aerospace applications. Table 1.2 lists an example of CNTs and VGCF as reinforcement within a polystyrene (PS) polymer matrix [19]. The higher elastic modulus of nanotubes with a tensile strength an order of magnitude higher than that of

conventional carbon fibers qualifies the nanotubes as a desirable reinforcement in polymer composite materials.

1.3 Carbon Nanotubes-Reinforced Polymer Composites for Use as ICF Targets

1.3.1 Inertial Confinement Fusion

The main mission of the Laboratory of Laser Energetics (LLE) at the University of Rochester is to investigate inertial confinement fusion (ICF) using the direct-drive approach. Inertial confinement fusion is a process where the fuel is confined by its own inertia for a sufficiently long time at very high density and temperature for the fusion reaction to occur. This is achieved by uniformly illuminating a target that consists of a thin-wall shell with a concentric solid fuel (DT or D_2) with the sixty beams of the 30 kJ Omega laser thereby compressing its contents to a density and pressure sufficient to initiate nuclear fusion. The laser beams instantaneously ionize the atoms in the outermost layer of the target and heat the resultant plasma. As the plasma ablates and expands outwards, the remainder of the fuel accelerates inwards, compressing the central region until the fuel is 1000 liquid density, which

raises the fuel temperature to trigger the fusion reaction [20]. The schematic of direct-drive ICF process is shown in Figure 1.4.

1.3.2 Target Requirements

A spherical target typically consists of a thin-wall polymer capsule that is ~1 mm in diameter with a wall thickness of 3-5 μm and a uniform solid fuel (DT or D_2) layer (100 μm thick) on its inner surface. Foam shells having densities of 70 - 120 mg/cc and thickness of 40 – 60 μm will be coated with a normal density plastic layer. The preparation of these targets will be greatly facilitated if the capsule possesses the following properties: (i) high gas permeability at elevated temperature to allow a rapid fill with DT; (ii) high strength and elastic modulus to withstand greater buckling/bursting pressures and thus be filled more rapidly than current targets; (iii) good thermal conductivity that may help the layering process by creating a more isothermal environment for the ice; (iv) substantial transparency in the visible spectrum to allow observation during DT filling.

The design of the ICF target varies with the different laser facilities employed to conduct the experiment. Table 1.3 lists the target designs for the main current laser facilities [21, 22]. It is noted that direct-drive ICF experiments on the National Ignition Facility (NIF), whose energy is almost 50 times larger than OMEGA's energy, require targets with larger diameters (3.5mm) and comparable thick wall

for OMEGA targets (3 μm); achieving the surface smoothness, uniform wall thickness, and sphericity of these targets is considerable more difficult as the target size increases.

1.3.3 Carbon Nanotubes-Reinforced Polymer Microcapsules

Various materials have been used to fabricate shells for use as ICF fuel capsules [21]. Previous and current processes for the production of ICF targets have been dedicated to developing plastic shells for their mechanical properties, high permeability, optical transparency and low atomic number and low density. Those plastic materials that are available for use in the OMEGA application include polystyrene (PS) [23], poly-α-methylstyrene (PAMS) [24], vapor deposition polymerization (VDP) polyimide [25], and hydrocarbons capsules fabricated using a glow-discharge-polymerization (GDP) process [26]. Such materials with promising properties have been greatly beneficial in target fabrication. The next generation of shells for the NIF or Fusion energy will have to be permeation-filled more rapidly with the DT fuel, because the larger size has a comparably larger fuel inventory. Therefore, the possibility of making a strong plastic shell by reinforcing it with carbon nanotubes (CNTs) reinforcement is investigated to meet this challenge.

Carbon nanotubes could benefit target fabrication in the following two ways: First, due to the greater strength and toughness of the reinforcing CNTs and interfacial bonding for load transfer, "whisker-like" carbon nanotubes reinforcing the plastic shell wall, as shown in Figure 1.5 (a), can make the shell withstand greater buckling/bursting pressures and thus be filled more rapidly than current targets. The carbon content of nanotube reinforcement could also provide increased laser absorption with which the lower density would minimize the hydrodynamic penalty. Moreover, carbon nanotubes also possess high thermal conductivity that may help the layering process by creating a more isothermal environment for the ice. Second, carbon nanotubes can function like foams, inside a shell as shown in Figure 1.5 (b), to support DT ice and help creating an ideal structure for the target. The open connectivity of the CNTs-type foam would benefit the ice layering process by providing a more "open" and connective radial path through the foam wall.

1.4 Objective

Carbon nanotubes (CNTs) have been recognized as ideal reinforcement materials in other technology fields [7-14]. A great deal of recent research has focused on limiting the defects within the nanotubes (which are particularly detrimental from a mechanical property perspective) and increasing the production yields from

nanotube processing techniques. Current nanotubes-reinforced nanocomposites are usually prepared by "wet" processing methods, such as solution mixing and casting, melt dispersion, or extrusion and injection techniques. Those techniques; however, have few limitations and do not achieve expected properties due to, (i) poor separation of bundles: there are types of nanotubes that are produced as bundles. In order to have an optimal load transfer from the matrix to the nanotubes, they must be separated; (ii) week nanotube-polymer interface: these wet processing methods do not yield a homogeneous and stable interface between nanotube and polymer matrix. Also, at the moment the efforts to make CNTs or nanotube-reinforced composites at low temperature needed for ICF application have failed to achieve properties equivalent to those of high-temperature productions.

Therefore, the attraction of this study is the potential to determine the feasibility of making carbon nanotubes-reinforced polymer composite thin films or shells with desirable low temperature and great mechanical properties for target fabrication, and using only chemical vapor deposition (CVD) and vapor deposited polymerization processes.

The main goals are:

(1) Develop a fabrication process for production of vapor-deposited carbon nanotubes at low temperature with desirable mechanical properties and dimensions for ICF application.

(2) Optimize the vapor deposition with different processing conditions to produce other types of low temperature open-networked carbon nanostructures, including nano-foams and nano-walls.

(3) Develop a series of fabrication procedure to synthesize carbon nanotubes-reinforced polymer composites using only vapor deposition process.

(4) Identifying and characterizing the interfacial interaction between nanotubes and polymer matrix.

(5) Characterize the composites quality and properties relevant to the ICF applications, including tensile strength, mechanical modulus, composite densities, and shell wall thickness uniformity.

1.5 Tables and Figures

Materials	Diameter (nm)	Density (g/cm^3)	Modulus (GPa)	Tensile Strength (GPa)
CNTs	1-10	1.33-2.6	Up to ~1000	Up to ~200
C Nanoropes	10-100	1.3	563	~75
SiC fibers	10,000-20,000	2.3	190	2.8
Quartz	9,000	2.2	70	3.4
Steel	-	7.8	208	0.4
Epoxy	-	1.25	3.5	0.05
Wood	-	0.6	16	0.08

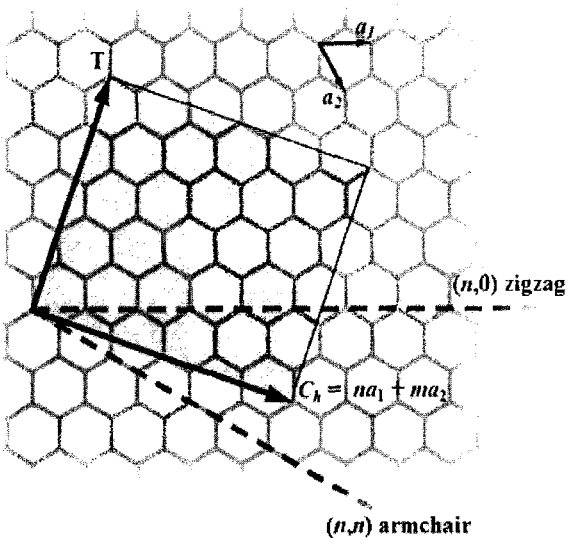
Table 1.1 Mechanical properties of CNTs compared with other materials [2,4-6,16,17].

Composite 1 wt% loads	VGCF or MWNT parameters		Composite tensile properties	
	Diameter (nm)	Aspect ratio (l/d)	Strength (MPa)	Modulus (MPa)
PS + VGCF	> 200	< 100	~ 1	1190
PS + MWNT	30	> 1000	16	1690

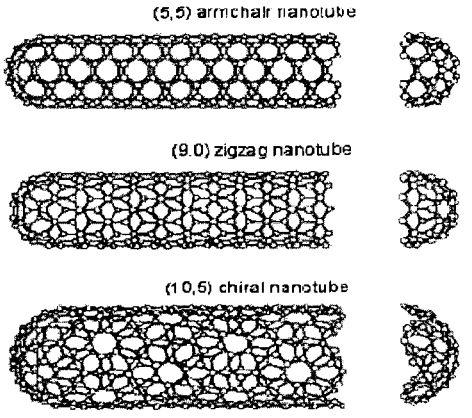
Table 1.2 Mechanical performance of the multi-walled carbon nanotubes (MWNTs) and vapor-grown carbon fibers (VGCF) as reinforcements for polystyrene (PS) composites [19].

Direct-Drive Targets	OMEGA Laser System (U of Rochester)	National Ignition Facility (NIF)
Capsule Diameter (μm)	~ 880	~ 3500
Capsule Wall Thickness (μm)	3-5	< 5
DT Layer Thickness (μm)	100	350

Table 1.3 Designs of Inertial Confinement Fusion (ICF) targets for various laser facilities [21,22].

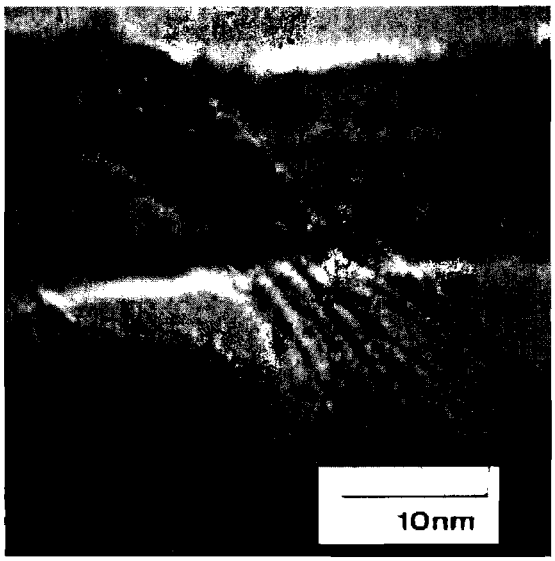


(a)

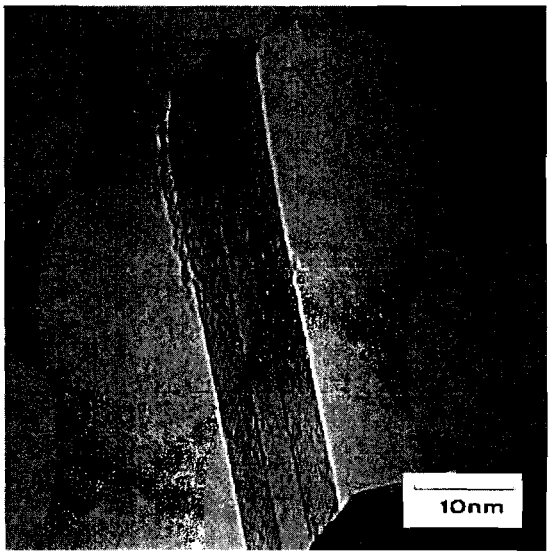


(b)

Figure 1.1 (a) A graphene sheet made of carbon atoms placed at the corners of hexagons forming the lattice with chiral vector, C_h=na_1+ma_2 (a_1 and a_2 are the unit vectors) denoting the rolling direction of the sheet to make (b) a (5,5) armchair nanotube, a (9,0) zigzag nanotube, and a (10, 5) chiral nanotube [14].



(a)



(b)

Figure 1.2 TEM images of typical (a) SWNTs, and (b) MWNTs [1,14].

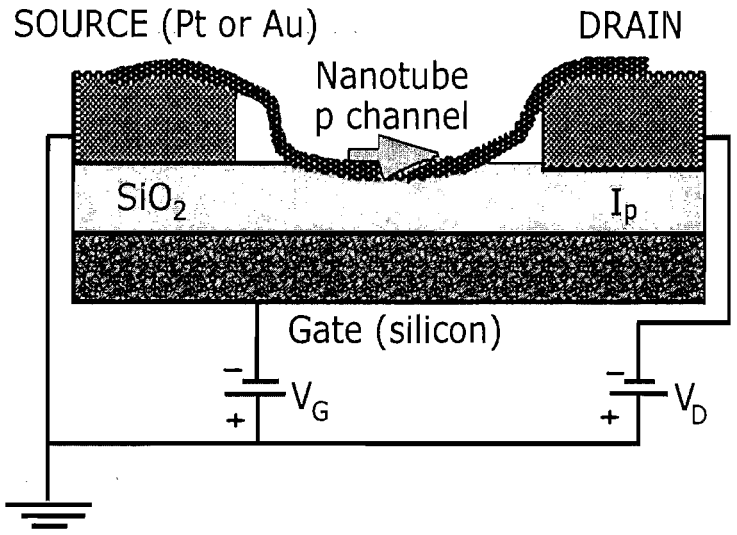


Figure 1.3 Schematic of the carbon nanotubes-based field effect transistor [9,10].

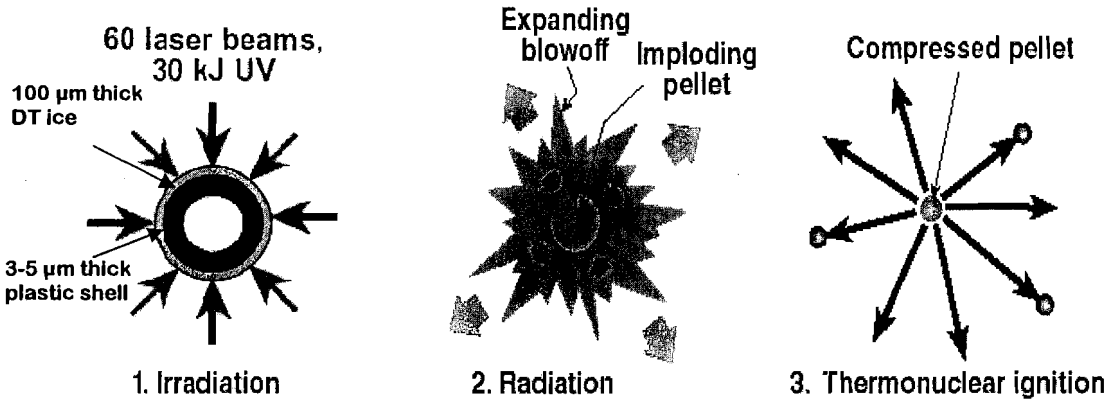


Figure 1.4 Schematics of the Inertial Confinement Fusion (ICF) process [20].

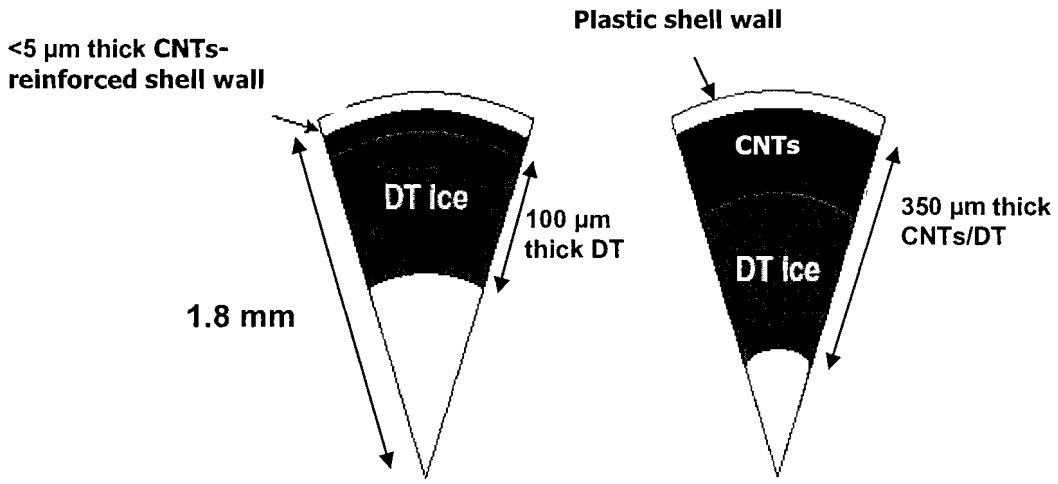


Figure 1.5 Schematics of the typical targets with (a) nanotubes-reinforced shell walls and (b) nanotubes-reinforced DT layers inside the walls.

Chapter 2. Fabrication of Carbon Nanotubes by Microwave Plasma Chemical Vapor Deposition

2.1 Introduction

2.1.1 Synthesis Methods of Carbon Nanotubes

For the synthesis of high yield and good quality carbon nanotubes, many methods were invented and developed. A summary of some standard nanotubes fabrication techniques is given in Table 2.1. The earliest approach to produce nanotubes was an arc-discharge process [27] as pioneered by Iijima [1]. This was shortly followed by a laser ablation technique developed by Smalley at Rice University [28]. Chemical vapor deposition (CVD) has become a common technique to grow CNTs in the last decade [29-34], with the interest of capable to be scaled for industrial production. Regardless of the applications and growth approach, the ability to control the properties of the nanotubes is critical to realize the promise of carbon nanotubes.

The arc-discharge process involves the use of two graphite electrodes under a gas atmosphere (such as argon or helium) and a voltage is applied until a stable arc is achieved [1,27,35]. This produces SWNTs in mixture of MWNTs and soot. To

synthesize pure SWNTs, an arc discharge with a cathode containing metal catalysts (such as cobalt, iron or nickel) mixed with graphite powder results in a deposit containing SWNTs [28]. The yield has been significantly increased by optimizing the catalyst mixture and the deposition condition.

In the laser ablation method, a target consisting of a mixture of graphite and a metal catalyst (such as cobalt or nickel) is placed in a horizontal quartz tube enclosed in a furnace and under a flow of inert gas at controlled pressure [1]. Laser pulses enter the tube and strike the target to vaporize graphite and nucleate CNTs through the reactor. The nanotubes are deposited on the cooler walls downstream from the furnace. Despite the high temperature (~1200 °C) of the furnace, this method has still become an important technique due to the high yield of CNTs (~70%).

Growth of CNTs using thermal chemical vapor deposition (CVD) is an alternative to the arc-discharge and laser ablation methods. It is relies on thermal generation of active radicals from the hydrocarbon gas over transition metals to grow CNTs on a substrate, where temperature is normally about 800-1500 °C. Usually, a catalyst is necessary to promote the growth from some form of hydrocarbon feedstock (CH_4, C_2H_2, C_2H_4...) [36]. It was also reported the yield and average diameter of CNTs could be varied by controlling the process parameters [37].