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#### SYNTHESIS AND CHARACTERIZATION OF

#### **3-DIMENSIONAL NETWORKS OF DIFFERENT NANOCARBONS**

A Dissertation in

Materials Science and Engineering

by

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## ABSTRACT

Carbon nanotubes (CNTs) exhibit unique optical, thermal, electrical and mechanical properties. Even though they have been around for more than two decades, there are still many challenges related to the viability of using them for practical applications. One of the main challenges is to engineer their assembly via covalent interconnections to produce macro-scale structures. The first part of this thesis describes recent findings related to a novel and innovative synthesis approach for synthesizing three-dimensional (3-D) CNT networks. In particular, this approach consists of fabricating 3-D covalently interconnected multi-walled carbon nanotubes (MWNTs) with silicon carbide (SiC) nano- and micro-particles. The material was synthesized by a two-step process involving the coating of MWNTs with silicon oxide (SiO<sub>x</sub>) via chemical routes, followed by spark plasma sintering (SPS). SPS enables the use of high temperatures and mechanical pressures, which are required for the carbothermal reduction of silica and the densification of the material into 3-D composite blocks. Covalent interconnections of MWNTs are created by a carbon diffusion process resulting in SiC formation. Interestingly, the 3-D MWNT composite exhibits high thermal conductivity values (16.72 W  $m^{-1}$  K<sup>-</sup> <sup>1</sup>); up to two orders of magnitude higher than comparable nanocarbon-based materials. From an electrical point of view, this material exhibits a semiconducting behavior with an electron hopping mechanism associated to 3-D variable range hopping (VRH). Our findings demonstrate that it is possible to fabricate macroscale MWNT-based composites with enhanced physical properties from covalent interconnections.

It is well known that varying growth conditions and precursor compositions drastically change the structural, physical and electronic properties of CNTs (multiand single-walled). Elemental doping of CNTs was also explored in thesis, in an effort to establish covalent interconnections between CNTs. The structure-property changes induced by doping were also carefully analyzed and studied. The synthesis of single-walled carbon nanotubes (SWNTs) doped with silicon (Si) is reported in Chapter 3 of this thesis. It was found that depending on the Si concentration, the bundle electronic transport of SWNTs could be tuned. The Si doped SWNT (Si-SWNTs) samples were grown using an aerosol assisted chemical vapor deposition (AACVD) approach. A detailed analysis of the Raman spectra and radial breathing modes (RBMs) of Si-SWNTs led to the conclusion that the diameter of SWNTs is reduced after Si doping. Experimental transport measurements revealed drastic changes in the electrical resistivity of Si-SWNTs when compared to pristine SWNTs.

The roles of sulfur and boron during the growth of MWNTs were also explored in this study. These elemental dopants were responsible for significant changes in the nanotube morphology and electronic properties. For example, boron doping induced the formation of "elbow"-like junctions on the MWNTs and entangled MWNTs networks, exhibiting a sponge-like texture. In addition, 3-D branched "tentacle"-like structures with numerous covalent junctions were synthesized by adding very small amounts (<1 at%) of boron and sulfur during the AACVD synthesis of MWNTs. Chapter 4 discusses the structure, properties and potential applications of these tentacle-like carbon morphologies. Finally, Chapter 5 describes future work and perspectives related to the controlled synthesis of covalently interconnected 3-D architectures with carbon nanotubes.

# TABLE OF CONTENTS

L	IST OF	F TA	BLES	ix
L	IST OF	FFIC	JURES	X
A	CKNO	WL	EDGEMENTS xv	<i>iii</i>
1	Intro	oduc	tion	1
	1.1	Carl	bon allotropes and hybrid forms	. 1
	1.1.	1	Hybridized forms of carbon and properties	. 1
	1.1.	2	Novel sp <sup>2</sup> hybridized carbon forms and their dimensionality	. 2
	1.1.	3	Brief history of CNTs	. 5
	1.1.4	4	Properties & applications of CNTs	. 6
	1.1.	5	CNT synthesis and characterization	. 8
	1.1.	6	AACVD	. 9
	1.1.	7	Electron microscopy	11
	1.1.	8	Raman Spectroscopy	14
	1.1.	9	Other characterization techniques	16
	1.2	3-D	Networks of nanocarbons	20
	1.2.	1	Research challenge and motivation	20
	1.2.1 surv	2 /ey	Synthesis and properties of 3D nano-carbon networks: a literature	24
	1.2.	3	Properties of 3D networks	31
	1.2.4	4	Applications of 3D CNT and graphene networks	34
	1.2.:	5	Achievements and Current Challenges	38
	1.3	Goa	ls of this study	39
2	3D (	cova	lently interconnected SiC-CNT nanocomposites	40
	2.1	Intro	oduction to carbon nanotube composites	40
	2.2	Syn	thesis and characterization of SiC-CNT composites	49
	2.2.	1	Fabrication of SiC-CNT nanocomposites	49
	2.2.2		Methods for structural and elemental analyses	51
	2.2.2	3	Methods to Measure Thermal Properties	52
	2.2.4	4	Methods to Measure Electrical Properties	53
	2.3	Res	ults and Discussion	53

2.3.1	Formation Mechanism of SiC-CNT Covalent Interconnections	53
2.3.2	Microstructure and Composition of the SiC-CNT Composite	54
2.3.3	Thermal properties of SiC-CNT Composites Compared to Other	
Carbon 1	Materials	61
2.3.4	Electrical Conductivity of the composite	63
2.4 Cor	clusions and Future work	66
3 Silicon-o	doped carbon nanotubes: controlling tube diameter and electronic	
transport		.68
3.1 SW	NT: growth, structure, packing, and doping	68
3.1.1	SWNT growth techniques: a brief history	69
3.1.2	Literature review of the growth mechanism of SWNT	71
3.1.3	SWNT structure	72
3.1.4	Doped SWNTs: a literature study	74
3.2 Adv	vantages of Si interconnects	77
3.3 Met	hod details: synthesis and characterization of Si-SWNTs	80
3.3.1	CVD synthesis of pristine and Si-SWNT	80
3.3.2	Transmission electron microscopy: technique	81
3.3.3	Raman spectroscopy of Si-SWNTs	81
3.3.4	Electrical measurements	81
3.4 Res	ults and Discussion	82
3.4.1	Structural changes in SWNTs on Si doping	82
3.4.2	Analysis of radial breathing modes	83
3.4.3	Raman peak shifts and intensity changes associated with Si dopin 85	g
3.4.4	Electrical properties of pristine and Si-SWNTs	88
3.5 Cor	clusions	94
4 3D netw carbon nanof	orks of doped multi-walled CNTs and radially grown CNTs on ibers	.95
4.1 Lite their prope	erature review on different methods to grow 3D CNT sponges and erties	95
4.1.1	Chemical routes for synthesizing 3D CNT networks	97
4.1.2	CVD growth of 3D CNT networks 1	01

	4.2	CV 104	D Synthesis and structure of B-doped and pristine MWNT sponges					
4.2.1		.1	CVD synthesis of pristine and B-doped (CB <sub>x</sub> MWNT) sponges 10	)4				
	4.2.2		Structural characterization (SEM, TEM, Raman, TGA) 10	)6				
4.2.3		.3	Testing the physical properties: density, surface area, porosity 114					
	4.2.4		Mechanical properties of MWNT sponges 11					
	4.3	App	plications of 3D MWNT based sponges11	18				
	4.4	Car	bon Nanotentacles	20				
	4.4	.1	Experimental Methods	21				
	4.5	Nar	notentacle growth mechanism	30				
	4.6	Cor	nclusions	31				
5	Co	nclus	ions13	33				
	5.1	Sun	nmary of contributions	33				
	5.2	Fut	ure work	37				
	5.3	List	t of publications	38				
Rł	EFER	ENC	ES14	42				
AI	PPEN	DIX		89				

# LIST OF TABLES

Table 2.1: Summary of electrical and mechanical properties observed in different CNT-inorganic
matrix composites
<b>Table 2.2.</b> Density ( $\rho$ ), thermal diffusivity ( $\alpha$ ) and thermal conductivity (k) of the SPSed SiC-CNT
material. A comparison with other graphitic materials measured at 27 $^{\circ}\mathrm{C}$ in the through-thickness
direction has also been included
<b>Table 2.3:</b> Resistivity ( $\Omega$ cm, ( $\hat{a}$ 300K) of the SPSed SiC-CNT material in comparison with other
SiC and CNT based materials
<b>Table 4.1</b> : Examples of porous materials used in different commercial applications
<b>Table 4.2:</b> Surface area values of different CNT based aerogels synthesized using different chemical
processes
Table 4.3: Liquid Nitrogen porosimetry results for MWNT and CB <sub>x</sub> MWNT sponges showing
values for BET surface area, pore volume and average pore size for each material115

# **LIST OF FIGURES**

<b>Figure 1.1:</b> (a) sp <sup>3</sup> hybridization of carbon and crystal structure of diamond showing tetrahedral
bonds of C atoms with 4 other C atoms. ( <i>source: https://en.wikipedia.org/wiki/Diamond_cubic</i> ) (b)
sp <sup>2</sup> hybridizations and graphite crystal structure showing hexagonal honey-comb structure of sp <sup>2</sup>
carbon atoms. (c) Phase diagram of carbon2
Figure 1.2: Different forms of sp <sup>2</sup> hybridized carbon: 0-D fullerene, 1-D carbon nanotube, 2-D
graphene and 3-D graphite
<b>Figure 1.3</b> : (a) A triply periodic minimal surface decorated with sp <sup>2</sup> carbon atoms: schwarzite (b)
3-D interconnected schwarzite structure (c)-(d) 3-D networks of CNTs interconnected by schwarzite
linkers
Figure 1.4: Computer models of (a) haeckelite tube, (b) carbon nanocone, (c) torus decorated with
graphene, and (d) helicoidal graphene5
Figure 1.5: (a) Hollow graphitic carbon fibers that are 50 nanometers in diameter discovered in
1952. (b) Electron Microscopy image showing a rolled sheet of graphene examined for its frictional
properties. (c) Chemical vapor deposition (CVD) growth of nanometer-scale carbon fibers reported
in 1976. (d) Microtubules of graphitic carbon discovered in the soot of arc discharge in 19916
Figure 1.6: CNT publication & patent statistics from 2004-2011, and examples of commercial
products that have used CNTs for their fabrication
Figure 1.7: (a) A photograph of the AACVD setup used for synthesizing CNTs in this study. (b) A
schematic illustration of the physical processes involved in CVD, starting with the decomposition
of gaseous precursors, followed by their adsorption onto the substrate, and reactions that lead to
nucleation of the products10
<b>Figure 1.8</b> : Electron beam interacting with a TEM specimen and generating different signals12
Figure 1.9: EEL spectra of highly-graphitized carbon, MWNT, manganese oxide/graphene oxide

Figure 1.10: Scattering events classified into first order and second order processes......15

(MnO/GO) composite and amorphous carbon, showing the characteristic  $\pi^*$  and  $\sigma^*$  peaks......14

**Figure 1.11**: (a) Raman features in different graphitic materials: (from top to bottom) graphene, highly oriented pyrolytic graphite (HOPG), SWNTs, damaged graphene, single walled nano-horn

(SWNH), and amorphous carbon. (b) Schematic pictures showing atomic vibrations of RBM, (c) G-
band and (d) D-band modes in SWNTs16

Figure 1.12: A decor	voluted XPS	spectrum of	carbon	overcoats	showing p	eaks co	orrespond	ing to
the $sp^2$ carbon, $sp^3$ car	rbon, C–O and	C = O bond	ling					17

**Figure 1.14:** (a) Atomically resolved STM images of individual SWNTs clearly indicating the tube chirality. (b) dI/dV data and the calculated density of states (DOS) for a (16,0) tube (right inset)...19

**Figure 2.5** (a) Raman spectra of spark plasma sintered SiC-CNT composite showing an average Raman spectrum and individual SiC and CNT spectra from regions 1&2 in Figure 2.5(b); (b) Raman

**Figure 4.1**:(a) Microstructure of a porous, chemically cross-linked 3D CNT solid and (b) schematic illustration of the Suzuki coupling reaction that enables the cross-linking of MWNTs. (c) Low magnification SEM image showing bundles of MWNTs within the walls of the porous structure. (d) MWNT aerogel fabricated via gelation of a MWNT dispersion using PTSPMA polymer. (e) A photograph of the aerogel and (f) SEM image showing a honeycomb-type porous structure with MWNTs decorating the pore walls. (g) A schematic of the gelation process is shown. (h)-(k) 3D freestanding foams fabricated by electrophoretic deposition of SWNTs on a nickel foam followed by etching away the nickel foam template. (l)-(m) Scanning electron micrographs of the pore structure of the 3D SWNT foam after etching away the template. (n) A comparison of the TGA

**Figure 4.3:** SEM images of (a)-(b)  $CB_xMWNT$  sponges and (c)-(d) pristine MWNT sponges, respectively. Arrows in (b) point at elbows in the  $CB_xMWNT$  sponge structure. From the SEM images it is evident that the pristine MWNT sponges comprise of mostly straight tubes whereas  $CB_xMWNT$  sponges have many elbow-like structures. (e) A photograph of  $CB_xMWNT$  sponge. The inset shows a water droplet on the sponge, demonstrating super hydrophobicity..................107

**Figure 4.4:** TEM images of (a)-(b)  $CB_xMWNT$  sponges and (c)-(d) MWNT sponges, respectively. The high resolution TEM image of a  $CB_xMWNT$  sponge in (b) shows multiple elbows on the same tube. Long metal particles observed within the hollow core of MWNT sponges. Average tube diameters are ~70nm and ~20 nm in  $CB_xMWNT$  and MWNT sponges, respectively......109

Figure 4.6: Raman spectra of (a) CBxMWNT sponges (b) pristine MWNT sponges.....111

Figure 4.12: CO<sub>2</sub> adsorption and desorption curves of CB<sub>x</sub>MWNT and MWNT sponges......119

Figure 4.13: CH<sub>4</sub> adsorption and desorption curves of CB<sub>X</sub>MWNT and MWNT sponge......120

**Figure 4.18**: (a) HAADF image of a nanotentacle subjected to EDS analysis. (b) Carbon, (c) iron and (d) sulfur EDS maps from the region shown in (a).....128

**Figure 4.19**: (a) HAADF image of a nanotentacle area mapped with EDS in (b). (b) The distribution of sulfur on the central CNT stem showing strong signals at the "bumps". (c)-(e) TEM, HAADF and EDS area map respectively of a magnified region of the nanotenacles. (f)-(h) Similar

observations were recorded another region of the sample many positive curvatures. The sulfur map in (h) corresponds to the area shown in the TEM image in (f) and HAADF image in (g).....129

Figure 5.1: Cover of Adv	. Funct. Mater. 2	25, (2015)	134
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## **1** Introduction

#### 1.1 Carbon allotropes and hybrid forms

#### 1.1.1 Hybridized forms of carbon and properties

Carbon is one of the most abundant and life-supporting elements found on earth. The importance given to carbon material research stems from this fact. The unique ways in which carbon can chemically bond with itself as well as other elements have enabled the formation of thousands of carbon based natural and synthetic materials. The existence of different carbon isotopes also makes it a suitable candidate for many avenues of research.<sup>1–3</sup> For example, the C<sup>14</sup> isotope has been very useful for carbon dating and has thus given important insights into evolution of nature and mankind.<sup>4</sup> The carbon atom has an electronic configuration that allows mixing of its electronic orbitals to produce hybridized orbitals. This gives rise to different ways in which carbon atoms can be bridged with each other and hence the existence of different allotropes such as graphite and diamond are possible. Each carbon atom can chemically bond with four other carbon atoms tetrahedrally through sp<sup>3</sup> hybridized orbitals to form a diamond like structure (**Fig. 1.1a**). Alternatively,  $sp^2$  hybridized orbitals in carbon atoms can result in strong in-plane covalent bonds, thus forming a honey-comb like structure, as shown in Fig. 1.1b. The naturally occurring form of  $sp^2$  carbon in nature is graphite where each layer is comprised of the sp<sup>2</sup> hybridized carbon atoms arranged in a hexagonal network as shown in Fig. 1.1b. Many differences in the properties between diamond and graphite exist. While graphite is an electrical conductor and black in

color, diamond is an electrical insulator and transparent. Strong in-plane covalent bonds and weak out-of-plane van der Waals forces result in the easy shearing of graphitic planes, thus making graphite soft and suitable as lubricants. Diamond, on the other hand, is one of the hardest substances discovered to date. Of the phases of carbon, graphite is known to be the most thermodynamically stable.<sup>5</sup> This is illustrated in the phase diagram of carbon (**Fig. 1.1c**).



**Figure 1.1:** (a) sp<sup>3</sup> hybridization of carbon and crystal structure of diamond showing tetrahedral bonds of C atoms with 4 other C atoms. (*source: https://en.wikipedia.org/wiki/Diamond\_cubic*) (b) sp<sup>2</sup> hybridizations and graphite crystal structure showing hexagonal honey-comb structure of sp<sup>2</sup> carbon atoms.<sup>6</sup> (c) Phase diagram of carbon.<sup>5</sup>

#### **1.1.2** Novel sp<sup>2</sup> hybridized carbon forms and their dimensionality

In the past few decades, new allotropes of carbon were discovered, such as fullerenes and carbon nanotubes (CNTs). The 0-D form of  $sp^2$  hybridized carbon known as fullerenes was discovered in 1985 by Kroto, Smalley and Curl *et al.*<sup>7</sup>

Although many types of fullerenes exist, the most stable one  $-C_{60}$  or buckminsterfullerene– is composed of 60 C atoms arranged in the form of a sphere, as shown in **Fig. 1.2**.



**Figure 1.2:** Different forms of sp<sup>2</sup> hybridized carbon: 0-D fullerene, 1-D carbon nanotube, 2-D graphene and 3-D graphite.

This spherical arrangement of a  $C_{60}$  molecule is made possible by joining twenty hexagons and twelve pentagons of sp<sup>2</sup> bonded carbon. However, a CNT – which is the 1-D allotrope of sp<sup>2</sup> carbon – is best imagined as a seamless cylinder formed by rolling a graphite layer. A graphite layer that is one atom thick (graphene) represents the 2-D allotrope and the stacked graphite is considered as the 3-D allotrope for sp<sup>2</sup> hybridized carbon.



**Figure 1.3**: (a) A triply periodic minimal surface decorated with sp<sup>2</sup> carbon atoms: Schwarzite (b) 3-D interconnected Schwarzite structure (c)-(d) 3-D networks of CNTs interconnected by Schwarzite linkers.<sup>8</sup>

Other 3-D forms that have been theoretically predicted are "Schwarzites" – which are triply periodic minimal surfaces decorated with  $sp^2$  carbon atoms with 6 (or more) member rings (**Fig. 1.3a**).<sup>9,10</sup> A primitive cell of the simplest Schwarzite can be visualized as a 3-D assembly consisting of 12 octagonal rings and 24 heptagonal rings of  $sp^2$  carbon that can serve as a junction between 6 single walled carbon nanotubes (SWNTs) (**Fig. 1.3c-d**). The non-hexagonal carbon rings add negative Gaussian curvatures to these structures. Haeckelites for example, constitute another family of  $sp^2$  hybridized carbon allotropes that have been theoretically predicted and consist of a planar graphene-like sheet with 5-, 6-, and 7-membered carbon rings.<sup>11</sup> These structures are energetically more stable than C<sub>60</sub> according to

theoretical calculations. Haeckelites can also be rolled to form seamless cylinders similar to rolling graphene sheets (**Fig. 1.4a**). Some of the other theoretically predicted carbon allotropes include nanocones (**Fig. 1.4b**), toroids (**Fig. 1.4c**) and helicoidal graphenes (**Fig. 1.4d**).<sup>10</sup>



**Figure 1.4:** Computer models of (a) haeckelite tube, (b) carbon nanocone, (c) toroids decorated with graphene, and (d) helicoidal graphene.<sup>10</sup>

#### 1.1.3 Brief history of CNTs

Following the accidental discovery of mechanically strong and flexible graphite whiskers in the 1950's, there was a lot of interest in studying tubular graphitic forms (**Fig. 1.5a**).<sup>12</sup> The carbon researchers at that time were not only intrigued by the mechanical properties of these materials, but also about their structural properties.<sup>13</sup> Some of the studies in the 1960's also focused on understanding the frictional properties of rolled-up graphene (**Fig. 1.5b**).<sup>14</sup> The growth of carbon fibers became a popular field in the late 1970's when various methods to grow filaments of graphitic carbon were developed.<sup>15,16</sup> Among these methods, a notable work was reported by Endo and coworkers in 1976 regarding hydrocarbon pyrolysis to produce filamentous carbon (**Fig. 1.5c**).<sup>17</sup> In 1991, Iijima discussed the observation

of helical microtubules of graphite, now popularly known as CNTs, using a transmission electron microscope (TEM) (**Fig. 1.5d**).<sup>18</sup>



**Figure 1.5:** (a) Hollow graphitic carbon fibers that are 50 nanometers in diameter discovered in 1952.<sup>13</sup> (b) Electron Microscopy image showing a rolled sheet of graphene examined for its frictional properties.<sup>14</sup> (c) Chemical vapor deposition (CVD) growth of nanometer-scale carbon fibers reported in 1976.<sup>17</sup> (d) Microtubules of graphitic carbon discovered in the soot of arc discharge in 1991.<sup>18</sup>

#### 1.1.4 Properties & applications of CNTs

CNTs are one-dimensional and exhibit large aspect ratios, i.e., their diameters are usually in the range of a few nanometers while their lengths can reach up to few centimeters.<sup>19,20</sup> This gives rise to extremely high surface areas that in theory can be greater than 1300 m<sup>2</sup>g<sup>-1</sup>.<sup>21</sup> The electronic properties of CNTs will be discussed in detail in **Chapter 3**. Briefly, their electronic properties are structure dependent for single-walled carbon tubes (SWNTs). Transport measurements have shown unusually high current densities (~ 10<sup>9</sup> A cm<sup>-2</sup>) for metallic SWNTs, surpassing copper nanowires.<sup>22</sup> CNTs are also stiff, strong and mechanically robust nanomaterials whose tensile strength (Young's Modulus) can reach values up to 1 TPa.<sup>23</sup> High thermal conductivity is another important property of CNTs where theoretical values surpass 6000 Wm<sup>-1</sup>K<sup>-1</sup> for SWNTs.<sup>24</sup> This is attributed to the large phonon mean free path in CNTs. In addition, their thermal stability at temperatures > 2000°C makes them suitable candidates for fabricating nanoelectronic devices, in which heat dissipation and thermal stability are needed.<sup>25</sup>

All of these remarkable properties have made CNT materials of significant research interest, which has resulted in an exponential growth of publications and patents related over the past decade. It is therefore not surprising that CNTs have found many uses in a variety of applications such as light-weight composites, coatings, adsorbents, nano- and micro-electronics, energy storage etc. (**Fig. 1.6**).<sup>26</sup>



**Figure 1.6:** CNT publication & patent statistics from 2004-2011, and examples of commercial products that have used CNTs for their fabrication.<sup>26</sup>

#### 1.1.5 CNT synthesis and characterization

Currently, various techniques are available for growing different types of CNTs including arc-discharge, hydrocarbon pyrolysis, laser vaporization of graphite targets, electrolysis of carbon electrodes in molten ionic salts, etc.<sup>27–30</sup> Hydrocarbon pyrolysis using transition metal catalysts has been a widely used technique for growing large quantities of crystalline multi-walled carbon nanotubes (MWNTs) and SWNTs.<sup>31–34</sup> Among the most popular catalysts are transition metals such as Fe, Co, Pd, Ni and Pt. The pyrolysis is usually carried out at high temperatures in an inert gas atmosphere and the CNTs are deposited on a substrate which could be the quartz tube reactor itself or a substrate that is pre-deposited with catalysts.<sup>33</sup> In

this study, the CNTs are produced by hydrocarbon pyrolysis using an aerosol assisted chemical vapor deposition (AACVD) technique. The following subsections describe the AACVD technique and also tools to characterize the CNTs synthesized using this technique.

#### **1.1.6 AACVD**

CVD is the most popular technique currently used for synthesizing CNTs due to its low-cost, easy scalability and high-yield.<sup>35,36</sup> Other advantages of CVD over conventional arc-discharge and laser ablation techniques are the possibilities of precisely controlling the growth parameters, carrying out the growth at ambient pressure conditions, and producing different forms CNTs, such as powders, solids, films and even on patterned substrates.<sup>35,36</sup>

The AACVD process differs from the conventional CVD process by the method used to deliver the carbon precursors to the reactor.<sup>36</sup> A photograph of the AACVD setup used in our studies is shown in **Fig. 1.7a**. The precursor solution containing a carbon source and catalyst is converted into a mist (solution droplets) by an ultrasonic nebulizer. The mist is transported into the quartz tube reactor by an inert carrier gas and vaporized as soon as it enters the hot zone of the furnace. The subsequent physical processes can take place as gas phase or substrate-driven reactions when heat is provided (**Fig. 1.7c**).<sup>36</sup>



**Figure 1.7**: (a) A photograph of the AACVD setup used for synthesizing CNTs in this study. (b) A schematic illustration of the physical processes involved in CVD, starting with the decomposition of gaseous precursors, followed by their adsorption onto the substrate, and reactions that lead to nucleation of the products.<sup>36</sup>

The physical processes involved in CVD are complex and governed by the interplay between thermodynamics, kinetics, and chemistry of the reactants and growth parameters. Due to its non-equilibrium nature, there are many constraints when it comes to theoretically predicting the outcomes of the reactions.<sup>37</sup> The important parameters that control the growth include: solvent (carbon precursor), catalyst, substrate, temperature, flow-rate (of the precursors into the hot-zone) and time of

the reaction.<sup>33,35,36</sup> The mechanisms proposed for the growth of CNTs during CVD will be discussed in detail in **Chapter 3**.

#### **1.1.7** Electron microscopy

Electron microscopy is by far the most useful technique for the structural and elemental analysis of nanomaterials. A scanning electron microscope (SEM) works on the principle of raster scanning a sample with a beam of electrons and subsequent image formation using secondary electrons generated from the surface of the sample. The secondary electrons and other signals emitted from the sample (such as backscattered electrons, auger electrons and X-rays) are useful for analyzing the morphology, structure, and elemental composition of nanomaterials. However, the resolution of an SEM is limited by the electron spot size and interaction volume with the sample which are both larger than atomic scale, thus making atomic resolution nearly impossible. TEM was first developed with the idea of overcoming the image resolution of a light microscope by making use of wavelike characteristic of electrons (which have shorter wavelengths - on the order of a few picometers - as compared to light). This helps in imaging specimens at the nano-scale and also at sub-angstrom scale with high resolution TEMs (HRTEMs). In a TEM, a beam of electrons is allowed to pass through the specimen that needs to be analyzed. As it passes through, the electrons interact with the atoms in the sample to generate a variety of signals that can be analyzed to obtain different information (**Fig.1.8**).<sup>38</sup> After the interaction, the transmitted electron beam forms an image which is viewed using a screen or captured by a CCD camera.



Figure 1.8: Electron beam interacting with a TEM specimen and generating different signals.<sup>38</sup>

TEM can be also operated in a diffraction mode, where the electrons satisfying Bragg's diffraction condition (after interacting with the specimen) interfere constructively to form diffraction patterns. These give valuable information about the degree of crystallinity of the sample, orientation of crystal planes, inter planar distances, etc. Currently, TEMs equipped with instrumentation for compositional analysis such as electron energy loss spectrometer (EELS) and also energy dispersive X-ray spectrometer (EDS) are also commercially available, thus making it possible to use the TEM for a variety of purposes apart from basic structural imaging.

EDS uses the X-rays generated when an electron beam strikes a specimen in a TEM to identify individual elements present in it. The fundamental principle behind detecting individual elements from their X-ray peaks is that each element has a unique atomic structure that gives rise to a unique set of peaks in its X-ray spectrum.<sup>38</sup> In other words, an atom that has been ionized by the electron beam with return to the ground state, emitting X-rays with very specific energies depending on the transitions that occurred. These X-rays are collected by a detector (usually semiconducting Si or Ge) which converts the incoming X-rays to voltage pulses. This is then displayed as counts per energy of X-rays detected. The detector is positioned in a very confined region between the objective pole pieces, above the sample, and is usually sensitive towards detection of heavier elements (above Li) in the periodic table.

The EELS technique is based on the principle of recording energy losses encountered by electrons that interact with a TEM specimen by inelastic scattering. The energy loss could be due to the electrons interacting with phonons in the specimen, or conduction and valence electrons in the specimen, or core shell electrons (by means of ionizations) etc. These energy losses of the emerging electron beam are recorded in the form of a spectrum that can give a lot of information about the specimen chemistry, electronic structure and bonding environments, band-gap, free electron density, etc.<sup>38</sup> The electrons emerging from the sample are made to pass through a magnetic prism which deflects the electrons according to the energy it possesses. The electrons that have lost more energy are deflected more than the ones that have lost zero energy. Thus, it is possible to create a spectrum of electrons that will give direct information about the electron intensity versus the energy loss.<sup>38</sup> Figure 1.9 shows sample EEL spectra of different forms of carbon. The C-K edge (~284 eV) in graphitic carbons show well-defined  $\pi^*$  and  $\sigma^*$  peaks that correspond to the ionization of electrons from the inner K-shell of carbon.



**Figure 1.9**: EEL spectra of highly-graphitized carbon, MWNT, manganese oxide/graphene oxide (MnO/GO) composite and amorphous carbon, showing the characteristic  $\pi^*$  and  $\sigma^*$  peaks.<sup>39</sup>

#### 1.1.8 Raman Spectroscopy

The basic principle of Raman spectroscopy is based on the inelastic (Raman) scattering of light. This occurs via (1) excitation of an electron from the valence to conduction band by absorption of a photon, (2) emission (Stokes) or absorption (anti-Stokes) of phonons via electron scattering and (3) relaxation of the electron from the conduction to valence band by the emission of a photon.<sup>40,41</sup> Therefore the emerging photon has a different energy compared to the incident photon, and this energy difference is monitored in a Raman spectrum to gain information about phonon frequencies in the material. Depending on the number of scattering events that occur, the order of the scattering process is defined as first order, second order, and so on (**Fig. 1.10**).



Figure 1.10: Scattering events classified into first order and second order processes.<sup>41</sup>

The simplest process is a one-phonon, first order scattering. The Raman spectrum of sp<sup>2</sup> hybridized carbon has a distinct G-band (close to 1580 cm<sup>-1</sup>) arising from the in plane C-C stretching, which is a first order mode. Another first order mode is radial breathing mode (RBM), which arises from the radial out-of-plane bond stretching and is characteristic of single walled carbon nanotubes. This peak gives very important information about the diameter and curvature of carbon nanotubes. A second-order scattering process gives rise to the disorder-induced D-band observed around 1350 cm<sup>-1</sup> – and is used for quantifying defects in the sp<sup>2</sup> network. Another feature characteristic of graphitic sp<sup>2</sup> materials is the 2D band (interchangeably referred to as G<sup>2</sup>) commonly observed between 2500 - 2800 cm<sup>-1</sup>. This feature arises from a second-order two-phonon Raman scattering process.<sup>40,41</sup> Examples of Raman spectra showing the characteristic features of different graphitic materials are shown in **Fig. 1.11**.



**Figure 1.11**: (a) Raman features in different graphitic materials: (from top to bottom) graphene, highly oriented pyrolytic graphite (HOPG), SWNTs, damaged graphene, single walled nano-horn (SWNH), and amorphous carbon.<sup>40</sup> (b) Schematic pictures showing atomic vibrations of RBM, (c) G-band and (d) D-band modes in SWNTs.

#### **1.1.9** Other characterization techniques

X-ray diffraction (XRD) has been a versatile tool in analyzing the crystallinity of materials, as well as phase transformations and compositional analysis. This tool is based on Bragg's law which states that the X-rays incident on a material are diffracted in specific directions based on the alignment of the crystal planes and the inter-planar spacing in the material.<sup>42</sup> The scattering angles and intensities of the diffracted X-rays are recorded to probe the crystal orientations and disorders present in the material.<sup>43</sup>

X-Ray photo-electron spectroscopy (XPS) is a surface sensitive quantitative spectroscopic technique useful for determining the elemental composition at parts per thousand range in nanomaterials.<sup>44</sup> The technique is performed by irradiating a material with X-ray photons and detecting the electrons emitted from the material and their kinetic energies. Each electron in an element has a characteristic binding energy depending on its bonding configuration. Therefore, XPS can give insights on the chemical bonding configurations and atomic compositions in the surface layers of the material.<sup>45</sup> **Figure 1.12** shows an XPS spectrum of a carbon overcoat (carbon based protective material used to layer magnetic hard disks) sample showing different bonding configurations of carbon in the form of sp<sup>2</sup>, sp<sup>3</sup>, C–O and C = O.<sup>46</sup>



**Figure 1.12:** A deconvoluted XPS spectrum of carbon overcoats showing peaks corresponding to the sp<sup>2</sup> carbon, sp<sup>3</sup> carbon, C–O and C = O bonding.<sup>46</sup>

Thermogravimetry (TGA) is a thermal analysis technique that measures the weight loss in a sample while heating it in air or in an inert atmosphere. As each
component in the material reaches its decomposition temperature, a corresponding weight loss is observed in the TGA spectrum, indicating the presence and amount of that component in the material (**Fig 1.13**.). This is useful in quantifying the weight% of different phases and impurities present in the material.<sup>47,48</sup>



**Figure 1.13:** TGA curves of CVD grown MWNTs at different methane flow rates (10 - 120 sccm). Weight loss and corresponding derivative curves are shown for the MWNTs as they were heated from 100°C to 800°C in air at a heating rate of 20°C/min.<sup>49</sup>

Scanning tunneling microscopy (STM) is a popular technique for atomicresolution imaging and surface manipulation of materials at the atomic scale.<sup>50</sup> In this technique, a conducting tip is brought very close to the surface of a sample, and on applying a bias between the tip and the sample, a tunneling of electrons between them is observed. The tunneling current is highly dependent on the bias voltage, position of the tip and the local density of states of the electrons in the sample.<sup>50</sup> STM has been a proven technique for studying correlations between the electronic properties of carbon nanotubes and their surface chemistries, especially the effects of doping and surface functionalization on electronic structure of the tubes (**Fig.1.14a**).<sup>51–53</sup> Scanning tunneling spectroscopy (STS) is a variant of STM that is useful for measuring the density of electrons of graphitic nanomaterials as a function of their energy. In STS, the STM tip is used to pass current signals through a sample, and the current (*I*) is recorded as a function of the applied bias voltage (*V*). The differential conductance (dI/dV) is proportional to the density of states of the sample (**Fig.1.14b**).<sup>53</sup>



**Figure 1.14:** (a) Atomically resolved STM images of individual SWNTs clearly indicating the tube chirality. (b) dI/dV data and the calculated density of states (DOS) for a (16,0) tube (right inset).<sup>53</sup>

Atomic force microscope (AFM) is another variant of the above technique and is a surface analysis tool, which operates by raster scanning a cantilever probe on the

surface of a material and measuring various forces on its surface as functions of the deflection of the cantilever.<sup>54</sup> AFM has been useful for studying the Van der Waals interactions, diameter profiles, mechanical and tribological behaviors of carbon nanotubes.<sup>55–57</sup>

## **1.2 3-D Networks of nanocarbons**

### 1.2.1 Research challenge and motivation

A carbon-carbon (C-C)  $sp^2$  bond is one of the strongest in nature, which is one of the reasons why nanostructures made from  $sp^2$  carbon bonds generally exhibit excellent mechanical properties. For example, CNTs are very stiff, strong and mechanically robust nanomaterials whose tensile strength (Young's Modulus) can reach values of up to 1 TPa.<sup>23</sup> Theoretical predictions indicate that if these nanostructures are used as building blocks for macro-structures, it is possible for the resulting material to achieve unusual mechanical and electronic properties.<sup>58</sup> Apart from these properties, very high surface areas (on the order of  $\sim 2,000 \text{ m}^2/\text{gm}$ ) can be obtained in these materials. However, in order to fabricate these structures, assembling nanostructures into ordered networks may be necessary, which poses a great challenge. Sp<sup>2</sup> hybridized carbon atoms can be arranged in a 2D or 3D network in a variety of ways. Various models of these networks have been proposed and their electronic transport properties have been studied.<sup>59</sup> Some models are based on ordered networks of CNTs while others are networks of interconnected graphene sheets, interconnected fullerenes, or graphene-CNT hybrids and fullerene-CNT hybrid networks. Self-assembly, as well as the incorporation of junctions on CNTs and graphene, are potential pathways to realize these theoretical 3D structures.

Theoretical models of 3D CNT and graphene structures were studied by Romo-Herrera *et al.*<sup>58,59</sup> These 3D structures were constructed by adding non-hexagonal carbon rings to the corresponding 1D (CNT) or 2D (graphene) building blocks.<sup>58</sup> "Multi-terminal" nodes comprised of covalently interconnected 1D CNTs in different configurations were used as the building blocks for creating hierarchical structures by translation. The electrical and mechanical properties of these 3D networks were determined. The conductivity of electrons as well as the density of states (DOS) spectra for these multi-terminal nodes in "super-square" (SS), "super-graphene" (SG), "super-cubic" (SC), and "super-diamond" (SD) types of units are shown in **Fig. 1.15a-d** respectively.

A remarkable feature of these materials is that surface areas, in the range of  $2,500 \text{ m}^2/\text{gm}$  and higher can be achieved with densities as low as  $0.009\text{g/cm}^3$ . In addition, the mechanical properties of these structures were found to depend on the strength of the nodes and not on the chirality of the CNTs. Overall, the mechanical strength of these materials for axial compression was found to surpass that of individual CNTs. The SD structure was able to withstand a compressive strain up to 50% in the [001] direction compared to 7% for CNTs. These enhancements in the mechanical strength, arising from the presence of strong covalent interconnections between the individual CNTs, are thus potentially useful for many applications that require a combination of light weight and robust mechanical support, such as shock absorbers.



**Figure 1.15:** (a-d) Super square, super graphene, super cubic and super diamond blocks made of  $sp^2$  carbon atoms and the calculated values of electrical conductivities as well as the density of states along different conduction pathways in the 3D network.<sup>58</sup> (e) Images of calculated 3D surfaces of  $sp^2$  carbon networks that resemble graphene foams: P8-1 and (f) I-WP8-1 structures. (g) Calculated values of Poisson's ratio for various schwarzite structures: D-Rot family shows a negative Poisson's ratio when rippled. <sup>60</sup>

The recent success in fabricating 3D monolithic graphene and CNT structures has prompted researchers to investigate the theoretical, mechanical and electronic properties achievable by these materials in more detail. In this regard, Terrones *et al.* performed DFT calculations on different giant schwarzite structures belonging to the primitive (P), diamond (D), gyroid (G), and I-graph – wrapped

package graph (I-WP) families that have similar structures as the 3D graphene foams.<sup>60</sup> Very interesting properties were observed in these structures, including a negative Poisson's ratio in rippled D-schwarzites, a remarkable resemblance of the P-type schwarzite to 3D graphene foams experimentally synthesized, and a dependence of the Young's modulus on the size of the schwarzites. Figure 1.11e-f show the structures of two triply-periodic minimal surfaces (TPMS) decorated with pentagons, hexagons and octagons belonging to the P8-1 and I-WP8-1 varieties calculated using the surface evolver code. The calculated values of Poisson's ratio for D, P, G and I-WP schwarzite families are shown in Fig. 1.11g. While the Pfamily shows the highest average values for Poisson's ratios (ranging from 0.4 to 0.18), the D-Rot type, which is a rotated configuration of the D-type, shows a negative average Poisson's ratio (-0.063) when the lattice size is increased and many ripples are created on its surface. These values are still higher than that observed in the 3D graphene foams experimentally obtained by Wu et al. because of the presence of topological defects in the latter material, which are not accounted for in the former case (**Fig. 1.16**).<sup>61</sup>



**Figure 1.16**: (a)-(b) Schematic illustration of the solvothermal conversion of ethanol-dispersed graphene oxide (GO) platelets into a 3D graphene sponge. (c) SEM image of the 3D graphene sponge showing an interconnected porous structure. (d) Photographs of graphene sponges. (e) The Poisson's ratio (in air) of graphene sponges as a function of applied strain in the axial direction. (c) Poisson's ratio (in air and in acetone) as a function of number of compression and release cycles along the axial direction.<sup>61</sup>

# **1.2.2** Synthesis and properties of 3D nano-carbon networks: a literature survey.

Three-dimensional networks of CNTs, graphene and their derivatives can be created using different approaches that are broadly classified under two categories: namely *growth* and *post-growth* processing. Growth based approaches typically involve the synthesis of 3D networks in-situ during a chemical process such as CVD and may involve the use of templates. Post growth processing involves solution based processing or the use of high energy processes such as electron beam welding, annealing, high temperature sintering, etc. of pre-synthesized CNTs to form 3D networks.<sup>61–65</sup> The following sections describe different approaches applied to synthesize CNTs, graphene and their hybrid 3D network synthesis.

### 1.2.2.1 Template-based approaches

Using metal based templates has recently emerged as an efficient route to create CNT and graphene networks.<sup>66–69</sup> Most often, these synthesis procedures involve the pyrolysis of carbon over porous transition metal templates. This novel class of 3D macro-porous materials is promising for adsorption, sensing, biological scaffolds, catalytic supports, flexible electronics, and energy applications.<sup>68,70–75</sup> One of the initial works directed towards CVD synthesis of 3D free-standing graphene foam-like structure was by Chen's group in 2010.<sup>66</sup> Chen et al. demonstrated that porous Ni scaffolds could be used to grow high porosity (~99.7%), light-weight, (~5 mg/cm<sup>3</sup>) 3D graphene foams (GF).<sup>66</sup> In their method, methane (CH<sub>4</sub>) was pyrolized at 1000°C over the Ni scaffolds, followed by coating them in poly(methyl-methacrylate) (PMMA) and etching away the Ni frame using hot hydrochloric acid (HCl). The PMMA coating of the graphene before etching the metal helped to maintain rigidity of the GF and prevented it from collapsing during the metal etching process. Afterwards, the PMMA was gradually removed using hot acetone. The resultant 3D interconnected graphene foams exhibited very high electrical conductivities (~10 Scm<sup>-1</sup>) on loading 0.5wt% GF with polydimethylsiloxane (PDMS). In addition, these PDMS-GF composites also displayed excellent electromechanical properties. Their resistivity only increased slightly (by ~2.7%), even after mechanically straining them to a bend radius of up to 2.5mm for approximately 10,000 cycles. Pan and coworkers recently used diatoms – unicellular algae – which possess silica cell walls (called frustules), as a removable template during a methane-based CVD growth of a 3D graphene structure (**Fig. 1.17a-d**).<sup>76</sup>



**Figure 1.17**:(a) Aulacoseira diatom frustule template used for CVD growth of 3D graphene structures. (b) Schematic of the CVD process for growing graphene on the frustule template followed by etching of the template that yields a 3D graphene replica of the frustule. (c)-(d) TEM images of the 3D graphene structures showing an interconnected pore structure.<sup>76</sup>

The transparent 3D graphene network obtained on removing the frustule replicated the internal morphology of the frustule and was extensively studied for gaining insights into its complex structure and development.<sup>76</sup> Sacrificial templates have also been employed in solution based processing approaches for obtaining 3D networks of nanocarbons. For example, bio-inspired hierarchical structures of graphene oxide (GO) have been fabricated by Sun *et al.* by using E. Coli bacterial cells as templates.<sup>77</sup>

## 1.2.2.2 High energy welding techniques

The idea of covalently interconnecting CNTs using high-energy techniques that help in breaking or re-arranging C-C bonds is a well-known and developed technique.<sup>63,64</sup> One of the early strategies used to explore this was using a high energy electron beam to weld CNTs (**Fig. 1.18a-f**).<sup>64,78</sup> Recently, spark plasma sintering (SPS) has emerged as a potential tool for creating large numbers of graphene-CNT, CNT-CNT and metal-CNT contacts and fabricating 3D bulk structures.<sup>62,79–81</sup> **Figures 1.18g-h** show sintered blocks of de-fluorinated MWNTs obtained using SPS. Inter-tube bridging occurred in these MWNT blocks during the sintering process as fluorinated MWNTs were subjected to high temperature (1273 K) and pressure (80 MPa) conditions during SPS.<sup>81</sup> This is attributed to the formation of many sp<sup>3</sup> hybridized carbon atoms that can create cross-links amongst the tubes. **Figures 1.18i-m** show SEM and TEM images of the fractured surfaces of the MWNT blocks.



**Figure 1.18:**(a)-(d) Tight binding molecular dynamics (TBMD) simulations showing electron beam welding of two crossing SWNTs. (e)-(f) Schematics showing X-junctions formed by electron beam irradiation and the presence of defects (heptagonal rings) at the point of crossing of the tubes.<sup>64</sup> (g)-(h) Sintered blocks of de-fluorinated MWNTs obtained after a SPS process. (i)-(j) SEM and (k)-(m) TEM images of fractured surfaces of the MWNT blocks. Cross-links between the tubes are established during a high energy sintering process of fluorinated MWNT powder.<sup>81</sup>

### 1.2.2.3 CVD and dopant-assisted CVD synthesis

One of the first reports on the CVD synthesis of monolithic free-standing CNT networks (sponges) was by Gui *et al.* in 2010.<sup>82</sup> The procedure consisted of injecting a precursor solution containing a carbon source and catalyst using a syringe pump into a heated reactor tube. The CNT sponges obtained from this CVD process were comprised of highly entangled CNTs that formed a macro, porous material (**Fig. 1.19a-e**). In 2011, Hashim *et al.* reported a new technique for creating 3D porous monolithic sponges composed of boron-doped CNTs.<sup>83</sup> A photograph that demonstrates the flexibility of these sponges is shown in **Fig. 1.19f**. This was achieved via a single step CVD synthesis through the addition of small amounts of

boron to the precursor containing carbon and the catalyst for CNT growth. The role of the boron during the synthesis was crucial to forming "elbow-like" kinks on the tube, which resulted in a highly entangled network of CNTs that created a sponge-morphology in the material (**Fig. 1.19g**). The mechanical properties of the boron-doped sponges were found to depend on these elbow-like junctions and have been extensively studied since then.<sup>84</sup> Density functional theory (DFT) calculations show that boron atoms can induce elbow shaped morphology in CNTs because of their tendency to occupy negative curvature regions (**Fig. 1.19h**).<sup>83</sup> Modification of the tubular morphology of CNTs through chemical doping was also pursued by Shan *et al.*, who obtained freestanding nitrogen-doped MWNT sponges through a CVD process.<sup>85</sup> These N-doped sponges demonstrate tunable mechanical and electrical properties depending on the CNT diameters.



**Figure 1.19**:(a) A block of 3D MWNT sponges synthesized using CVD process.<sup>82</sup> (b) SEM and (c) TEM image of MWNT networks that constitute the sponges.<sup>82</sup> (d) Schematic showing the 3D entangled tubes that give rise to a porous and spongy morphology.<sup>82</sup> (e) Photograph of the MWNT sponge in water. The hydrophobic nature of these sponges enables them to float in water. Pictures also show the flexibility of the sponges as well as the strain recovery from compressive stress.<sup>82</sup> (f) Photograph of the boron doped MWNT sponges (CB<sub>x</sub>MWNT).<sup>83</sup> (g) SEM image of CB<sub>x</sub>MWNT showing "elbow-like" kinks on the tube surface.<sup>83</sup> (h) DFT calculations showing energetically stable locations for boron atom in an elbow shaped nanostructure.<sup>83</sup>

## 1.2.2.4 Solution processing of CNT and graphene networks

Solution processing typically involves the gelation of MWNT or graphene oxide (GO) dispersions using organic or inorganic precursors, followed by drying the solvent. This leaves behind porous 3D MWNT or GO solids, also known as aerogels.<sup>86</sup> This approach is attractive due to the possibility of tuning the physical

properties of the resulting 3D networks by controlling the growth/fabrication parameters.<sup>87,88,88–90</sup> Details and variations of this approach are provided in **Chapter 4**, **Section 4.1**.

### **1.2.3** Properties of 3D networks

The 3D structures based on CNTs and graphene have a tremendous advantage over their 1D and 2D counterparts as they consist of networks with micro-, meso- and macro-pores that guarantees molecular transport through the entire structure and utilization of the internal surface area. In the case of CVD grown CNT sponges, the "pores" arise from random entanglement of individual CNTs. For 3D structures generated using post-growth approaches, however, manipulating the process parameters can control the morphology and alignment of pores. The porosity of these materials is often close to 99% or higher, with bulk densities around 5 - 25 mg /cm<sup>3</sup>.<sup>83,91</sup> Hydrophobicity and structural flexibility are a few other attractive properties that are characteristic in these materials. For example, Wu and coworkers reported CVD-grown pristine CNT sponges with a contact angle of 156° for water droplets.<sup>91</sup> Not only were the sponges lightweight, but also structurally flexible and mechanically robust. They could be compressed to more than 95% volume reduction ( $\varepsilon > 95\%$ ) at low stress values (<0.25 MPa).<sup>91</sup> CNT sponges grown using the CVD technique reported by Gui et al. not only exhibited flexibility for bending, stretching, and twisting, but also large elastic and reversible strain deformations.<sup>82</sup> Mechanical testing of CVD grown boron-doped, nitrogen-doped, and pristine (undoped) MWNT sponges was performed by Zhao et al.<sup>84</sup> A constitutive model was used to fit the stress-strain curves of the 3D CNT sponges under compression and the effective modulus of the bulk material was reported for the first time. The  $CB_xMWNT$  sponges showed controllable viscoelastic properties that were dependent on the covalent junctions present (**Fig. 1.20a-b**). The presence of these covalent junctions also endowed them with higher compressive modulus (~100 GPa) when compared to the 3D CNT sponges without covalent junctions.

CNT sponges with a truss-like structure, prepared by Dai *et al.* using CVD, show excellent mechanical stability due to strong inter-tube interactions. Compressive stresses were recorded as a function of increasing strain (10% up to 90%), and the curves resemble behaviors of other foam-like structures, with an initial linear portion, followed by a plateau and a steep hike in the stress.<sup>92</sup> Interestingly, the slope of the linear portion remains almost constant for different strain values, indicating the consistency in its mechanical strength. These materials also performed well during a 0.016 Hz cyclic loading/unloading at a strain of 60% at 400°C, which demonstrates superior stability compared to polyurethane sponges (**Fig. 1.20c**). The covalent interconnections amongst the truss-like CNTs provide an additional support and suppress the collapse of the tubes after the tube buckling occurs under higher strains.



**Figure 1.20**:(a)-(b) Stress-strain curves of  $CB_xMWNT$  sponges as a function of the number of "elbow-like" junctions and the elastic modulus of the junctions, respectively.<sup>84</sup> (c) Cyclic compressive strain tests performed on the 3D CNT "truss-like" networks showing better fatigue resistance as compared to polyurethane (PU) sponges.<sup>92</sup>

It is well known that CNTs and graphene have exceptional electrical properties when viewed individually. Due to the free electrons in the 6-member carbon rings that make up nanotubes and graphene, very high electrical conductivities are achievable. It is also possible to control whether nanotubes are semi-conducting or metallic by altering the helical nature of the tubes. These properties carry over when formed into 3D networks. If ohmic junctions are formed between different nanotubes/graphene sheets, then the electrical conductivity extends into all three dimensions, instead of being limited to 1- or 2D. When combined into composites with other materials for electrical applications, these 3D networks can provide high conductivity to the added materials<sup>93</sup>.

### **1.2.4** Applications of 3D CNT and graphene networks

Owing to the above-mentioned properties, 3D graphene/CNT networks show fascinating prospects in numerous applications including absorption. electrochemical sensing, bio-composites, and devices for energy storage and conversion.<sup>94–97</sup> The highly hydrophobic and oleophilic surfaces of graphene and CNT-based sponges have been demonstrated as absorbers for a wide variety of oils, alkanes, dyes, and organic solvents with remarkable absorption rates and capacities.<sup>65,98–100</sup> The CNT sponges synthesized by Gui et al. had adsorption capacities ranging from 80 to 180 times their own weight for various oils and solvents.<sup>20</sup> These values are several times higher than polymeric sponges and activated carbons. The high adsorption capacity and fast adsorption rate results from physisorption of organic molecules that can be stored inside sponge pores. The adsorbed oils and solvents could be salvaged by mechanical compression or direct burning in air without significantly affecting the sponge properties. This is mainly due to the high porosity of the macrostructure allowing quick diffusion of the generated heat.<sup>20</sup> 3D graphene/CNT foams are also attractive candidates for the removal of air pollutants owing to the micro- and meso-pores present in 3D networks. Gas adsorption by 3D CNT/graphene networks is a relatively unexplored area of research and only a small number of papers starting from 2013 reported graphene foams as adsorbents of gases such as acetone<sup>101</sup>, CO<sub>2</sub><sup>102</sup>, and formaldehyde<sup>103</sup>. Graphene/CNT sponges with large surface area (~ 850 m<sup>2</sup>/g),

high conductivity (~ 10 S/cm), and electron transfer properties serve as excellent candidates for electrochemical sensors to detect trace agents. For example, Yavari et al. reported the use of robust CVD-graphene sponges to detect  $NO_2$  and  $NH_3$ gases.<sup>73</sup> For this purpose, the sponge sheets were cut in 0.5 cm<sup>2</sup> strips and attached to a four-probe chip with copper interconnects. The sensor was able to reliably detect resistance changes upon exposure to 20 ppm  $NH_3$  and 20 ppm  $NO_2$  gases at room temperature, with steady-state response times around 5–10 minutes. Desorption of the gas was achieved with joule heating. The measured sensitivity was an order of magnitude higher than that of a conducting polymer also operated at room temperature and with similar time response. The graphene sponge sensors also provide a less expensive gas detection method than semiconducting metal oxide sensors that operate at higher temperature.

3D carbon networks are also useful for a wide range of energy applications such as catalyst supports for use in direct methanol fuel cells and microbial fuel cells as well as for lithium-ion battery electrodes.<sup>104–106</sup> They are also promising for composite supercapacitor electrodes. Wang *et al.* recently created 3D carbon nanotube foam/nickel hydroxide composites (CNTF/Ni(OH)<sub>2</sub>) for use in supercapacitor electrodes.<sup>93</sup> The grown composites achieved a specific capacitance of up to ~1400 F g<sup>-1</sup>, an extremely low equivalent series resistance of 0.22 $\Omega$ , and a capacitance retention of 94% after 2000 cycles.<sup>93</sup> These values indicate that the composite CNTF/Ni(OH)<sub>2</sub> operated well as a supercapacitor electrode. The CNTF provided a backbone for the nickel hydroxide, relieving stress caused by volume changes and allowing large capacitance retention over many cycles. The CNTF also provided great electrical conductivity, lowering the series resistance and allowing the charging/discharging to occur more rapidly<sup>93</sup>.

CNTs are popular materials for strain sensing applications primarily due to their high electrical conductivity and strong coupling between their electrical and mechanical properties. In addition, a high aspect ratio provides an additional advantage for CNT networks. They can form effective percolating networks that maintain active conduction pathways even when they are mechanically perturbed.<sup>107</sup> The property of piezo-resistance - wherein mechanical strain effects can change the conductivity of the material - has been previously demonstrated in CNTs.<sup>108</sup> This property has also been utilized for developing CNT-polymer composites-based strain gauges and strain sensors.<sup>109</sup> CNTs have found to be sensitive to mechanical degradation, such as crack formation, within the polymer composites.<sup>110</sup> However, buckling of the tubes when strained in tension can still limit their use in strain sensors because of the non-linear change in resistance with applied strain. In this regard, Shi et al. recently developed a hybrid CNTembroidered graphene (CeG) material that exhibited a linear strain response. Due to the flexibility and optically transparent nature of the films, they are excellent candidates for wearable strain sensors.<sup>111</sup> The buckling of CNTs when stretched or compressed under strain was avoided because of the strong interaction with graphene, which also helped maintain the electrical conductivity across the material. 3D sponges of N-doped CNTs (N-CNTs) have also recently shown excellent strain response.<sup>112</sup> The N-CNTs were acidified and treated with hyperbranched polyglycerol (HPG), thus enabling covalent interconnections between the tubes via interactions between the -COOH groups on the N-CNTs and -OH groups on the HPG. The N-CNTs-HPG were impregnated with Ag nanoparticles and then freeze dried to form N-CNTs/Ag sponges. After a preconditioning treatment, the material showed very stable and linear strain response as well as a gauge sensitivity factor of 1.4.

Previous results for 3D carbon nanomaterials pave new avenues for their use in the field of bio-applications. Crowder *et al.*<sup>113</sup> used 3D GF as cell culture substrates for human bone marrow-derived mesenchymal stem cells (hMSCs) (**Fig. 1.21**). GFs maintained the hMSC viability and stimulated changes in the morphology and protein expression patterns, indicating that spontaneous osteogenic differentiation occurred without extrinsic biochemical inputs. Recently, Song *et al.*<sup>114</sup> investigated the pro- and anti-inflammatory responses of microglia in GF culturing systems. They found that GFs supported the growth of microglia and showed comparable biocompatibility with commercially available tissue culture polystyrene (TCPS).



**Figure 1.21:** (a)-(c) SEM images showing hMSCs cultured on GFs for four days. Protrusions up to 100  $\mu$ m in length (yellow arrowheads) were observed from the small cell bodies (black arrows) within the porous regions of the GF.<sup>113</sup>

## **1.2.5** Achievements and Current Challenges

Many approaches are currently available for the synthesis, characterization and utilizing the exceptional properties of nano-carbon based 3D structures, as detailed above.<sup>8</sup> However, one of the remaining challenges is the precise control of the assembly of their individual building blocks.<sup>58</sup> Successful endeavors in this direction would allow researchers to engineer the structure and properties of these 3D structures and tailor it to suit different applications. There is emerging interest in combining nano-carbon structures with novel 2D materials beyond graphene, such as transition metal dichalcogenides, to develop 3D structures (**Fig. 1.22**).<sup>115–120</sup>



Figure 1.22: Schematic illustration of a solvothermal method that combines GO and  $MoS_2$  to create  $MoS_2/RGO$  hybrids.<sup>120</sup>

These materials are able to combine the intrinsic properties of their individual components and thus exhibit improved performance for hydrogen evolution reaction (HER), water splitting and as electrode materials in Li-ion batteries.<sup>115–119</sup> Moving forward, further research and innovation is required to harness the

properties of 3D CNT/graphene networks in order to achieve next generation of performances for several applications.

## **1.3** Goals of this study

The main goals of this study were to investigate novel synthetic approaches for producing multi-functional 3D networks of CNTs by facilitating covalent interconnections between CNTs and to analyze the resulting structure-property changes. In the first strategy, a multi-functional composite of covalently interconnected CNTs with silicon carbide (SiC) nano- and micro-particles was fabricated using spark plasma sintering. These lightweight SiC-CNT composites exhibited enhanced thermal and electrical conductivity as a result of strong intertube bridging. The second approach involved establishing inter-tube bridging of SWNTs using silicon (dopants) as atomic welders. This resulted in major structural and electronic property changes in the nanotubes. In the third approach, doping of CNTs with sulfur and boron during chemical vapor deposition (CVD) was performed to synthesize hierarchical porous structures with many covalent junctions. The doping resulted in morphological changes in the CNTs, giving rise to high surface area, macro-porous structures. Detailed structural characterization of these novel materials was performed and potential applications were explored.

## 2 Three-dimensional covalently interconnected SiC-CNT nanocomposites

## 2.1 Introduction to carbon nanotube composites

Ceramics and metal matrix composites are materials that are common around us. From burner components in the kitchen to gas turbine blades in aircrafts, they have carved a niche in the materials realm.<sup>121-124</sup> Many years of research in this field have contributed to the development of novel technologies to fabricate functional materials as well as improve their properties. In 1996, carbon nanotubes (CNTs) gained attention as promising candidates for reinforcing ceramic matrix composites.<sup>125</sup> The combination of a very high Young's modulus (~TPa range), exceptional stiffness, high aspect ratio and low density makes CNTs ideal for improving the overall performances of lightweight composites.<sup>125</sup> Most of the early studies in this area were directed towards using CNTs as reinforcements in polymer matrices.<sup>126–128</sup> The high electrical conductivity and aspect ratio of CNTs enabled the formation of percolating and conducting paths in polymer composites while also providing mechanical stability (Fig. 2.1a).<sup>128</sup> As a result, many researchers explored the possibility of using CNTs as reinforcements in metal oxide composites.<sup>129</sup> There were some efforts in the mid 1990's to synthesize nanocomposites by filling the inner hollow cores and the gap between the concentric walls of multi-walled carbon nanotubes (MWNTs) with metal oxides (Fig. 2.1c).<sup>130,131</sup> It was not until the late 90's that the idea of utilizing CNTs as reinforcements in metal oxide composites (CNT-Fe-Al<sub>2</sub>O<sub>3</sub>, CNT-Co-MgO, etc) to improve their electrical conductivity gained attention.<sup>132,133</sup> In this context, a study revealed that when a hot extrusion process was used to fabricate CNT- metal oxide nanocomposites, the resulting CNTs were aligned within the densified composite, thus leading to anisotropic electrical conductivity.<sup>129</sup> In addition to improving electrical conductivity, CNTs were also found to be beneficial in pinning down grain boundaries and limiting grain growth in ceramics at high sintering temperatures.<sup>129</sup> This gave rise to better mechanical properties, especially superior fracture toughness of the composite. However if severe sintering conditions were used, such as high temperatures up to ~1600°C, the CNTs were degraded (**Fig. 2.1b**).<sup>133</sup>



**Figure 2.1** (a) CNTs exhibiting fiber pull-out in a CNT- polymer composite.<sup>128</sup> (b) SEM image of CNT–Fe/Co–MgAl<sub>2</sub>O<sub>4</sub> (CMD) composite showing a web-like CNT network amidst the metal oxides.<sup>133</sup> (c) Diagrammatic representation of a CNT core getting filled with molten metal oxide due to capillarity.<sup>130</sup>

Although preliminary studies using CNTs as reinforcement for oxide materials showed interesting results, the field gained momentum when researchers started to explore CNTs as toughening agents for a variety of ceramic materials.<sup>134–137</sup> It was expected that CNTs would finally help to solve some of the inherent problems associated with ceramic materials, including poor fracture toughness, thermal shock resistance, and electrical conductivity. However, many challenging questions began to surface. What is the best way to obtain a uniform and well dispersed CNT distribution in ceramic matrices? How the reinforcement-matrix interaction could be improved in order to induce maximum load-bearing capacity in the composite. Which specific type of CNT would perform the best in a composite? What is the most suitable fabrication technique for CNTs?

Since late 1990's, some of the techniques that demonstrated potential for fabricating CNT-ceramic composites included powder processing (hot pressing, hot isostatic pressing, hot extrusion), chemical vapor deposition (CVD), electrophoretic deposition, colloidal and sol-gel processing. Direct CVD based, insitu growth of CNT-ceramic composites was reported by Peigney *et al.* in 1998.<sup>138</sup> Mixtures of methane (CH<sub>4</sub>) and hydrogen (H<sub>2</sub>) were passed over supported catalysts (Fe, Co, Fe-Co alloys) dispersed within metal oxide solid solutions (for e.g.: Al<sub>2-2x</sub>Fe<sub>2x</sub>O<sub>3</sub>) at high temperatures (900 – 1100°C). Subsequently, the resulting powder mixture was hot pressed.<sup>138</sup> In another approach by Xia *et al.*, CVD was used to grow MWNTs within the nano-channel pores of an alumina template that was predeposited with a transition metal catalyst.<sup>139</sup> They performed an extensive study on the crack deflection mechanism of CNTs, when the reinforced composite is

fractured. Powder processing techniques have also been explored by many groups.<sup>140</sup> In this technique, CNTs are initially mixed with ceramic powders *via* chemical methods and then densified by applying pressure and/or temperature. Spark plasma sintering (SPS) is a modification of this technique and will be discussed in detail in the forthcoming sections. By adding 10wt% CNTs to borosilicate glass through a conventional powder processing route, followed by hot pressing between two graphite dies at 750°C for 2-3 hours, compacted specimen with 5 orders of magnitude lower electrical resistivity than the glass have been achieved.<sup>141</sup> **Table 2.1** gives an overview of the functional properties of CNT-inorganic matrix composites.

Composite fabrication [Ref]	Temperature / pressure/ hold time	Material	Electrical resistivity	Elastic modulus /fracture strength/ fracture toughness
Hot pressing [141]	750°C/ 20 MPa/ 2-3 h	Duran® glass	$10^5 \Omega cm$	63 MPa/ 106 MPa/ 0.72 MPa m <sup>1/2</sup>
		Glass – 10% MWNT	13 Ωcm	54 MPa/ 63 MPa/ 0.80 MPa m <sup>1/2</sup>
Freeze casting [142]	−60°C/ 1.3 KPa / 72 h	100% 45S5 Bioglass	-	111.50 MPa/ 2.08 MPa/ -
		MWNT (0.25 wt%) – 45S5 Bioglass composite	-	266.59 MPa/ 4.56 MPa/-
SPS [135],[144]	1150°C/ - / 3 min	Al <sub>2</sub> O <sub>3</sub>	$10^{13} \Omega cm$	- / - / 3.3 MPa m <sup>1/2</sup>
		10-vol % SWNT/Al <sub>2</sub> O <sub>3</sub>	6.6 x 10 <sup>-2</sup> Ωcm	- / - / 8.1 MPa m <sup>1/2</sup>
		15-vol % SWNT/Al <sub>2</sub> O <sub>3</sub>	3 x 10 <sup>-2</sup> Ωcm	-
Hot Isostatic pressing [144]	1700°C/ 100 MPa/ 1h	$Si_3N_4$	$10^{13} \Omega cm$	-
		1.8 wt% MWNT/Si <sub>3</sub> N <sub>4</sub>	1.26 Ωcm	-
SPS [145]	1050°C/ 50 MPa/ 5 min	SiO <sub>2</sub>	$10^{14} \Omega cm$	-
		10-vol% MWNT/SiO <sub>2</sub>	1.5 Ωcm	-

**Table 2.1:** Summary of electrical and mechanical properties observed in different CNT-inorganic matrix composites.

More recently, a freeze-casting process has been used to fabricate bio-active glass-CNT composite scaffolds that have tremendous potential for use in tissue regeneration.<sup>142</sup> In 1998, Ma and co-workers prepared hot pressed CNT-silicon carbide (SiC) composites in an attempt to improve the mechanical properties of ceramic matrix composites.<sup>146</sup> The bending strength and fracture toughness improved by 10% when small amounts (10 wt%) of CNTs were incorporated into the SiC. They also demonstrated that CNTs preserve their structure and properties after being subjected to a high temperature (2273 K) and high pressure (25 MPa) sintering treatment.

Fabrication of SiC-vertically aligned MWNT composites have been reported by Gu *et al.*, using chemical vapor infiltration.<sup>147</sup> Sheets of vertically aligned MWNTs were placed on a graphite beam support and loaded inside an alumina tube under high vacuum (2 x  $10^{-3}$  Torr). Using a mixture of argon and hydrogen, methyltrichlorosilane was bubbled through the tube which was heated to  $1000^{\circ}$ C.<sup>147</sup> This was followed by annealing at temperatures ranging from 700-1600°C. An enhancement in the fracture toughness (~66.4 J/m<sup>2</sup>) was observed in the resultant composite when compared to bulk SiC.

SPS is a relatively new technique used for densifying a large variety of ceramics, composites, and metals.<sup>148</sup> In essence, SPS is a pressure-assisted furnace in which the heating is provided by a pulsed direct current supplied to the graphite die containing the powders to be sintered. In addition, current-assisted heating allows rapid heating rates up to high temperatures. SPS has recently been used for fabricating a variety of nano-carbon (particularly graphene and CNT) reinforced metal and ceramic matrix composites (**Fig. 2.2**).<sup>149–151</sup> These materials are sought after various industrial applications, particularly in automobile and aerospace industries.<sup>26</sup> In recent studies, SPS was successfully used to fabricate dense, homogeneously dispersed SiC/graphene nanoplatelets (GNPs) composites by liquid-phase sintering of SiC-GNPs powder mixtures with up to 20 vol.% of GNPs.<sup>80</sup> In addition, SPS has been used to manufacture SiC/graphene composites by the in-situ synthesis of graphene sheets at SiC grain boundaries during the SPS

densification of SiC ceramics.<sup>79</sup> This and other studies indicate that SPS is a novel, cost-effective technique to produce composites.



**Figure 2.2:** (a) SEM image of a polished fractured surface of CNT-hydroxyapatite composite fabricate by SPS at 900°C.<sup>151</sup> (b) SEM micrograph of polished and plasma etched surface of Si<sub>3</sub>N<sub>4</sub>-CNT composite sintered using SPS.<sup>150</sup> (c) Fracture surface of the SiC-based composite containing 10 vol.% GNPs.<sup>80</sup> (d) TEM images of a grain boundary with formation of a graphite island in an SiC-graphene composite sintered using SPS.<sup>79</sup>

In this chapter, we will describe the successful fabrication of a composite material embedding 3-dimensionally interconnected CNTs by SPS.<sup>62</sup> The covalent interconnections among CNTs network were facilitated by a carbon diffusion process that resulted in the formation of SiC when silica (SiO<sub>2</sub>) coated CNTs were subjected to high temperatures. The use of SPS for fabricating novel SiC-CNT composites reported here allowed high temperatures and pressures that are required

for the carbothermal reduction of silica to be reached. SPS also allowed the material to densify into a stable 3-D CNT composite block.

## 2.1 Spark Plasma Sintering (SPS)

SPS has gained a lot of attention recently as a method to fabricate CNT reinforced ceramic composites.<sup>152</sup> A simple schematic of the SPS process is shown in Figure 4b. The basic arrangement consists of a graphite die, two punches and spacers. The powder to be contacted is kept in between the punches and the die. The entire assembly is then placed between the two electrodes of the SPS setup inside a vacuum chamber. Some of the advantages of SPS include reduced sintering temperatures, reduced sintering time (on the order of a few minutes), faster heating rates (up to 600°C/min), and the absence of a direct heat source. Both temperature and pressure aid in the consolidation of the material *via* a mass transfer process. Heat is produced by Joule heating of the die (powder in case of conducting samples).<sup>152</sup>

A reduction in grain growth and an enhancement in densification has been observed in samples sintered using SPS.<sup>153–155</sup> The reduction in sintering temperature makes SPS different from the conventional hot pressing method. Another major difference between SPS and other conventional sintering processes is the heating technique. In conventional processes, the sample is generally heated using heat transfer methods such as radiation or convection within a furnace with the help of heating elements or hot inert gases. However, current assisted heating occurs in SPS by passing a pulsed current through conducting graphite electrodes into the sample.<sup>152</sup>

The heating rate, applied pressure, and current were found to be the main parameters that influence sintering and densification in SPS.<sup>152</sup> Although many studies have been carried out to determine the effects of these parameters on the final grain sizes of sintered ceramics and metal oxides, as of yet there is no consensus.<sup>148,152,153,156</sup> Many research indicate that better densification of materials is achieved using SPS as compared to other pressure-less sintering processes. For example, Shen *et al.* have reported that the use of higher sintering pressures resulted in a better densification in an alumina sample produced using SPS.<sup>157</sup> They also observed that the grain sizes were significantly reduced when the heating rates were increased from 50°C/min to 600°C/min for sintering temperatures of 1300° and 1400°C. On the other hand, Kim *et al.* were able to obtain finer grain sizes when using slower heating rates for alumina sintering.<sup>156</sup> Balazsi et al. performed extensive studies on using SPS for CNT based composites.<sup>137,158</sup> When compared to a conventional hot pressing process for consolidating CNT-silicon nitride composites, these authors found that SPS not only enabled higher densification at significantly lower temperatures, but also considerably improved the mechanical properties of the resultant composite.<sup>137</sup>

## 2.2 Synthesis and characterization of SiC-CNT composites

#### 2.2.1 Fabrication of SiC-CNT nanocomposites

In order to synthesize the composite, we first produced pristine MWNTs using an aerosol assisted chemical vapor deposition (AACVD) process.<sup>159</sup> A precursor solution of toluene ( $C_7H_8$ ) and 2.5wt.% ferrocene ( $C_{10}H_{10}Fe$ ) was ultrasonically sprayed into a quartz tube heated to 860°C. Specific details about the CVD setup and schematics are provided in **Section 4.2**. Ultra-high purity (UHP) argon was used as a carrier gas at a flow rate of 2.5 l/min in order to introduce the solution mist into the quartz tube. The reaction took place for 30 minutes. Subsequently, the tube was cooled down to room temperature and CNTs were scraped off from the walls of the tube using a metal scraper. The as-synthesized tubes were dispersed in hydrogen peroxide ( $H_2O_2$ ) at a concentration of 1mg ml<sup>-1</sup> for an oxidation treatment. The dispersion was ultrasonicated for 8 hours in order to break apart the tube bundles and improve their dispersion in the subsequent sol-gel process.

To obtain the SiC-CNT composites, a two-step fabrication process was followed. In the first step, the peroxide treated CNTs were subjected to a sol-gel process as described by Seeger *et al.*<sup>160</sup> Typically, 1g of peroxide treated CNTs was ultrasonically dispersed in 0.25 wt.% polyethylenimine (PEI). When the peroxide treated CNTs are subjected to ultrasonication in PEI, positive charges developed on the surface of the tubes and further broke down bundles of tubes. Any excessive PEI was removed by ultracentrifugation at 5000 rpm for 1-2 h and rinsed thoroughly with water.



**Figure 2.3** (a) Schematic of the sol-gel process; (b) TEM image of a MWNT before the sol-gel process; and (c)  $SiO_x$  coated MWNT after the sol-gel process.

During the second half of the sol-gel process, negatively charged colloidal  $SiO_x$  particles were adsorbed onto the outer surface of CNTs (**Fig. 2.3a-c**). This was carried out by mixing tetraethoxysilane (TEOS) with water and ethanol that lead to a hydrolysis-condensation reaction to form  $SiO_x$ . This mixture was then added to the CNT dispersion at a 1:5 mass ratio and agitated for 6-8 hours in an ultrasonic bath where the CNT outer walls adsorbed the colloidal silica onto its outer walls. The resultant gel was washed and centrifuged in ethanol to get rid of excess  $SiO_x$ 

and left to dry in an oven at 50°C overnight. A schematic of the sol-gel process of coating CNTs with  $SiO_x$  is shown in **Fig. 2.3a**.

The second step in fabricating SiC-CNT composites involved SPS of the SiO<sub>x</sub>-CNTs. Discs of 15 mm diameter and ~2 mm thickness were obtained by SPS (SPS-510CE, Fuji Electronic Industrial Co.,Ltd.) using a maximum temperature of 1800 °C, heating rate up to 133 °C·min<sup>-1</sup>, holding time of 10 min, and 4 Pa of vacuum atmosphere. SiO<sub>x</sub>-CNT powder composition (1 g) was loaded into the SPS graphite die and pressed at 20 MPa at room temperature. An uniaxial pressure of 80 MPa was applied during the first minute of the heating process (while the temperature was below 600 °C), and maintained during the heating-holding cycle. Upon cooling, the pressure was decreased to 20 MPa.

### 2.2.2 Methods for structural and elemental analyses

Structural analyses were performed to detect SiC formation in the composites. Raman spectra were acquired using a Renishaw in-via micro-Raman spectrometer with a 514 nm laser wavelength. Spectra were taken from both the surface of the sintered block as well as from the exposed fracture surfaces. Typical spectra were recorded with 20 seconds of exposure time for 2 accumulations using a ~1  $\mu$ m laser spot. Raman mappings were also acquired from 10 $\mu$ m x 10 $\mu$ m areas using 0.2 sec exposure per pixel with a 6 pixel per micron spatial resolution using a Ramanatomic force microscope – model Alpha300 WITec GmbH.

XRD studies of the sintered composite were carried out in a PANalytical Empryean X-Ray diffractometer with a copper K $\alpha$  radiation source. The patterns were

collected from different regions on the sample by varying 20 from 5° to 80°. The microstructure of the sample was determined using a SEM (FEI NanoSEM 630) with a field emission source operated at an acceleration voltage of 5 kV. HRTEM was performed with a JEOL 2010F at an operating voltage of 200 kV in order to study the interfaces between the SiC and CNTs within the composite. In order to generate electron transparent specimens for HRTEM, the standard procedure of cutting, gluing, slicing, grinding, dimpling, and ion milling was performed. Ion milling of the dimpled sample to electron transparency was carried out using a low-angle gentle (3 kV) ion beam (Fischione 1010 with a cooling stage) at liquid-nitrogen temperatures. EDS analysis of the specimens were also carried out using the same microscope. A JEOL 2010 TEM equipped with a LaB<sub>6</sub> filament (200 kV operating voltage) was used for EFTEM characterization.

### 2.2.3 Methods to Measure Thermal Properties

Through-thickness thermal diffusivity ( $\alpha$ ) was measured by the laser-flash method (Thermaflash 2200, Holometrix Netzsch) at room temperature in an Ar atmosphere, using 8.8 mm x 8.8 mm square specimens with ~1 mm of thickness. The data reported here corresponds to the average of at least three measurements. The thermal conductivity (k) was then calculated *via* the following expression:  $k = \alpha \cdot \rho \cdot Cp$ , where  $\rho$  is the density of the specimen (1.74 g·cm<sup>-3</sup>) and Cp is the specific heat of the material (0.7096 J·g<sup>-1</sup>·K<sup>-1</sup> for graphite).

### 2.2.4 Methods to Measure Electrical Properties

In order to understand the electronic transport behavior of the SiC-CNT composite, four probe electrical measurements were carried out using a physical property measurement system (PPMS) (Evercool Quantum Design). Thin strips (1.2 mm x 3 mm x 1.4 mm) were obtained by cutting the samples with a diamond cutter. The samples were attached to four terminal Cu electrodes with Ag paint. Current was passed through the material at a constant voltage, and the electrical resistivity values were calculated after measuring the dimensions of the sample. The dependence of electrical resistivity on temperature was studied by varying the temperature from 2 K to 375 K.

## **2.3 Results and Discussion**

### 2.3.1 Formation Mechanism of SiC-CNT Covalent Interconnections

Although various theories have been proposed for the carbothermal reduction of  $SiO_2$  to form SiC, the general consensus is that at temperatures above 1400 °C silica melts and in the presence of carbon, SiC can nucleate. The reaction between Si and C is described by **Equation 2.1**.<sup>161,162</sup>

$$SiO_2(s,l) + 3C(s) \rightarrow SiC(s) + 2CO(g)$$
 (2.1)

The amount of synthesized SiC depends on the activity of the carbon and the partial pressure of CO gas that is a byproduct of the reaction between  $SiO_2$  and C. The ease with which CO gas escapes from the pores during sintering is believed to enhance the densification of the material and also the SiC formation.<sup>163</sup> Early studies on
carbothermal reduction processes of SiO<sub>2</sub> mention a link between the final particle sizes of the SiC crystallites and the size of carbon clusters (precursors), time of reaction, and the reaction temperature.<sup>164,165</sup> In general, for sintering processes the final grain structures are highly dependent on the sintering temperature and time. Krstic *et al.* also mentioned that the SiC crystallite size depends on the size of SiO<sub>2</sub> clusters. Their findings indicate that the reaction rate (for the conversion of SiO<sub>2</sub> to SiC) governs the SiC domain formation, and it is dependent on SiO<sub>2</sub> cluster size. For small SiO<sub>2</sub> particles in contact with carbon; they observed an enhanced rate of solid-state reaction between the carbon and SiO<sub>2</sub>. In addition, once the solid-state reaction starts, the gas formed (CO) has to be continuously removed from the system for the reaction to proceed. Furthermore, the diffusion of Si and C through the SiC further limits the reaction. Since CNTs have high surface areas (~54 m<sup>2</sup>/g), however, we are able to overcome some of these limitations that would otherwise suppress the reaction.<sup>166</sup>

## 2.3.2 Microstructure and Composition of the SiC-CNT Composite

SEM micrographs of fracture surfaces in a SiC-CNT composite sintered at 1800°C and 80 MPa are shown in **Fig. 2.4c-d** A dense composite material with a high CNT loading was clearly observed when compared with other SiC-CNT composites previously reported in the literature.<sup>146,167</sup> The high densification was assumed to be a direct result of using high pressure in addition to high temperature during sintering.



**Figure 2.4** (a) Schematic diagram representing the carbothermal reduction of silica and 3D CNT network formation during SPS; (b) Schematic view of the SPS experimental setup; and (c)-(d) SEM images of SiC-CNT composite.

Interestingly, it was also observed that the extremely high uniaxial pressure could give rise to partial 2D alignment of CNTs perpendicular to the direction of the applied pressure. Although some CNT appeared slightly damaged, the CNTs were well adhered in general. The length of the tubes ranged from a few hundred nanometers to a few microns while the diameters varied from 20 to 70 nm.

The average Raman spectrum of the sample sintered at 1800 °C (**Fig. 2.5a**) revealed the coexistence of graphitic species (D-, G-, and 2D-bands for sp<sup>2</sup> hybridized carbon) and SiC (~ 800 and 972 cm<sup>-1</sup>). From this spectrum, it was possible to identify the spatial distribution of each component on the scanned map as well as their characteristic spectra. A Raman image in false colors was created using these data (**Fig. 2.5b**), mapping the intensity of the G-band (in blue) and the SiC band at 800 cm<sup>-1</sup> (in red). Two representative spectra at different positions of the Raman image (marked as 1 and 2 in **Fig. 2.5b**) were extracted and are shown in Figure 5a. In this context, the spectrum at position 1 (blue) corresponds to crystalline CNTs, which was confirmed by the low intensity ratio between the D- and G- bands (I<sub>D</sub>/I<sub>G</sub> = 0.45) observed even after the extreme SPS conditions. The spectrum at position 2 (red) confirmed the formation of SiC, depicting two clear peaks ascribed to the transverse-optical (TO, ~ 800 cm<sup>-1</sup>) and longitudinal-optical (LO, ~ 972 cm<sup>-1</sup>) modes of  $\beta$ -SiC. In addition, the Raman map also displayed the homogenous distribution of SiC within the CNT network.

To further probe the crystalline structure of the composite, XRD was employed. The XRD pattern of the SiC/CNT composite after the sintering process is shown in **Fig. 2.5c**. Peak fitting analysis of the diffractogram revealed the prominent peaks belonging to CNTs and  $\beta$ -SiC.<sup>168,169</sup> The presence of SiC was clearly indicated by the peaks located at 2 $\theta$  values 36°, 42°, 61° and 72°, corresponding to SiC(111), (200), (220), and (311) interplanar spacing. A splitting of the C(002) peak is observed and this could be attributed to the formation of small graphitic domains during the carbon diffusion process. These domains were expected to be turbostratic in nature with an offset in their d-spacing.

From both the Raman spectroscopy and XRD measurements, a fairly good degree of crystallinity within CNT was observed after the SPS process. When these measurements are correlated with the SEM images of the composite, it was observed that the crystalline structure of most of the CNTs were preserved, even after they were subjected to high temperature (1800°C) and extreme pressure (80 MPa).



**Figure 2.5** (a) Raman spectra of spark plasma sintered SiC-CNT composite showing an average Raman spectrum and individual SiC and CNT spectra from regions 1&2 in Figure 2.5(b); (b) Raman image (in false colors) on a scanned area of  $10 \,\mu m \times 10 \,\mu m$  created by mapping the intensity of the G-band of CNT (blue), and the 800 cm<sup>-1</sup> band of SiC (red), and (c) XRD pattern of SiC-CNT composite showing the graphitic C(002) reflection and the presence of the  $\beta$ -SiC phase in the composite.

The  $I_D/I_G$  value of 0.45 observed in the Raman spectrum of SiC-CNT composite revealed smaller amounts of damage to the tubes when compared to other studies that report a higher  $I_D/I_G$  ratio of CNTs after SPS process.<sup>170</sup> Although the starting CNT material reported here had an  $I_D/I_G$  of 0.35, it was believed that the sintering conditions used (1800°C, 80 MPa of pressure for 10 min) did not result in significant damage to the tubes. Newly formed SiC domains of different sizes (ranging from 5-10  $\mu$ m) were observed throughout the composite that served to bundle as well as interconnect CNTs. Those bundles were expected to be composed of junctions of CNT and SiC, which is further confirmed by HRTEM. HRTEM images (**Fig. 2.6**) of the composite showed CNTs in a mixed amorphous and crystalline matrix. A Fast Fourier transformation (FFT) of the lattice fringes as well as the interplanar spacing helped to identify CNTs and SiC within the sample.



**Figure 2.6** (a)-(d) HRTEM images of SiC/CNT composite showing SiC domains around the graphitic planes of MWNTs. Inset in (b) shows the FFT of SiC region.

From the low magnification images, it was observed that the SiC nucleation occured very close to the CNT walls (**Fig. 2.6a**). Smaller domains of SiC were first formed when carbon atoms from the CNT walls reacted with the SiO<sub>x</sub> that surrounded them. At this point, SiC domains sometimes merged to form larger crystallites on the order of ~10  $\mu$ m in size. On a closer look at the high- resolution images of the composite, lattice fringes of SiC deriving from the CNT walls were clearly identified (**Fig. 2.6b-d**). This further confirmed the occurrence of carbothermal conversion of silica into SiC.

EDS was used to obtain microscopic elemental information of the synthesized samples. A representative EDS spectrum showed characteristic peaks for C, Si and Fe, as shown in Fig. 2.7a. EFTEM imaging has been previously used in the literature for analyzing the 3-D nature of composites containing CNTs, especially in cases where the CNTs are embedded in an amorphous matrix.<sup>171</sup> In the EFTEM maps obtained from the SiC-CNT composite, CNTs are embedded in a matrix containing carbon and silicon. The zero loss map in Fig. 2.7b can be compared to a regular bright field HRTEM image of the specimen, in which the bright portion corresponded to vacuum and the dark portions corresponded to thick regions of the sample. Figure 2.7c shows an elemental map in which the brighter areas corresponded to the region with carbon. As expected, the carbon signal was observed throughout the sample (from CNTs as well as SiC) and the presence of the CNT within the matrix was revealed by the brighter, elongated areas within the SiC particles. The distribution of CNTs in the matrix was more evident in the corresponding silicon map (Fig. 2.7d), which displayed a strong correlation with the carbon map, with the exception of dark, elongated areas that corresponded to the location of CNTs (**Fig. 2.7c**).



**Figure 2.7** (a) Presence of silicon and carbon was further confirmed using EDS in a HRTEM, and (b)-(d) EFTEM elemental maps of zero-loss, carbon and silicon map (respectively), clearly showing CNTs embedded in a SiC matrix.

The TGA analysis of the sintered SiC/CNT sample was performed using a TGA Q5000 IR Thermogravimetric Analyzer. The sample (0.7 mg) was loaded on a high temperature (H.T.) platinum pan. The balance purge was done with N<sub>2</sub> gas at 10ml/min while the sample purge was done using air at 25ml/min. The weight loss was recorded while the sample was heated at a 10°C/min ramp from room temperature (R.T.) up to 1000°C. A small initial weight loss (~3%) was observed at ~300°C that could have been due to volatile impurities, particularly from amorphous carbon within the material. Most of the weight loss (~30%) observed in

the sample occurred around ~600°C, corresponding to the loss of graphitic carbon from the CNTs. The derivative weight curve was also computed and recorded as a function of temperature (**Fig. 2.8**).



**Figure 2.8**: TGA weight loss (black) and derivative weight curves of the SiC-CNT sample heated from R.T. to 1000°C in air.

# 2.3.3 Thermal properties of SiC-CNT Composites Compared to Other Carbon Materials

Thermal conductivity (*k*), diffusivity ( $\alpha$ ) and density measurements ( $\rho$ ) were carried out on the sintered sample. Since the specimens exhibited a high surface roughness, the maximum surface roughness ( $R_{max} = 39 \ \mu m$ ) was used to correct the experimental  $\alpha$  data. According to previous studies, the value of actual thickness was obtained by subtracting twice the value of  $R_{max}$  from the measured thickness.<sup>172,173</sup> The obtained values are listed in **Table 2.2**. "*k*" values of the sintered block before and after the correction were 16.72 and 14.15 W m<sup>-1</sup> K<sup>-1</sup>, respectively. These results were compared to those previously reported for similar nanocarbon-based materials, such as CNT buckypaper and bulk specimens of pressed GNPs.<sup>174</sup> Analysis of the thermal properties of the SiC-CNT composite in a through-thickness direction revealed thermal conductivity values about two orders of magnitude higher than those observed for buckypaper, which was expected to the lower density of buckypaper.

Material [Ref]	ρ (g cm <sup>-3</sup> )	$\alpha$ (cm <sup>2</sup> s <sup>-1</sup> )	k (W m <sup>-1</sup> K <sup>-1</sup> )
Buckypaper [172]	0.51	0.0056	0.20
GNPs [172]	1.80	0.0283	3.62
SiC-CNT (this work)	1.74	0.1354	16.72
SiC-CNT* (this work)	1.74	0.1146	14.15

\* Data corrected using Rmax

**Table 2.2.** Density ( $\rho$ ), thermal diffusivity ( $\alpha$ ) and thermal conductivity (k) of the SPSed SiC-CNT material. A comparison with other graphitic materials measured at 27 °C in the through-thickness direction has also been included.

It was previously found that adding small weight fractions of CNTs to a thermally conducting matrix increased anisotropy in the thermal conduction behavior of the resulting composite.<sup>174</sup> A strong correlation between the amount of CNT and the reduction in the through-thickness value of k (in the uniaxial pressing direction) has also been found. This was attributed to the presence of thermal interfaces existing between the CNTs and the matrix material, as well as inter-tube interactions. There are reports of CNT blocks sintered using SPS without the addition of any matrix material having thermal conductivity values in the range of 12 W m<sup>-1</sup> K<sup>-1</sup>.<sup>175</sup> In this case, a percolation network of CNTs was believed to create a 3-D phonon

conduction mechanism when high sintering temperatures (>1500  $^{\circ}$ C) were employed. In the present work, the creation of inter-tube and SiC-CNT junctions lead to 3D phonon conduction pathways that improve the thermal conductivity of the SiC-CNT composite.

#### **2.3.4** Electrical Conductivity of the composite

From the electrical measurements, it was observed that the resistivity in the SiC-CNT material rapidly decreased with increasing temperature in the regime 2-10 K. On further increasing of the temperature, the resistivity decreased more gradually. This is a typical response observed for semiconducting materials.

Material [Ref]	Resistivity (Ω cm, @ 300K)	
CNT-Reinforced SiC [164]	0.334 - 0.065	
Nano β-SiC α-SiC SiC [82][176][177]	0.99 1.25 x 10 <sup>6</sup> 1 x 10 <sup>8</sup> - 1 x 10 <sup>20</sup>	
MWNT blocks [177]	2 x 10 <sup>-3</sup> - 3 x 10 <sup>-3</sup>	
Cross-linked CNT (CL-CNT) blocks [178]	4.16 x 10 <sup>-2</sup>	
SiC-CNT (this work)	4.72 x 10 <sup>-2</sup>	

**Table 2.3:** Resistivity ( $\Omega$  cm, @ 300K) of the SPSed SiC-CNT material in comparison with other SiC and CNT based materials.

A comparative study was also performed by measuring the resistivity of the SiC-CNT sample sintered at 1800 °C and of a sample sintered at 1700 °C, while the rest of the experimental conditions were kept constant. The resistivity values of the SiC- CNT composites sintered at 1800 °C, and 1700 °C were found to be 4.77 x  $10^{-2} \Omega$  cm and 5.19 x  $10^{-3} \Omega$  cm, respectively **Fig. 2.9a**. These values are significantly lower than that of pure SiC, as reported in the literature.<sup>179</sup>

Table 2.3 shows a comparison of the electrical resistivity for different SiC-based materials.<sup>79,167,177,178,180,181</sup> We have also compared the electrical resistivity to pure CNTs samples in order to determine where our sample fits in. The addition of CNTs to SiC was previously found to improve the electrical conductivity of SiC by 96%.<sup>167</sup> The SiC/CNT composite fabricated here had an optimum value of electrical conductivity, integrating the properties of electrically insulating SiC and conductive CNT.<sup>175,179,182</sup> From the TGA curve of the SiC-CNT sample, a weight loss of  $\sim$ 30% was observed close to 600 °C, which was an indication of the amount of residual graphitic carbon content in the sample after the sintering process. Having formed a large fraction of SiC during the sintering process, it was expected that the composite would be more insulating when compared to a block of sintered CNTs without any SiC. On the contrary, the electrical conductivity of our composite was comparable to other CNT based materials, thereby suggesting that the high electrical conductivity of the SiC-CNT is a direct consequence of interlinking of CNT during the SPS process. The resistivity value measured for the sample sintered at 1800 °C was one order of magnitude higher than that of the sample sintered at 1700 °C. The probable reason for this behavior was the elevation in the carbothermal reduction rate by increasing the sintering temperature.

We also used variable range hopping (VRH) models to predict the electron hopping mechanism in these composites, as shown in Figure 9. VRH was proposed by Mott

in 1969.<sup>183</sup> These models were obtained by plotting  $\ln(\rho T^{-1/2})$  as a function of T<sup>-</sup>  $\frac{1}{(n+1)}$  where n=1, 2 or 3 indicates the dimensionality of the sample. Figures 2.9b**d** show VRH models for n=1,2 and 3, respectively for the SiC-CNT composite fabricated in this study. Fitting the linear region of the above mentioned plot gave an insight into the conduction mechanism that dominated in the sample. The best fit corresponded to the one with the highest correlation coefficient ( $\mathbb{R}^2$ ). For the SiC-CNT composite, the value of the regression coefficient was found to be highest for the linear portion in the 3-D VRH model fitting, indicating that the electron hopping mechanism in the SiC-CNT composite occurred in three dimensions. From previously reported studies regarding electron conduction mechanisms in CNT composites, 1-D VRH is the most prominent form of charge transport.<sup>184</sup> This arises from the expected charge tunneling property of CNTs. Nevertheless, the carbothermal reduction process for the SiC-CNT samples resulted in the creation of an interconnected CNT network through carbon diffusion. Charge transport is facilitated in the bulk sample through these 3-D charge pathways as a result of the crystallization of SiC from SiO<sub>x</sub>/CNT.



**Figure 2.9:** (a) Electrical resistivity as a function of temperature measured for SiC-CNT samples sintered at 1700 °C and 1800 °C. At 1800°C we believe that a more efficient reduction of SiO<sub>2</sub> to SiC takes place that results in lower electrical conductivity values. (b)-(d) Variable range hopping models for SiC-CNT composites. The 3D VRH model shows the highest regression value.

# 2.4 Conclusions and Future work

We reported here a novel approach to fabricate CNT based 3-D composite materials using a post-processing technique that involved the coating of CNTs with SiO<sub>x</sub> followed by SPS (at high temperature). SiO<sub>x</sub> underwent a carbothermal reduction during the sintering process at 1800 °C to form SiC by a carbon diffusion process between the CNT and SiO<sub>x</sub>. The newly formed SiC matrix interconnected the CNTs in the SiC-CNT composite. SPS has shown excellent potential for creating numerous CNT interconnections for the fabrication of 3-D bulk structures. The presence of SiC in the sintered composite was confirmed through spectroscopic studies and microstructural analysis. Thermal and electrical properties of the sintered composite were outstanding and provided an indicator into the formation of covalent interconnections between the tubes. It has already been established that the addition of CNTs could considerably lower the electrical resistivity of ceramic materials.<sup>167</sup> By incorporating CNT in a SiC matrix, we not only improved the electrical conductivity values, but also preserved the excellent thermal conductivity of the material. This could potentially serve as an emerging ceramic/CNT composite for electromagnetic shielding which is very important for aircrafts and space applications.

# **3** Silicon-doped carbon nanotubes: controlling tube diameter and electronic transport

# 3.1 SWNT: growth, structure, packing, and doping

Depending on the atomic layer thickness of their walls, carbon nanotubes (CNTs) can be classified into single, double, or multi walled. The basic structural difference between these types of CNTs is shown in **Fig. 3.1**. A single-walled nanotube (SWNT) consists of a single layer of  $sp^2$  bonded carbon atoms forming a seamless cylinder, whereas a double-walled nanotube (DWNT) is similar but with two concentric walls in the cylindrical structure. Multi-walled nanotubes (MWNT) consist of multiple concentric tubes of  $sp^2$  bonded carbon atoms.



Figure 3.1: An illustration of a (a) SWNT (b) DWNT and (c) MWNT.

#### **3.1.1** SWNT growth techniques: a brief history

The carbon-arc discharge method was among the first well established techniques that yielded the growth of CNTs. However, initial observations of the tubes collected from the arc discharge setup were almost entirely what we now call "multi-walled" CNTs.<sup>18,27,185</sup> Most of the theoretical work in the early 1990's that shed light on the structure, electronic and physical properties of this new wonder material was based on their single-shell structures.<sup>186,187</sup> In order to validate these predictions, there was a need to experimentally synthesize SWNTs. By adjusting the parameters of the carbon arc discharge setup, Iijima et al. were able to accomplish SWNT growth in 1993.<sup>188</sup> In a typical arc discharge setup that was traditionally used for fullerene synthesis, two carbon electrodes were separated by few cm within an enclosed chamber. An inert gaseous environment was flowed into the chamber while a D.C. current across the electrode terminals produced an electric discharge, thus vaporizing the carbon from the cathode. "Single-shelled tubes" (in other words, SWNTs) were deposited in the form of a carbon soot in their arc discharge experiment, where iron was used as the catalyst (embedded in the carbon cathode) and the gaseous environment consisted of methane and argon in the discharge tube. The diameters of the SWNTs ranged from 0.7 to 1.6 nm with lengths reaching up to 700 nm.<sup>188</sup> Coincidentally, a parallel work was carried out by Bethune *et al.* who reported a similar approach to obtain SWNTs using a cobalt catalyst assisted arc discharge setup.<sup>189</sup> A more extensive study in this direction was performed by Ajayan et al. investigating the dependence of the cobalt catalyst concentration, chamber pressure, and the use of bi-metallic catalysts on the growth of SWNTs.<sup>190,191</sup> They observed that increasing the catalyst concentration and the chamber pressure in a carbon arc discharge experiment yielded higher quantities of better quality "web-like" SWNTs. A higher yield was also observed for Co-Pt bimetallic catalysts systems. Simultaneously, there were many investigations on the arc discharge based growth of SWNTs with the help of catalysts such as Ni, La, Gd, Y, etc.<sup>192–195</sup> However, the exact mechanism of formation as well as the process of isolating single defect-free tubes still remained unsolved challenges. Towards this end, Smalley and coworkers explored another route for synthesizing SWNTs that involved laser heating and vaporizing graphitic carbon anode targets embedded with metal catalysts.<sup>29</sup> This method produced SWNTs with a better carbon conversion rate (15% of the vaporized carbon converted to SWNTs) and less amorphous carbon coating of the nanotubes. It also proved to be a feasible path for scaling-up the synthesis of SWNTs,<sup>196</sup> although there were efforts to utilize the arc discharge process towards realizing this goal.<sup>197</sup> The arc discharge and laser heating methods were still limited to the production of gram quantities of tubes. Following this, Hafner *et al.* reported the synthesis of SWNTs *via* the decomposition of carbon precursors such as CO and CH<sub>4</sub> using metal catalysts (Mo and Fe/Mo) deposited on substrates with an alumina support.<sup>198</sup> In this study, they were able to limit the carbon supply to the catalytic particle (because of the slow disproportionation of CO at 1atm pressure) and hence favor the growth of SWNTs over DWNTs and MWNTs. The supported metal catalyst assisted hydrocarbon pyrolysis route was also explored by other groups.<sup>199,200</sup> This technique evolved as "chemical vapor deposition" (CVD) in the following years, wherein carbon precursors were passed over supported metal catalysts inside a hot reaction chamber to synthesize SWNTs.<sup>201</sup>

All the above mentioned experiments were carried out with the metal catalyst present in the solid phase before the commencement of heating or arc discharge. A fresh perspective to the synthesis approach was provided by Smalley *et al.* in 1999 by using a gas phase catalysis for SWNT growth.<sup>202</sup> Along with the gaseous carbon precursor, gaseous catalyst (Fe(CO)<sub>5</sub>) was also introduced into a heated quartz tube reactor (800°C to 1200°C). At the cool end of the tube, SWNT mats were deposited and collected using a filter.

# 3.1.2 Literature review of the growth mechanism of SWNT

Even after two decades since the time CNTs were first discovered, there is still no universal consensus regarding their growth mechanisms. Growth mechanisms of catalyst assisted CVD synthesis of SWNTs have been explained using two different theories, referred to as base-growth and tip-growth, which were initially formulated for explaining the growth of carbon filaments/whiskers in the 1970's and 80's.<sup>203</sup> In general, the following processes are involved in nanotube growth: (1) adsorption and decomposition of the hydrocarbon on the catalyst particle surface, (2) diffusion of carbon into the catalyst particle, and (3) precipitation of the carbon from the super-saturated catalyst particle (depending on the solubility limit). The base-growth model assumes that the catalyst particle remains at the base of the growing nanotube, providing a continuous feedstock of carbon atoms to the lengthening tube. Another assumption for this model is that the growing tip has a closed end

cap which is particle-free, and this has been experimentally observed by multiple groups.<sup>194,201,204,205</sup> This model also accounts for the interaction between the support (used for the growth) and the catalyst particles.<sup>206</sup> On the other hand, the tip-growth model is formulated on the basis that the metal catalyst particle remains at the tip of the growing tube. This particle supplies the carbon feedstock as it continues to lengthen the tube on one of its sides, and prevents tube closure on the other side. Most of the evidence suggests that the SWNTs grow by the base-growth model, especially in the arc-discharge and laser-evaporation synthesis methods.<sup>207</sup> Firstly, the metal particles have never been found at the closed tip of the nanotube after the growth. Secondly, the metal particle diameters have been observed to be much higher than the tube diameters. Schematic illustrations of both growth models are presented in **Fig. 3.2.** 



Figure 3.2: Schematic illustrations of (a) "tip-growth" and (b) "base-growth" models of CNT growth. <sup>206,208</sup>

# 3.1.3 SWNT structure

One of the most interesting discoveries regarding SWNTs is the fact that their electronic properties are dependent on their "chirality," or in other words, the

orientation of the honey comb lattice with respect to the tube axis.<sup>186</sup> The chirality of a SWNT is mathematically defined by its chiral vector  $C_h$  as shown below in **Equation 3.1**:<sup>186,209</sup>

$$C_h = ma_1 + na_2 \tag{3.1}$$

In the above equation,  $a_1$  and  $a_2$  are the unit lattice vectors of the SWNT and (m, n) are the lattice points that are super-imposed to the origin (denoted by (0,0) by the chiral vector, indicating the rolling direction of the graphene sheet (**Fig. 3.3a**). The diameter of an SWNT (*d*) is also determined by the chiral vector as follows (**Equation 3.2**):<sup>210</sup>

$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi}$$
 3.2

A graphene sheet can be rolled into a cylinder in many unique ways, as shown **Fig. 3.3 b**. Thus, SWNTs can be classified into armchair (m = n,  $\theta = 30^{\circ}$ ), zigzag (m = 0 or n = 0,  $\theta = 0^{\circ}$ ) or chiral (other values of m and n,  $0 < \theta < 30^{\circ}$ ) depending on their chiral vectors and chiral angle  $\theta$ . The chiral angle  $\theta$  is defined in **Equation 3.3**:<sup>210</sup>

$$\theta = \arctan\left[-\frac{\sqrt{3}n}{2m+n}\right]$$
 3.3

Armchair SWNTs are generally metallic in nature, whereas for the other helicities, the metallic character is present if the relation 2m + n = 3k (where *k* is any non-zero integer) is satisfied.<sup>186</sup>



**Figure 3.3:** Graphene sheet showing lattice vectors  $a_1$  and  $a_2$ , chiral vector  $C_h$  and chiral angle  $\theta$ . (b) Different chiral configurations of CNTs showing armchair, zigzag and chiral tubules.<sup>10</sup>

# 3.1.4 Doped SWNTs: a literature study

It is often necessary to manipulate CNTs through chemical modification in order to exploit specific properties for practical applications.<sup>83,211,212</sup> Elemental doping of CNTs has proven to be an effective route when achieving this goal and provides important insights to their structure-property relationships, particularly changes in their electronic structure and chemical reactivity.<sup>213–217</sup> Doping can be achieved by intercalation of atoms between crystalline planes, by encapsulation of atoms or molecules within the nanotubes' hollow core or by substitution of carbon atoms by other heteroatoms (**Fig. 3.4**).<sup>214</sup> Each of these routes introduces structural and property changes within CNTs.<sup>214,218–220</sup> While some groups have focused on achieving better chemical reactivity of the CNT surface's seeking applications as catalytic materials as well as in gas and molecular adsorption/sensing, many others have paid more attention to diameter selectivity as a result of doping.<sup>211,221–228</sup>

Doping of CNTs has also been found to improve the matrix-reinforcement interaction in polymer-CNT composites.<sup>229</sup>



**Figure 3.4**: Schematic illustrations of (a) endohedral doping or encapsulation, (b) exohedral doping or intercalation and (c) substitutional or in-plane doping.<sup>214</sup>

One of the first studies aimed at investigating the effects of substitutional doping of CNTs with boron (B) and nitrogen (N) was published in 1993.<sup>230</sup> Following this report, there were many subsequent studies carried out related to this topic.<sup>231–235</sup> Substitutional doping of CNTs with N was found to occur in two different configurations.<sup>234</sup> The first substitution involved the direct replacement of a C atom by one N atom while the second, known as a "pyridinic" type configuration (**Fig. 3.5b**), has the N bonded to two other C atoms. The pyridinic configuration is found to give rise to density of states (DOS) in the conduction band close to the Fermi level (E<sub>f</sub>). B doping on the other hand, has shown to give rise to DOS in the valence band close to E<sub>f</sub> (**Fig. 3.5a**). Thus, doping is able to introduce both acceptor and donor states near E<sub>f</sub> in CNTs.<sup>214</sup>



**Figure 3.5**: (a) Theoretical DOS of a (10,10) CNT doped with B and N, showing acceptor states below  $E_f$ , and donor states above  $E_f$ , respectively. (b) A molecular model showing two different N-doping configurations on a CNT: direct substitution (blue color single N atom) and a pyridinic configuration (three N atoms) marked within the small and large red circles respectively. (c) LDOS of pyridinic N-doped (top) armchair (10,10) and (bottom) zig-zag (17,0) CNTs showing donor states in the  $E_f$  after doping (black curve represents LDOS after doping and orange curve represents LDOS before doping). (d) Electronic band structure depicted in real space for P-doped (10,0) CNT. (e) Electronic band dispersions for N-doped and P-doped (10,0) CNT. <sup>234–237</sup>

Interestingly, N doping is theoretically predicted to cause the tubes to become metallic, irrespective of their chiralities.<sup>235</sup> Strong donor states are seen above the  $E_f$  in pyridinic N doping of armchair as well as zig-zag type of tubes (**Fig. 3.5c**).

Phosphorus (P) doping of CNTs has also been studied, although it is more challenging to dope CNTs with a larger element like P in which the valence electrons occupy the third shell.<sup>217,237</sup> Density functional theory (DFT) calculations indicate that the formation energy decreases for P-doping of smaller diameter tubes because of a reduction in the strain energy for accommodating a larger atom like P on the CNT.<sup>237</sup> P-doping gives rise to highly localized states very close to the P atom (**Fig. 3.5d**), resulting in a sharp DOS near the  $E_f$  and the formation of dispersion-less bands related to spin polarization (**Fig. 3.5e**).

While B, N, P and S have been popular elements for doping CNTs, primarily because of their close proximity to C in the periodic table and thus in their similar atomic size and structure, Si – an element that lies directly below C in group 6, has not been studied much as a doping element.<sup>83,217,221,223,233,237–239</sup>

# **3.2** Advantages of Si interconnects

Theoretical studies of Si doping in SWNTs have indicated an inclination towards forming smaller diameter tubes when Si is incorporated into the carbon lattice.<sup>240</sup> Baierle *et al.* reported this work in 2001.<sup>240</sup> Their findings showed that the Si atoms protrude out from the lattice when replacing a C atom in a SWNT due to the inability of Si to form sp<sup>2</sup> hybridization as well as the large size of the Si atom. First principles calculations performed based on DFT by Baierle *et al.* studied two types of tubes, including a (6,6) metallic and a (10,0) semiconducting tubes with diameters of 8.14 and 7.82 Å respectively. By incorporating Si into both types of tubes, lattice distortions (bumps) developed at points where Si atoms

substitutionally replaced C atoms (**Fig. 3.6a-b**). The Si-C nearest-neighbor distances and the distances by which the nearest neighbor C atoms moved outward from the tube were different in both systems.



**Figure 3.6**: Molecular models of Si doped (a) (6,6) and (b) (10,0) CNTs. (c) LDOS of (6,6) and (d) (10,0) CNT.<sup>240</sup>

Changes in the electronic structure were also observed for Si-doped systems as seen in **Fig. 3.6c-d**. When comparing the local density of states (LDOS) of undoped and Si-doped SWNTs, Baierle *et al.* observed that a new localized level was created 0.6 eV above the top of the valence band for the (10,0) semiconducting SWNT. Another energy state was created at 0.7 eV above the Fermi level for the (6,0) metallic SWNT. It has also been illustrated that the new states in the LDOS arise due to the incorporation of Si within the tube matrix.<sup>240</sup> Thus, doping of SWNTs with Si appears to have a prominent impact on the electronic properties of SWNTs. In addition, Si doping can introduce very reactive sites within SWNTs, thus making it an amphoteric center for attracting or adsorbing other atoms or molecules.<sup>241</sup> Furthermore, by incorporating a heavy element such as Si into the C lattice, one could in principle synthesize small diameter tubes.<sup>240</sup>

Here we report the successful synthesis of Si-SWNTs by aerosol assisted chemical vapor deposition (AACVD). The effect of Si on diameter selectivity of SWNTs was carefully studied using Raman spectroscopy. The analysis of the radial breathing modes (RBMs) in the Raman spectra suggests the incorporation of Si into the carbon lattice. We also observe an increase in the D band in the Raman spectra of Si-SWNTs, suggesting the creation of more defect sites in the carbon lattice by Si doping. Electronic transport measurements and theoretical calculations of the Si-SWNTs bundles show different electronic transport properties when compared to pristine SWNTs, which confirms the doping of Si atoms into the carbon lattice. The Si doping mechanism in SWNTs is elucidated by comparing experimental evidence of structural changes and electrical properties of Si-SWNTs with theoretical calculations. In addition, this work emphasizes the effectiveness of doping as a suitable method for controlling SWNT diameters during CVD growth.

From the perspective of forming 3D SWNT networks, this study also aims at investigating Si atoms as inter-tube bridging agents for SWNTs. Such interconnections are significant for building macro structures that have robust mechanical, electrical and thermal properties. Inter-tube bridging within SWNT bundles has been theoretically and experimentally observed by changing the local hybridization of interstitial carbon atoms in SWNTs, as reported by Kis *et al.*<sup>242</sup> However, a novel approach we suggest here is to use dopant atoms such as Si to

interconnect the nanotubes within a bundle. We also discuss in **Section 3.4.4** the results of quantum transport calculations performed using the density functional tight-binding method that indicate an improvement in the quantum conductance across tubes in a SWNT bundle with Si doping. This is due to the tendency of Si atoms to form covalent interconnections between SWNTs resulting either in a C-Si-C bridging or a C-Si-Si-C dimer (where two adjacent tubes have neighboring Si dopant sites). Although there is no direct experimental evidence to the inter-tube bridging, the electronic transport measurements carried out indicate a strong possibility that these types of connections are present within our samples.

## **3.3** Method details: synthesis and characterization of Si-SWNTs

#### 3.3.1 CVD synthesis of pristine and Si-SWNT

An AACVD technique was used to synthesize the Si-SWNTs.<sup>159,243</sup> The precursor solution for AACVD consisted of ethanol, ferrocene  $(FeCp_2)$ and methoxytrimethylsilane (MTMS) in various concentrations (0.015 wt%, 0.030 wt%, 0.060 wt%, 0.075 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%). The reaction temperature and time were maintained at 1000°C for 30 minutes. Upon heating the quartz reaction tube was kept in an inert atmosphere (argon). Once reaching the desired temperature, the argon flow was raised to 0.7ltr/min in order to effectively transport the solution droplets into the hot zone of the quartz tube. The Si–SWNTs were collected from the quartz tube walls downstream - near the furnace exit, after the quartz reactor cooled down to room temperature. A metal rod was used to twist off the Si-SWNT strands that formed a grey film on the quartz tube.

#### **3.3.2** Transmission electron microscopy: technique

High-resolution transmission electron microscopy (HRTEM) was carried out using a JEOL 2010F with a field emission source operating at 200 kV. In order to prepare the samples for HRTEM observations, the Si-SWNTs were well dispersed in acetone using a horn sonicator for 10 minutes. A drop of this well-dispersed suspension was collected on a 300 mesh holey carbon copper grid.

#### 3.3.3 Raman spectroscopy of Si-SWNTs

Raman spectroscopy was carried out using a Renishaw inVia confocal micro-Raman spectrometer with a 50× objective and using the following laser excitation wavelengths: 488 nm and 514.5 nm ( $E_{laser}$ : 2.54 eV and 2.41 eV respectively). Lorentzian profiles were used to fit the Raman peaks for the RBMs, D-band, Gband, 2D-band and the  $I_D/I_G$ .

#### **3.3.4** Electrical measurements

Electrical resistivity measurements were performed using a Quantum Design physical property measurement system (PPMS). Electrodes for the Si-SWNT strands were attached to copper wires using conductive silver paste. Prior to the measurements the chamber was heated at 100°C for one hour under vacuum to degas the samples. The dependence of electrical resistivity on temperature was studied by varying the temperature from 2.5 K to 380 K.

# **3.4 Results and Discussion**

#### 3.4.1 Structural changes in SWNTs on Si doping

HRTEM observations of the samples revealed bundles of SWNTs in all the synthesized materials (**Fig. 3.7**). The bundle diameters have been found to vary between 5 and 20 nm in the studied samples. Carbon nanotubes with little amounts of residual catalysts and amorphous carbon are observed in the pristine and Si-SWNTs under the presence of small Si content in the precursor solution. When increasing the MTMS concentration beyond 0.010 wt%, the residual catalyst particles agglomerated into bigger structures surrounding the SWNT bundles. The presence of spherical particles of varying diameters distributed around the nanotubes, have been previously reported.<sup>28,221,222,243</sup>

These particles mainly consist of metallic impurities from the catalyst, silicon oxide (byproduct from the decomposition of MTMS) and in some cases, ternary products of the reaction between Si, Fe and O. In early reports regarding the growth of nitrogen doped SWNTs, the amount of these residual particles in the sample increased when increasing the N-dopant concentration in the precursor solution.<sup>221,234,244</sup> The density of tubes was strikingly higher for lower doping concentrations as compared to higher amounts of MTMS. This led us to believe that increasing the amount of Si beyond 0.15 wt% poisoned the activity of the catalyst.



**Figure 3.7**: (a-h) TEM images of pristine and Si doped SWNTs synthesized at various Si precursor concentrations. Bundles of SWNTs are observed in all the samples, typically ranging from 5-20 nm in diameter. Residual catalyst particles and carbonaceous materials are observed surrounding the bundles. The yield of tubes seems to be lower at higher Si concentration.

#### **3.4.2** Analysis of radial breathing modes

Raman spectra of SWNTs have been extensively analyzed to obtain information about chirality, crystallinity, defects, hole or electron doping and nanotube diameters.<sup>40</sup> The characteristic Raman features observed in SWNTs are: the RBMs that arise from the radial stretching vibration of the SWNTs perpendicular to their axis (thus being directly related to the tube diameter); the 2D band, which results from a double resonance process involving a phonon at the K point of the graphitic lattice in the nanotube; the disorder induced D peak; and the G band, which is originated from the C-C bond stretching vibrations, parallel to the nanotube axis.<sup>40</sup> Using Raman spectroscopy, the effect of Si doping in SWNTs was analyzed with a particular focus on the changes in the RBMs. Raman spectra of pristine and Si doped samples were recorded using two different laser excitation energies (2.54 eV and 2.41 eV), and their D, G, 2D, and RBM modes were analyzed.

While several RBMs were observed in the ranges from 160 to 260 cm<sup>-1</sup> for the pristine SWNTs, most of the RBM peaks have been detected in a narrower range, from 190 to 235 cm<sup>-1</sup> for most of the Si-SWNT analyzed samples (**Fig. 3.8**). The spectra shown in **Fig. 3.8** were acquired while exciting the samples with a 488 nm wavelength laser ( $E_{laser} = 2.54 \text{ eV}$ ), and represent an average of five different spectra collected from different spots on each sample. In order to analyze the effect of Si on tube diameters, we used the established equation  $\omega_{RBM} = 248/d_t$  that relates the RBM mode frequencies ( $\omega_{RBM}$ ) to the tube diameters ( $d_t$ ).<sup>245</sup>



**Figure 3.8:** Raman spectra of pristine and Si doped SWNTs acquired with  $E_{laser} = 2.54 \text{ eV}$ . The RBMs are compared for samples obtained from experiments using different MTMS (Si precursor) concentrations in the AACVD precursor solution. The pristine sample shows higher intensity peaks at lower frequencies. By adding Si into the precursor solution we observe that the low frequency

peaks decrease in intensity and higher frequency peaks become more intense. On further increasing Si, we restrict the tube diameters to a narrow range close to 1.22 nm.

The intensity of the 161 cm<sup>-1</sup> peak was the highest in pristine SWNT samples, followed by the peaks at 202 cm<sup>-1</sup> and 258 cm<sup>-1</sup>. Using the relation between  $\omega_{RBM}$  and  $d_t$  mentioned above, the tube diameters were estimated to be 1.54 nm, 1.22 nm and 0.96 nm, respectively. **Figure 3.8** exhibits a variation in the distribution of peak intensities as Si precursor percentages are varied in the pyrolyzed solution. For Si-SWNTs with 0.015wt% of MTMS in the precursor solution, the 161 cm<sup>-1</sup> peak's intensity decreased and the highest intensity RBM was observed at 202 cm<sup>-1</sup>. A similar trend was witnessed for all the other Si-SWNT samples, with two main RBM features located at 202 cm<sup>-1</sup> and at 225 cm<sup>-1</sup>. These results clearly indicated that the addition of Si limited the range of tube diameters in the Si-SWNTs. Similar trends in RBM frequency distribution and mode intensities were observed in Raman spectra acquired while exciting the samples with E<sub>laser</sub> = 2.41 eV (details provided in appendix).

#### 3.4.3 Raman peak shifts and intensity changes associated with Si doping

A comparison of the Raman spectra of Si-SWNTs and pristine SWNTs depicting RBMs, D, G and 2D peaks acquired with  $E_{laser} = 2.54 \text{eV}$  is shown in **Fig. 3.9a**. The intensity ratios of the D and G bands ( $I_D/I_G$ ) were analyzed for all samples (**Fig. 3.9b**). The D-band arises from a one-phonon second order Raman scattering process and it is highly sensitive to perturbations in the sample crystallinity. A higher D-band in the material is usually indicative of more defects within the C

lattice.<sup>40</sup> For Si-doping, the induced defects were expected to be higher with higher amounts of dopants.

The results observed were as expected, with  $I_D/I_G$  values for Si-SWNTs synthesized from precursor solutions containing 0.03, 0.06 and 0.075 wt% MTMS being 0.11, 0.08 and 0.12 respectively, compared to a value of 0.03 in pristine SWNTs. The  $I_D/I_G$  ratio for the pristine sample was lower than all Si-doped samples (**Fig. 3.9b**). Nevertheless, we did not observe a linear trend in  $I_D/I_G$  with increasing amounts of Si in the solution. This could be due to the fact that upon increasing the Si amount beyond a certain threshold, the catalytic activity was reduced owing to a reaction occurring between Fe, Si and O, thus resulting in the formation of less number of tubes and more ternary compounds and carbonaceous by-products. Some evidence of these by-products is observed in the TEM images of samples synthesized in the presence of higher amounts of Si.



**Figure 3.9:** (a) D, G<sup>-</sup> and G<sup>+</sup> peaks and (b)  $I_D/I_G$  of pristine and Si doped SWNTs acquired with  $E_{laser} = 2.54$  eV. The D peak intensity increases significantly when Si is added in the system, suggesting the incorporation of doping induced defects in the carbon lattice.

Another feature carefully studied in the Raman spectra was the G band (Fig. 3.10). The splitting of G band to  $G^+$  and  $G^-$  was observed in all Raman spectra. This behavior is usually seen in semiconducting CNTs and it is a result of the unequivalent transverse and longitudinal optical phonons in the  $\Gamma$  point of the CNT Brillouin zone, contrary to what is observed in graphene. This is also a direct consequence of the tube curvature within CNT.<sup>246,247</sup> The G<sup>-</sup> mode, which arises due to the transverse optical phonon, usually undergoes softening when there are perturbations in the hexagonal C lattice that create bond distortions perpendicular to the axis of the tube.<sup>246</sup> A dependence of  $G^-$  on tube diameter has been reported for small diameter tubes.<sup>247</sup> The transverse optical phonon predominantly changes as the tube curvature increases -i.e., with smaller diameters. From the Raman peak fittings of G<sup>+</sup> and G<sup>-</sup> of the pristine and Si-SWNT samples it was observed that the peak shape resembled that of semiconducting tubes. The G<sup>+</sup> peak in SWNTs is generally located at around 1590 cm<sup>-1</sup> and the  $G^-$  close to ~ 1552 cm<sup>-1</sup>. All the spectra were normalized with respect to the G<sup>+</sup> band intensity, which is the most intense peak compared to all the other peaks in each spectrum.



**Figure 3.10:** (a) Raman spectra depicting the D,  $G^-$  and  $G^+$  peaks and (b)  $G^+$  and  $G^-$  peak positions plotted as a function of Si concentration acquired with  $E_{laser} = 1.92 \text{ eV}$ . A considerable downshift of  $G^-$  peak is observed in Si-SWNTs as compared to pristine SWNTs.

A downshift in G<sup>-</sup> was clearly seen when increasing the Si precursor solution concentration. The Raman spectra acquired with  $E_{laser} = 1.92eV$  also provided further confirmation (**Fig. 3.10a**). **Figure 3.10b** shows the peak positions of G<sup>+</sup> and G<sup>-</sup> in the samples with different doping levels in comparison to that of pristine SWNT. The position of G<sup>+</sup> at 1590 cm<sup>-1</sup> did not significantly vary whereas G<sup>-</sup> was downshifted by as much as 45 cm<sup>-1</sup> in the Si-SWNT sample synthesized with 0.10 wt% MTMS in the precursor solution. This was larger when compared to that of pristine SWNT which showed 32 cm<sup>-1</sup>, further suggesting that the CNTs were effectively doped with Si.

### 3.4.4 Electrical properties of pristine and Si-SWNTs

The electronic properties of SWNTs are extremely sensitive to the structure of the tubes.<sup>186</sup> The remarkable electronic properties of CNTs have made them popular for field effect transistors (FETs). However, the device performance is greatly

dependent on the transport properties, which in turn are sensitive to the quality of the tubes, presence of defects, etc. From another perspective, the sensitivity of the transport properties also makes it possible to change the transport properties through chemical doping.

The electrical resistivity ( $\rho$ ) values of pristine SWNTs, as well as the Si-SWNTs synthesized from precursors containing 0.06% MTMS, 0.10% MTMS and 0.2% MTMS were measured as a function of temperature within the range of 2.5 < T (K) < 380 and plotted in **Fig. 3.11**. While  $\rho$  values of the pristine sample could be measured down to 2.5K, the current *I* values for the Si-doped samples at lower temperatures (below 30 K for 0.2% MTMS, 10 K for 0.10% MTMS and 0.06% MTMS), were below the detection limit of the PPMS and hence could not be recorded.


**Figure 3.11:** Electrical measurements on Si doped (with MTMS) and pristine (no MTMS) SWNT samples. (a)  $\rho$  vs. temperature showing higher resistivity values in Si-SWNT samples as compared to pristine. (b)-(d) VRH models were plotted for  $\rho$  vs T<sup>-1/2</sup>, T<sup>-1/3</sup> & T<sup>-1/4</sup> and linear portion of the curves were fit to straight lines in the low temperature regime. The Si doped samples show mixed 2D-3D VRH whereas the pristine SWNT sample shows 3D VRH.

As expected, significant differences were seen in the Si-doped and pristine SWNT samples. Semiconductor-type behavior was observed in all the samples – wherein the  $\rho$  increased on decreasing the temperature. However, the  $\rho$  values for the doped samples were almost four orders of magnitude higher than the pristine sample. There was a sharp increase or a "kink" below 30K for pristine and Si-SWNT samples. This behavior has been reported previously and has been attributed to the presence of defects on the tubes as well as inter-tube interactions within a bundle.<sup>248</sup>

Mott's variable range hopping (VRH) models were used to understand the dominant electron hopping conduction mechanism in the studied samples. Mott's law models the relationship between the electrical resistivity and temperature by plotting  $\ln(\rho T^{-1/2})$  as a function of  $T^{-1/(n+1)}$ , where n=1,2 or 3 indicate the dimensionality of the electron conduction.<sup>183</sup> Depending on the best fit between ln  $(\rho T^{-1/2})$  and  $T^{-1/n}$  in the linear portion (low temperature regime), the electronic hopping conduction mechanism could be determined within the SWNTs. Previous studies have been conducted along this direction, and SWNT bundles have generally shown a good fit for 3D VRH hopping.<sup>248</sup> Very noticeable inter-tube interaction and electronic transport within the bundles through the contacts established at points of tube-overlap have shown to be contributing factors for 3D VRH conduction in SWNT bundles. In this study, the linear fittings for the pristine SWNT sample showed a maximum regression coefficient  $(R^2)$  value for the 3D VRH model. The Si-SWNTs on the other hand exhibited mixed 2D-3D VRH conduction. The linear fittings for the Si-SWNT sample synthesized with 0.06% MTMS showed equal R<sup>2</sup> values for 2D and 3D VRH, which was slightly higher than the corresponding value for 1D VRH. The Si-SWNT sample with 0.10% MTMS displayed the highest value of  $R^2$  for the 3D VRH linear fit, closely followed by 2D VRH. This mixed 2D-3D behavior observed in the Si-SWNTs could have been a result of having more local scattering sites that inhibited a complete 3D electron hopping, as the number of on-tube defects increased with more Si doping. This was also seen in the Raman spectra where the I<sub>D</sub>/I<sub>G</sub> ratio increased with higher Si doping. The Si-SWNT sample synthesized with 0.2%

MTMS showed very high resistivity values. Interestingly, the least value for  $R^2$  was found in the T<sup>-1/2</sup> dependence of  $\rho$  for all the samples measured. This was an indicator of the absence of Coulomb's gap in all the samples in the measured temperature range.<sup>249</sup>

In order to better understand the changes observed experimentally on the electronic properties of these Si-SWNTs, electronic structure and quantum transport calculations were performed on pristine, silicon-doped, and double-silicon-doped two-SWNT systems (**Fig. 3.12**). The initial atomic relaxation and electronic structure calculations were carried out using a self-consistent density functional tight-binding method as implemented in DFTB+.<sup>250,251</sup> The mat-sci set of Slater-Koster parameters<sup>252</sup> was chosen as it has previously been found to accurately reproduce the electronic structure of *sp*<sup>2</sup>-bonded carbon systems calculated with Density Functional Theory methods.<sup>253</sup> Hamiltonian and Overlap matrices were then extracted and used to perform multi-terminal electronic transport calculations following the Landauer-Buttiker formalism.<sup>254</sup>

We analyzed the conductance across two SWNTs that share a region where the nanotube walls were parallel, where a single or a double Si atom defect could have been present. In order to achieve this, the active region of the two-SWNT system was coupled to nanotube electrodes that were calculated in the absence of a parallel nanotube. The atomistic models employed are depicted in **Fig. 3.12a-c**. The quantum conductance between parallel pristine SWNTs presented in **Fig. 3.12d** was several orders of magnitude below that of a single SWNT lead, and was due to the weak interactions between the nanotubes.



**Figure 3.12:** (a)-(c) Models of CNTs used for calculating the conductance across two pristine tubes, tubes with a single Si defect and double Si defects respectively. (b) Quantum conductance values calculated for the above mentioned configurations of nanotubes. An increase in the inter-tube conductance is observed on Si-doping.

Substitutional doping of one of the SWNTs with silicon caused a protrusion on the nanotube wall at the doping site as well as the presence of a localized defect state. The consequent reduction of the distance to a neighboring nanotube and the increase in their coupling resulted in an increase in the inter-nanotube conductance, which was reduced to only one order of magnitude below the SWNT conductance. It was also observed that if two silicon doping sites on opposing nanotubes were in close proximity these would form a Si-Si bridge, which resulted in the covalent attachment of two SWNTs and a further increased in the quantum conductance across nanotubes.

#### 3.5 Conclusions

In conclusion, the synthesis of Si-SWNTs has been achieved through AACVD by introducing Si in the pyrolyzed precursor solution. Structural characterization using TEM revealed bundles of SWNTs with thickness ranging from 5 to 20 nm. Pristine and Si-SWNTs synthesized in the presence of low concentrations of MTMS led to samples with less amount of byproducts. Si doping was confirmed by Raman spectroscopy. Raman spectra revealed shifting of the RBMs, an increase in the  $I_D/I_G$ ratio, and a significant downshift of  $G^{-}$  in the doped samples. Mott's VRH models were employed to analyze the electron hopping mechanism in these materials. The differences in the electrical properties of pristine and Si-SWNTs helped further to presence of Si doping. Electronic transport calculations of a Si-doped dual-SWNT system confirmed that the presence of Si within SWNT bundles increased the coupling and quantum conductance across nanotubes, which was consistent with the experimentally observed mixed 2D and 3D-like transport regimes. Further increase of Si content could have resulted in the presence of covalent bonds across nanotubes which would further increase the transport across them. This work constitutes a step forward in the understanding of elemental doping of CNTs and provides important insights to their structure-electronic property relationships.

## 4 3D networks of doped multi-walled CNTs and radially grown CNTs on carbon nanofibers

# 4.1 Literature review on different methods to grow 3D CNT sponges and their properties

Large surface areas and porosities are useful traits while considering new materials for applications such as filters, adsorbents, flexible sensors, scaffolds and catalysis.<sup>72,255–258</sup> These applications also require the materials to be mechanically robust and tolerant to different chemical and thermal environments for high performance in varying conditions.<sup>259,260</sup> It is also important to have materials with low-cost production and handling, as well as easy scale-up capabilities in order to commercialize them.<sup>261</sup> In these regards, porous carbon-based 3D structures are exceptional, because they also offer the added advantage of being lightweight materials (**Table 4.1**).

There is an emerging class of materials that are made up of graphitic building blocks but are 3D in nature. These materials range from foams or aerogels, and are comprised of carbon and/or graphene to hybrid materials consisting of a mixture of one or both with graphene oxide (GO).<sup>72,95,258</sup> These new materials are not only capable of gas and liquid adsorption (particularly for oil spilling), but also useful for chemical and strain sensing as well as scaffolds for cell growth.<sup>72,107,258,262</sup>

Material	BET surface area (m²/g)	Density (g/ cm <sup>3</sup> )	Commercial applications	Ref.
Silica aerogels	100 - 830	0.048 - 0.38	<ul> <li>Desiccant</li> <li>Thermal insulation</li> <li>Drying and adsorption of organic solvents</li> </ul>	[263]–[268]
Zeolites	100 - 1800	0.48 - 1.5	<ul> <li>Air and water purification</li> <li>Drying and separation of gases and organics (paraffin)</li> <li>CO<sub>2</sub> recovery</li> <li>Catalysts and catalytic supports</li> </ul>	[269]–[273]
Polymer resin based carbonaceous adsorbents	500 - 2400	0.68 – 1.6	<ul> <li>Removal of phenol and derivatives from water</li> <li>CO<sub>2</sub> capture</li> </ul>	[274]–[277]
Activated alumina	250 - 350	0.6 - 0.8	<ul> <li>Desiccant</li> <li>Arsenic and fluoride removal from water</li> </ul>	[278]–[280]
Activated carbons	300 - 3000	0.25 – 0.65	<ul> <li>Gas separation and storage</li> <li>Water purification</li> <li>Adsorption of organic compounds</li> </ul>	[281]–[284]
Carbon black	600 - 2100	0.2 - 0.68	Electrochemical double layer capacitors	[285]

Table 4.1: Examples of porous materials used in different commercial applications.

Some of these materials have been found suitable for electrode materials with high electrochemical performance.<sup>286</sup> It is therefore clear that graphite-like materials hold great promise in many of these applications primarily due to their unique electronic and mechanical properties.<sup>287,288,289</sup> Changes in the chemical and physical environments have been found to alter the electronic properties of graphitic materials, thus creating the fundamental basis for exploring their potential in many applications.<sup>290</sup> The striking feature common to these novel 3D carbonbased materials is their high pore accessibility. In addition, the presence of sp<sup>2</sup> hybridized carbon provides a favorable environment for other elements and molecules, particularly gas molecules, to be able to electronically interact and create physiological changes.<sup>262</sup> Another advantage of having a strong sp<sup>2</sup> bonded carbon framework is that it endows mechanical robustness and flexibility to these porous structures.

#### 4.1.1 Chemical routes for synthesizing 3D CNT networks

Various experimental approaches have been used to synthesize 3D CNT-based porous solids.<sup>8</sup> Chemical cross-linking is an effective strategy to interconnect individual CNTs in order to build 3D architectures. Some studies in this direction have utilized chemical reactions such as the amidation and Suzuki coupling reaction to create covalent C-C junctions between CNTs, resulting in robust, free-standing, and macroscopic 3D CNT blocks.<sup>291,292</sup> Highly porous (surface area ~ 177 m<sup>2</sup>/gm) free-standing 3D structures of covalently interconnected MWNTs have been synthesized by Ozden *et al.* using the Suzuki coupling cross-linking approach, as seen in **Fig. 4.1a-c**.<sup>291</sup> These foams have demonstrated potential for oil spill remediation, with sorption capacities exceeding 120 gm/gm.<sup>291</sup>

Solution based processing and self-assembly of CNTs into 3D structures with the help of various binders have also gained significant interest over the past decade.<sup>293</sup> Chen *et al.* demonstrated the cross-linking of SWNTs by using different mass ratios of ferrocene-grafted poly(p-phenyleneethynylene) (Fc-PPE) in a chlorobenzene solution, followed by solvent exchange of chlorobenzene with ethanol and critical point drying.<sup>294</sup> In a similar solution-based approach, Zou *et al.* modulated the interaction potentials between MWNTs in such a way that it decreased the percolation threshold necessary for effective cross-linking and gelation of MWNTs.<sup>86</sup> This was achieved by functionalizing MWNTs with a polymer- poly(3-(trimethoxysilyl) propyl methacrylate) (PTMSPMA). The polymer not only stabilized the MWNT dispersion, but also underwent hydrolysis-condensation to form the cross-linked polysilsesquioxane, which established strong chemical bonds between the MWNTs. This resulted in gelation of the MWNT dispersion and subsequently formed very light-weight aerogels (~4 mg/mL) when the solvent was removed (**Fig. 4.1d-e**).<sup>86</sup> A schematic of this process is shown in **Fig. 4.1f**. Amino acids, organogelators and conjugated polymers have also been extensively used for the gelation of CNTs in recent years.<sup>295–297</sup>

One of the versatile routes established to fabricate porous SWNT aerogels involves dispersing SWNTs in water using a surfactant (such as sodium dodecyl sulfate) followed by freeze-drying. Bryning and coworkers reported this in 2007 and were able to obtain SWNT aerogels that were electrically conducting (conductivity ~ 1 S cm<sup>-1</sup>).<sup>298</sup> In addition, they were also able to improve the mechanical strength of the aerogels through polyvinyl alcohol (PVA) reinforcement – a step added just before freeze drying the aerogels. With the PVA:SWNT mass ratios ranging from 1:6, they were able to obtain aerogels with mass densities in the range of 40-60 mg/mL that could support objects up to 8000 times their weight without large amounts of deformation.<sup>298</sup>



**Figure 4.1**:(a) Microstructure of a porous, chemically cross-linked 3D MWNT solid and (b) schematic illustration of the Suzuki coupling reaction that enables the cross-linking of MWNTs. (c) Low magnification SEM image showing bundles of MWNTs within the walls of the porous structure.<sup>291</sup> (d) MWNT aerogel fabricated via gelation of a MWNT dispersion using PTSPMA polymer. (e) A photograph of the aerogel and (f) SEM image showing a honeycomb-type porous structure with MWNTs decorating the pore walls. (g) A schematic of the gelation process is shown.<sup>86</sup> (h)-(k) 3D freestanding foams fabricated by electrophoretic deposition of SWNTs on a nickel foam followed by etching away the nickel foam template.<sup>299</sup> (l)-(m) Scanning electron micrographs of the TGA curves of SWNT foams prepared with and without surfactant. A higher thermal stability is observed in the foams fabricated using a surfactant-free approach.<sup>299</sup>

Very large surface areas (~1291 m<sup>2</sup> g<sup>-1</sup>) have been achieved in aerogels fabricated using surfactant-based SWNT dispersions as the starting material.<sup>300</sup> Surfactant free approaches to disperse SWNTs and fabricate 3D porous structures

from their dispersion have also been tested by other groups.<sup>299</sup> One example for this involved the dispersion of SWNTs in a polar solvent (n-methylpyrrolidone), followed by electrophoretic deposition of the nanotubes onto porous nickel foam attached to the negative electrode in the electrolysis cell. The nickel foam was then etched away using HCl, leaving behind a free-standing 3D SWNT monolith (**Fig. 4.1h-m**).<sup>299</sup> The foams prepared using this method showed an improved thermal stability as compared to the foams prepared with surfactants. The corresponding TGA curves are shown in **Fig. 4.1n**. In addition, these surfactant-free 3D SWNT foams outperformed the surfactant-prepared SWNT foams during electrochemical impedance measurements. This was attributed to the inhomogeneous electrochemical interfaces between the surfactant-prepared SWNTs with the electrolyte.<sup>299</sup> **Table 4.2** summarizes the surface area values of the above mentioned CNT aerogels.

Material	Synthesis route	Surface Area (m²/g)	[Ref]
3D SWNT, DWNT	Chemical cross-link using	141 - 679	[301]
aerogeis	Chamical functionalization		
3D MWNT aerogels	& cross linking using PTMSPMA	580	[302]
3D SWNT aerogels	Surfactant assisted	1291	[303]
3D MWNT macroporous solids	Cross link: Suzuki coupling	177	[304]

**Table 4.2:** Surface area values of different CNT based aerogels synthesized using different chemical processes.

#### 4.1.2 CVD growth of 3D CNT networks

The addition of dopant atoms has also been found to yield 3D networks of CNTs during CVD. For example, in the dopant assisted CVD process, addition of elemental dopants, such as boron (B) and sulfur (S) has resulted in morphological changes of multi-walled carbon nanotubes (MWNTs) in such a way that it induces a network formation.<sup>83,239,305,306</sup> This shows significant promise in forming junctions between CNTs through covalent interconnections, as reported in previous studies (Fig. 4.2a-b).<sup>239,307</sup> Interestingly, doping also helps to create local perturbations in the electronic structure of CNTs, thereby enabling their electronic properties to be tuned.<sup>236</sup> However, doping of SWNTs often lead to local deformations of the carbon lattice, and often fail to create substantial morphological changes on the tubes unlike MWNTs. Villalpando-Paez et al. observed the formation of corrugations on SWNTs with N-doping (> 14 wt%), in addition to significant changes in the tube diameters and a decrease in the overall crystallinity of the samples.<sup>232</sup> It has been suggested that these defect sites can be used for anchoring other molecules that can serve as covalent linkers for the tubes.<sup>232</sup>

Macroscopic, free-standing 3D networks of CNTs have also been synthesized with the help of porous templates, chemical dopants, as well as floating catalysts in the CVD process.<sup>82,83,308</sup> Li *et al.* were the first to report the growth of large numbers of aligned Y-junction CNTs (**Fig. 4.2c**) using a nano-channel alumina (NCA) template.<sup>69</sup> In their approach, cobalt catalyst particles were deposited within the pores of the NCA template with Y-shaped channels, followed by pyrolysis using acetylene at 650°C after reducing the catalyst in a carbon monoxide (CO) atmosphere. This was extended one step further by Meng *et al.* who created hierarchical channels within anodic aluminum oxide (AAO) templates that enabled the synthesis of multi-level junctions and branches of CNTs (**Fig. 4.2d**).<sup>309</sup> A fascinating feature of this approach is the availability of a number of different templates for growing graphene and CNTs in 3D.<sup>74,310,311</sup> Using a single-step CVD method, Dai *et al.* demonstrated the growth of large surface area and radially aligned CNTs (RACNTs) bounded by cylindrical graphene layers.<sup>312</sup> Anodized alumina wires were used as templates to enable the formation and deposition of layers of sp<sup>2</sup> carbon on the anodized areas, thereby taking up the shape of radial cylindrical pillars within a cylindrical fiber. On removal of the template, hollow fibers of graphene with RACNT arrays on the inner walls remained. A schematic of the process is shown in **Fig. 4.2f-i**. The lengths of the CNTs were dependent on the amount of anodization and thickness of the alumina wire. The length of the fiber itself was determined by the starting alumina wire.



**Figure 4.2**:(a)-(b) SEM images of sulfur doped MWNTs. Conical branches arise from the central tubes as a result of "stacked-cup" morphology of the tube walls triggered by sulfur.<sup>239</sup> (c) A CNT Y-junction synthesized using CVD with an AAO template.<sup>69</sup> (d) Hierarchical CNT multi-terminal junctions created using a template based CVD method.<sup>309</sup> (e) Schematic of a 3D hierarchical CNT structure with multiple branches.<sup>309</sup> (f)-(h) Schematic showing synthesis of 3D CNT structures synthesized using AAO wire as template in a CVD technique.<sup>312</sup> (i) Model of a 3D-CNT structure with graphene at its base.<sup>312</sup>

### 4.2 CVD Synthesis and structure of B-doped and pristine MWNT sponges

CVD is an efficient, reproducible and scalable method to produce 3D spongelike structures entirely made up of CNT networks. Both the CVD technique and dopant assisted CVD technique for growing porous 3D MWNT networks have been used in this study and will be discussed in detail in the following sections. A comparative study of the gas-adsorption performance of boron-doped and pristine 3D MWNT sponge-like materials is reported in **Section 4.3**. These materials demonstrate remarkable adsorption capacities for CO<sub>2</sub> and CH<sub>4</sub>. Brunauer– Emmett–Teller (BET) measurements indicate that the surface areas, pore structures and active surface sites contribute synergistically towards enhancing their adsorption capacities.

The synthesis of porous hierarchical structures by co-doping CNTs with boron (B) and sulfur (S) has also been explored in this study (**Section 4.4**). Interestingly, these materials exhibit tentacle-like structures, with short branches protruding outwards from a thick CNT stem.

#### 4.2.1 CVD synthesis of pristine and B-doped (CB<sub>x</sub>MWNT) sponges

Two types of porous 3D CNT based sponge-like materials were used in this study: pristine MWNT sponges and B-doped MWNT (CB<sub>x</sub>MWNT) sponges. The materials were synthesized using an aerosol assisted CVD (AACVD) process.<sup>82,83</sup> The synthesis procedure involved the pyrolysis of a precursor solution typically containing a hydrocarbon source and catalyst, at temperatures suitable for CNT growth and ambient pressure conditions. A 1" diameter quartz tube reactor was used in all of the experiments and a Minimite furnace equipped with a programmable temperature controller provided the heating ramps for carrying out the necessary reactions. The precursor solution was kept inside a cylindrical glass vessel fitted with an ultrasonic piezoelectric transducer. The transducer was powered by a generator source which had a variable frequency/power range. The purpose of the piezoelectric was to agitate the precursor solution into a mist consisting of fine liquid droplets. The cylindrical vessel was connected to one end of the quartz tube reactor using a conical glassware adapter while the other end was connected to a liquid trap for filtering out the exhaust. An inert carrier gas was flowed at a low rate (0.5 ltr/min) to purge the setup while the furnace was being heated. Once the furnace reached the reaction temperature, the generator was turned on and the solution mist was led through the quartz tube reactor using a higher flow of inert gas (2.5 ltr/min). The carrier gas flow and the density of the mist determined the solution feed rate into the reactor. The size and density of the mist droplets were varied by changing the power/frequency parameters of the generator source. Sonication was carried out for the desired amount of time (usually varying between 30 minutes and 1 hour), after which the quartz reactor was cooled down to room temperature.

The procedure detailed above was used to synthesize pristine MWNT sponges using 1,2 dichlorobenzene as the carbon source and ferrocene as the catalyst.<sup>258</sup> The precursor solution was sprayed into a 1" diameter quartz tube reactor using an ultrasonic aerosol generator and Ar-15% H<sub>2</sub> mixture carrier gas at

2.5 ltr/min flow rate. The reaction was carried out at 860°C for 1 hour. Following this, the reactor was allowed to cool down. The pristine MWNT spongy blocks were collected by carefully scraping the walls of the quartz tube. Typically, a 1-hour long synthesis yielded around 100 mg of pristine MWNT sponges.

CB<sub>x</sub>MWNT sponges were obtained in a similar process using a precursor solution of toluene, ferrocene and triethylborane.<sup>83</sup> The solution was sprayed into a quartz tube using an ultrasonic aerosol generator. The reaction temperature was 860°C and the synthesis was carried out for 30 minutes. An extensive study of the structural differences between both types of sponges was carried out. New aspects in the structure – property correlations of these materials were investigated using Raman spectroscopy, X-ray diffraction (XRD) and thermogravimetric analysis (TGA). In addition, the potential of these sponges for oil absorption and gas adsorption (CO<sub>2</sub> and CH<sub>4</sub>) was explored.

#### 4.2.2 Structural characterization (SEM, TEM, Raman, TGA)

The CB<sub>x</sub>MWNT and pristine MWNT sponge samples were carefully analyzed using field emission scanning electron microscopy (FESEM) in a LEO1530 and an FEI Nova NanoSEM630, both operated at 5kV. The sponges used in this study consisted of entangled tubes that were randomly oriented to create an intricate network with micropores, as shown in **Fig. 4.3**. From numerous SEM images, the average tube diameters were estimated to be ~20nm and ~70nm in the MWNT and CB<sub>x</sub>MWNT sponges, respectively. Although both materials were composed of MWNTs, striking differences in their tube morphologies and overall structure were observed, as seen in the SEM images. The B atoms helped in the formation of kinks (elbows) in the carbon nanotubes during the growth of CB<sub>x</sub>MWNTs and hence led to their entanglement and resulting network formation. **Figures 4.3a-b** depict the entangled nature of the CB<sub>x</sub>MWNT sponges. The presence of kinks or elbow-like structures has been associated with highly B-doped sites, as confirmed by Electron Energy Loss Spectroscopy (EELS) in a previous study.<sup>83</sup> Density Functional Theory (DFT) calculations in the previous study also showed that the B atoms induced elbow-shaped morphology in CNTs because of their tendency to occupy the negative curvature regions on the nanotubes.<sup>83</sup> The pristine MWNT sponges, on the other hand, were composed of mostly straight tubes without any junctions, as shown in **Fig. 4.3c-d**. It is also noteworthy that these materials were extremely hydrophobic in nature (see **Fig. 4.3e** inset), where the contact angle they made with water surpassed 150°.



**Figure 4.3:** SEM images of (a)-(b)  $CB_xMWNT$  sponges and (c)-(d) pristine MWNT sponges, respectively. Arrows in (b) point at elbows in the  $CB_xMWNT$  sponge structure. From the SEM images it is evident that the pristine MWNT sponges comprise of mostly straight tubes whereas  $CB_xMWNT$  sponges have many elbow-like structures. (e) A photograph of  $CB_xMWNT$  sponge. The inset shows a water droplet on the sponge, demonstrating super hydrophobicity.

A closer look at the structure of the carbon nanotubes (that provide the framework for both the materials) using a TEM clearly showed that the pristine MWNT sponges were composed of thin and straight tubes with many residual catalyst particles trapped within their hollow cores. High-resolution TEM images of both the materials indicating these structural and morphological differences are shown in **Fig. 4.4**. Although the amount of residual particles in the B-doped tubes were considerably lower, both of these materials were endowed with superior magnetic properties. This magnetic response offers the ability to easily move the sponges around while being used as adsorbents, particularly for liquids.



**Figure 4.4:** TEM images of (a)-(b)  $CB_xMWNT$  sponges and (c)-(d) MWNT sponges, respectively. The high resolution TEM image of a  $CB_xMWNT$  sponge in (b) shows multiple elbows on the same tube. Long iron carbide particles observed within the hollow core of MWNT sponges. Average tube diameters are ~70nm and ~20 nm in  $CB_xMWNT$  and MWNT sponges, respectively.

TGA was performed on the pristine and  $CB_xMWNT$  sponges under air with a heating ramp of 10°C/min (**Fig. 4.5**). Both materials were found to be resistant to oxidation below 500°C. This was an indirect evidence of the presence of negligible amounts of non-crystalline carbon impurities such as amorphous carbon, which, if present, would burn at around 400°C or lower temperatures.<sup>313</sup> Once the oxidation commenced, the loss of carbon appeared to be smooth in the pristine MWNT sponges, whereas in case of CB<sub>x</sub>MWNT, there was a step in the weight loss. This was also reflected in the corresponding derivative weight loss curves. The derivative weight loss curve of pristine MWNT sponges showed a single sharp peak indicating a high purity material. The splitting in the oxidation for the case of CB<sub>x</sub>MWNT sponges could have been a result of B addition. Since the defective regions (elbows) were expected to oxidize at a lower temperature, the peak at 642°C before the complete oxidation of the CB<sub>x</sub>MWNTs at 714°C, could be attributed to this. It is also interesting to note that the oxidation of doped sponges started at a slightly higher temperature when compared to pristine sponges (610°C). This further demonstrates the effect of B-doping in improving the oxidation resistance of CNTs and was also consistent with other studies.<sup>314</sup>



**Figure 4.5:** Thermogravimetric analysis of 3-D spongy networks of MWNT showing weight loss and differential curves at a heating rate of  $10^{\circ}$ C/min in air: (a) CB<sub>x</sub>MWNT sponges and (b) pristine MWNT sponges.

Raman spectroscopic analysis of the sponges was carried out using a Renishaw inVia confocal micro-Raman spectrometer using a 50x objective and 514.5 nm as the laser excitation energy. The corresponding spectra of the samples are shown in **Fig. 4.6**. In both of the materials, the characteristic features of  $sp^2$  carbon – G peak, D peak and 2D peak – were observed. The ratio of D-band

intensity to G-band intensity  $(I_D/I_G)$  was higher for  $CB_xMWNT$  sponge as compared to pristine MWNT sponges, indicating the presence of more defects in the  $CB_xMWNT$  sponge as a result of boron doping.



Figure 4.6: Raman spectra of (a) CB<sub>x</sub>MWNT sponges (b) pristine MWNT sponges.

XRD measurements were also conducted in both types of MWNT sponges. The graphitic (002) peak was visible (~26°) in the XRD spectra of both  $CB_xMWNT$  and pristine MWNT sponges (**Fig. 4.7**). However, when comparing the full-width half maximum (FWHM) of the G(002) reflection in both materials, the  $CB_xMWNT$  sponges showed a lower value (sharper peak) than the pristine MWNT sponges, indicating a better degree of crystallinity in the B-doped material. The pristine MWNT material could have had a stacking disorder that caused a slight broadening of the (002) reflection. Iron carbide peaks were also clearly present in the pristine MWNT sample, when compared with a broad signal around  $45^{\circ}$  for the CB<sub>x</sub>MWNT sponges. This was consistent with the TGA data that exhibited a larger amount of residue (an indication of the oxides formed by catalyst particles) for the pristine MWNT sample after the sample was subjected to thermal analysis.



**Figure 4.7:** X-Ray diffraction analysis of (a)  $CB_xMWNT$  sponges (b) pristine MWNT sponges. The characteristic graphitic (002) reflection is visible in both spectra. However, many peaks corresponding to reflections of the residual catalyst particles are observed in the pristine MWNT sponges.

XPS characterization was used to determine the chemical bonding states and atomic quantification of carbon and oxygen in both the materials as well as that of boron in the CB<sub>x</sub>MWNT sponges (**Fig. 4.8**). The XPS analysis was performed using a Kratos Axis Ultra equipped with an Al-K $\alpha$  (1486 eV) X-ray source. The Xray spot was focused at 1 mm x 0.5 mm. XPS survey spectra were acquired with a pass energy of 80 eV, dwell time of 150 ms and step size of 0.3 eV. High resolution scans were carried out with a pass energy of 20 eV, dwell time of 800 ms for C1s, B1s and O1s, and 1200 ms for C11s, with a step size of 0.1 eV.



**Figure 4.8:** (a) XPS spectra of  $CB_xMWNT$  (red) and pristine MWNT sponges. (b)-(c) Deconvolution of the C1s and O1s spectra of both the samples. (d) B1s signal in the  $CB_xMWNT$  sponge sample indicating various B bonding states. (e) A noisy signal is observed for Cl 1s in the pristine MWNT sponge sample, indicating that the Cl atomic % is below the detection limit of XPS.

The C1s spectrum of both CB<sub>x</sub>MWNT and pristine sponges revealed one main peak at 284.2 eV attributed to the C-C sp<sup>2</sup> bonding configuration (**Fig. 4.8b**). The O1s spectra showed peaks close to 532.7 eV associated with O-C bonding states (**Fig. 4.8c**). Upon deconvolution of the B1s spectrum in CB<sub>x</sub>MWNT sponges, three underlying peaks were observed, corresponding to 187 eV (B-C bonding states), 189.7 eV (BC<sub>2</sub>O) and 192.9 eV (B<sub>2</sub>O<sub>3</sub>) (**Fig. 4.8d**). The overall atomic contents of each of these elements – B, O, and C - in the CB<sub>x</sub>MWNT were found to be 1.89 at%, 2 at% and 96.1 at%, respectively. Boron was mostly present in the higher energy state corresponding to  $B_2O_3$  (1.2 at%). The presence of  $B_2O_3$  in the CB<sub>x</sub>MWNT substantiated the TGA results that showed a higher oxidation resistance for this sample when compared to the pristine MWNT sponge sample. A high resolution scan of the Cl ls signal was also acquired to detect traces of chlorine in the pristine MWNT sponges since a chlorinated hydrocarbon was used as its growth precursor (**Fig. 4.8e**). However, the Cl 1s signal was not resolvable for accurate peak fitting analyses. The atomic percentages of O and C in the pristine MWNT sponges were 1.2% and 98.8%, respectively.

#### 4.2.3 Testing the physical properties: density, surface area, porosity

The surface area and porosity of CB<sub>x</sub>MWNT and pristine MWNT sponges were studied using liquid nitrogen porosimetry at -196°C. A comparison of adsorption and desorption behaviors of both materials is shown in **Fig. 4.9**. A continuous intake of N<sub>2</sub> was observed with increasing pressure along with a hysteresis on desorption, which are characteristics of a mesoporous materials. A gradual increase in the adsorption values was observed for relative pressures <1. This was followed by a steep rise in the adsorption values for a relative pressure close to ~ 1, particularly in the pristine MWNT sponge. This behavior, commonly observed in mesoporous materials, suggested the occurrence of capillary condensation.<sup>315</sup> During capillary condensation, the pores or capillaries in a porous material fills up with an adsorbate following an initial layer getting adsorbed on the walls of the pores. The BET surface area, pore volume and average pore sizes were determined and tabulated in **Table 4.3**. Although the nanotube diameters observed within  $CB_xMWNT$  sponges were much larger than those in pristine MWNT sponges, the surface area of  $CB_xMWNT$  sponges (68 m<sup>2</sup>g<sup>-1</sup>) was lower than that of the pristine MWNT sponges (105 m<sup>2</sup>g<sup>-1</sup>). These values were almost an order of magnitude lower than previously reported values.<sup>83</sup> The difference in the surface area values could be attributed to the tube morphology, particularly in  $CB_xMWNT$  sponges. The number of "elbow"-shaped junctions in the  $CB_xMWNT$  sponges was found to vary with the density of sponges as per other studies.<sup>84</sup> These junctions played a vital role in determining the ease of access of the gas molecules through the inner hollow regions and the inter-layer spacing of the multi-walled tubes. However, the average pore volumes were comparable for both the materials, with values of 0.23 cm<sup>3</sup>g<sup>-1</sup> for the CB<sub>x</sub>MWNT sponge, and 0.24 cm<sup>3</sup>g<sup>-1</sup> for the pristine, MWNT sponge.

Material	BET Surface Area (m <sup>2</sup> g <sup>-1</sup> )	Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	Avg. Pore Size (nm)
MWNT Sponge	105	0.24	6.82
CB <sub>x</sub> MWNT Sponge	68	0.23	9.62

**Table 4.3:** Liquid Nitrogen porosimetry results for MWNT and CB<sub>x</sub>MWNT sponges showing values for BET surface area, pore volume and average pore size for each material.



Figure 4.9: Nitrogen adsorption and desorption curves of  $CB_XMWNT$  and MWNT sponge at -196°C

#### 4.2.4 Mechanical properties of MWNT sponges

Mechanical testing of both of the sponge samples (with densities ranging from 12 mg cm<sup>-3</sup> to 29 mg cm<sup>-3</sup>) was performed using a custom built micro-indenter on sample sizes of 1mm in thickness and a 3 mm diameter. The results indicated significant differences in the plastic deformation behaviors of the pristine MWNT and CB<sub>x</sub>MWNT sponges (**Fig. 4.10**). The pristine MWNT sponges showed density-dependent behavior in plastic deformation, indicating that their plasticity could be tailored with density. The CB<sub>x</sub>MWNT sponges, on the other hand, exhibited density-independent behavior.



**Figure 4.10**: Plastic deformation (%) plotted as a function of density for CB<sub>x</sub>MWNT (red hollow triangles), pristine MWNT sponges (solid black squares) and a linear fitting for the pristine MWNT showing its density dependent behavior.

**Figure 4.11** shows the stress-strain curves of both the sponges at a compressive loading rate of 1µm s<sup>-1</sup> for up to eight cycles. The stress-strain curve of CB<sub>x</sub>MWNT (density 25.5 mg/cm<sup>3</sup>) showed typical strain-dependence that is usually found in polymers, biological material etc., unlike the pristine MWNT sponge (density 24.2 mg cm<sup>-3</sup>).<sup>316</sup> Hysteresis in the two stress-strain curves indicated viscoelasticity in both materials. The pristine MWNT sponges' average plastic deformation attained 12% ( $\rho = 17 \sim 25$  mg cm<sup>-3</sup>) while for the CB<sub>x</sub>MWNT sponges, the measured value was 4.6% ( $\rho = 13 \sim 29$  mg/cm<sup>-3</sup>). The area under the stress-strain curve gives an indication of the stiffness of a material. Thus, from the stress-strain curves obtained for both types of sponges it was observed that the pristine MWNT sponge.



**Figure 4.11**: Stress vs. Strain curves showing 1<sup>st</sup>, 2<sup>nd</sup>, 7<sup>th</sup> and 8<sup>th</sup> loading-unloading cycles for (a) Pristine MWNT sponge with density 24.2 mg/cm<sup>3</sup> and (b) CB<sub>x</sub>MWNT sponge with a density 25.5 mg/cm<sup>3</sup>.

#### 4.3 Applications of 3D MWNT based sponges

A comparison of CO<sub>2</sub> and CH<sub>4</sub> gas-adsorption performance of B-doped and pristine 3D MWNT sponges was carried out. The sponges exhibited remarkable adsorption capacities for CO<sub>2</sub> and CH<sub>4</sub>. The CO<sub>2</sub> adsorption-desorption isotherms for the two types of sponges are shown in **Fig. 4.12**. The pristine MWNT sponge, which had a higher surface area between the two materials, displayed a remarkable adsorption of CO<sub>2</sub> with an uptake capacity of 28 mmol g<sup>-1</sup> at higher pressures. This suggested that the pristine MWNT sponge had an accessible pore structure, and hence the CO<sub>2</sub> gas molecules could easily reach its active surface sites when compared to the CB<sub>x</sub>MWNT sponge. Large hysteresis was also observed while comparing the adsorption and desorption curves, particularly in the pristine MWNT sponge sample. This could have arisen from strong adsorbent-adsorbate interactions between the CNTs and CO<sub>2</sub> molecules. Other porous carbons that have demonstrated potential for CO<sub>2</sub> adsorption possess surface areas that are an order of magnitude higher than the materials used in this study.<sup>317</sup> However, the CO<sub>2</sub> adsorption capacities of pristine MWNT sponge surpassed the values reported for other porous graphitic carbon materials, such as graphene oxide derived carbons (GODCs) even at higher adsorption pressures (35 b).<sup>317</sup> Although the surface areas have previously shown a direct correlation with the adsorption capacities of these porous carbons, the synergy among the structure of the material, pore size, pore volume, and accessibility of the pores is also an important factor to consider in this study.



Figure 4.12: CO<sub>2</sub> adsorption and desorption curves of CB<sub>X</sub>MWNT and MWNT sponges.

The methane adsorption patterns (**Fig. 4.13**) for both of the materials were also in correlation with their BET surface areas. The pristine MWNT sponges, with higher BET surface area, exhibited a superior performance while a negligible adsorption of  $CH_4$  on the  $CB_xMWNT$  sponges was observed. The hysteresis loop of MWNT

sponges for CH<sub>4</sub> adsorption-desorption was indicative of the strong interactions of CH<sub>4</sub> on the carbon nanotubes.



Figure 4.13: CH<sub>4</sub> adsorption and desorption curves of CB<sub>X</sub>MWNT and MWNT sponge.

These results and other studies on liquid adsorption indicate that CNT based porous sponge-like materials are able to provide a suitable framework for the adsorption of liquids and gases.<sup>82,83</sup> Moreover, the mechanical, chemical and thermal stabilities of these sponges, as seen from TGA studies, render them to be robust for gas adsorption compared to other porous carbons.<sup>317–320</sup> In addition, these materials are highly multi-functional in nature and their electromagnetic shielding efficiencies were also studied recently.<sup>321</sup> Investigations of these materials for bio-applications are currently underway.

#### 4.4 Carbon Nanotentacles

The effect of sulfur and boron on CNT growth has been a subject of interest among carbon researchers for more than a decade now.<sup>83,238,322</sup> There have been

many reports on the role of sulfur during CNT synthesis.<sup>305,322–325</sup> In some cases, sulfur has been effective in promoting CNT growth whereas in other cases, adding minute quantities of sulfur has resulted in tube branching.<sup>307,323</sup> Previously reported theoretical and experimental results have also shown that sulfur favours the formation of stacked-cone morphology in CNTs.<sup>239</sup> However, doping CNTs with boron has shown dramatic changes in the tube morphology, such as introducing "kinks" or "elbow-shape" junctions.<sup>83</sup> In addition, changes in the vibrational properties have been observed using Raman spectroscopy, such as increased D-band intensity and shifting of 2D band.<sup>326</sup>

Here we report the effects of substitutional co-doping of boron and sulfur on the structure and properties of CNTs. Upon adding doping levels (<1 at%) of boron and sulfur in the precursor solution during CVD, the growth of hierarchical structures consisting of 3D-branched CNTs resembling "tentacles" was observed. This appears to be the first systematic study involving the synergy between boron and sulfur in promoting 3D CNT network growth. Elemental and high resolution imaging analyses were performed using HRTEM. When comparing these results with previous theoretical calculations, a possible growth mechanism for the growth these novel "nanotentacles" could be rationalized.

#### 4.4.1 Experimental Methods

Carbon nanotentacles were synthesized using an AACVD process involving a floating catalyst. The precursor solution containing a carbon source (toluene), catalyst (2.5wt% ferrocene) and dopants (0.15wt% thiophene as the sulfur source and 0.7wt% triethylborane as the boron source) was sprayed into a quartz reactor

tube kept inside a furnace, heated to 860°C. Argon was used as the inert carrier gas to transport the mist through the reactor tube. While the furnace ramped up to 860°C, the argon flow rate was kept at 0.5 ltr/min. Once the furnace temperature reached 860°C, a higher argon flow rate (2.5 ltr/min) was introduced. The reaction was carried out for 30 minutes, after which the tube was allowed to cool down. The nanotentacles were collected from the inside of the tube, between 3-6 inches of the tube within the furnace.

Structural analysis of the nanotentacles was carried out using an FEI Nova630 SEM equipped with a field emission source at a 5kV operating voltage. A small amount of the sample was dispersed onto a holey carbon copper grid (200 mesh) for HRTEM and compositional analysis. JEOL 2010F operating at 200 kV, and FEI Titan<sup>3</sup> G2\* were employed for the HRTEM as well as for EDS and EELS.

#### 4.4.2 Results and discussion

The yield from the AACVD process described in the previous section typically ranged from 10 - 30 mg of material. The microstructure of the black soot collected from the inner walls of the quartz tube reactor was analyzed using SEM (**Fig. 4.14**).



**Figure 4.14:** SEM images of carbon nanotentacles. (a)-(b) Low magnification images showing entangled carbon fiber like structures. (c) Conical branches growing out of CNTs in three dimensions are observed in high magnification SEM images.

It was observed that the addition of small amounts of B and S helped to create very peculiar nanotube morphologies, as seen in the SEM images. Low magnification images revealed numerous tubular structures consisting of CNTs and carbon nanofibers (CNFs) entangled with each other. At higher magnifications, tentacle-like protrusions or branches from these tubes were noted (**Fig. 4.14c-e**). Typically, these nano-tentacles consisted of a thick hollow central core made of CNTs which were 1 - 5 um long and 50 - 300 nm in diameter. The conical branches from CNT stems were usually 200-400 nm in length.

**Figure 4.15** shows TEM images of the nanotentacles with many residual catalyst particles (Fe and  $Fe_xS_y$ ) attached to the branches. It should be noted that

most of the particles were seen trapped within the hollow core of the conical branches, close to the tip of the branches. This was indicative that the catalyst particles attached themselves onto the central stem of the tentacle and catalyzed the growth of the secondary branches. The size of the inner core diameters of the branches were also consistent with the catalyst particle sizes observed.



**Figure 4.15:** TEM images of carbon nanotentacles showing 3D branching and network formation. Different morphological features such as (a) multi-node CNTs with branches, and (b) thick carbon nanofibers with branches are shown. (c) The hollow core within the central CNT is shown in this TEM image. (d) Numerous residual catalyst particles are seen entrapped within the branches in the nanotentacles.

From the HRTEM images in **Fig. 4.16**, the tubular branches arising from an inner CNT stem are clearly seen. These branches were mostly perpendicular to the

inner core and also featured uncapped ends. In some tubes, these branches were more widely spaced than in others. High magnification images revealed a hollow structure within the inner core/stem from which the conical branches grew outward (**Fig. 4.16b**). The growth of these branches were initiated from small "bumps" that formed on the central CNT stem as seen in **Fig. 4.16c**. The observation of these bumps were consistent with previous studies that revealed sulfur atoms induced positive curvatures on the CNTs. As we explain later in our proposed growth model, these bumps act as anchoring sites for the iron catalyst particle to enable the growth of branches on the CNTs. The graphitic planes in the CNT walls were also stacked at an angle to the central axis (**Fig. 4.16c-d**). These "stacked cone" type of morphological features also helped to confirm the effect of sulfur doping as previously reported.<sup>239,305</sup>


**Figure 4.16:** (a) HRTEM image of carbon nanotentacles showing the cone shaped branches growing perpendicularly outward from the central CNT. (b) An isolated CNT stem with a hollow core, showing initial stage of branch formation. "Bumps" are seen on the tube surface, which enable the anchoring of catalyst particles for branch growth. (c) High resolution image showing the hollow stem and the graphitic planes stacked at an angle to the central CNT axis. (d) High resolution image of a bump showing positive curvature induced on the tube surface.

In order to thoroughly examine the elemental distributions within the nanotentacles, we performed EELS and EDX analysis. Representative EELS spectrum (collected from the region circled in the inset of **Fig. 4.17a**) of a nanotentacle exhibiting the presence of B and C is shown in **Fig. 4.17a**. The peaks at 188 eV and 284 eV belonging to the k absorption edges of B and C were observed, respectively. As expected, the signal counts from C were many orders of magnitude higher than that from B. High resolution EELS area maps were acquired

from the branches as shown in **Fig. 4.17b-e**. The signal from B was found to increase close to the tips of the branches as shown in **Fig. 4.17c-d**. EELS signal from S was not within detectable limits and hence we used EDS to confirm the presence of sulfur within samples.



**Figure 4.17**: (a) EELS spectrum acquired from the nanotentacles (from the region showed in the inset). (b) and (d) HAADF images of the region from which high resolution EELS scan was performed. The corresponding EELS maps showing the distribution of boron and carbon are shown in (c) and (e) respectively.

EDS area scans were performed on the nanotentacles as shown in **Fig. 4.18a** and confirmed the presence of sulfur by observing its characteristic K $\alpha$  peak at 2.3 keV. The presence of residual particles was also indicated by the peak corresponding to Fe - K $\alpha$  at 6.4 keV. Copper peaks observed in the spectrum originated from the copper TEM grid used for sample support.



**Figure 4.18**: (a) HAADF image of a nanotentacle subjected to EDS analysis. (b) Carbon, (c) iron and (d) sulfur EDS maps from the region shown in (a).

From the EDS area maps, it was evident that the sulfur tends to occupy the regions where the "bumps" start to form and these start accumulating catalyst. The regions with fully grown branches did not show strong sulfur signals. **Figure 4.19** shows more EDS area maps of sulfur acquired from nanotentacles with many "bumps", where the branches were just beginning to form. Strong signals were observed at the regions with positive curvature within the tube walls.



**Figure 4.19**: (a) HAADF image of a nanotentacle area mapped with EDS in (b). (b) The distribution of sulfur on the central CNT stem showing strong signals at the "bumps". (c)-(e) TEM, HAADF and EDS area map respectively of a magnified region of the nanotenacles. (f)-(h) Similar observations were recorded another region of the sample many positive curvatures. The sulfur map in (h) corresponds to the area shown in the TEM image in (f) and HAADF image in (g).

The EDS results are consistent with previous reports showing the presence of sulfur at regions on the CNTs where branching occurred.<sup>239</sup> This also established the reason why "cup stacked" morphology was observed for the CNT walls in these samples, as sulfur tends to widen the tube diameters.<sup>305</sup>

### 4.5 Nanotentacle growth mechanism

The dramatic morphological changes induced by adding small amounts of boron and sulfur during the CNT synthesis were correlated with the elemental analyses results in order to propose the following growth model. It is expected that the starting CNT material that form during the growth process consists of tubular stems with "stacked cone" morphology. Molecular dynamics (MD) calculations have previously shown that sulfur has the tendency to widen CNT diameters by forming heptagonal carbon rings, thus leading to the formation of graphitic walls stacked at certain oblique angles to the central CNT axis. This is presumed to be the first step in the growth of nanotentacles (Fig. 4.20a). As carbon species agglomerate, the widening of the nanotube diameters leads to the formation of bumps on the tubular surface (Fig. 4.20b). From EDS analyses, sulfur was detected close to the bumps on the newly forming branches. These bumps create a rough surface which facilitates the accumulation of Fe nanoparticles. In addition, the sulfur atoms also diffuse into the catalytic iron particles to form  $Fe_xS_y$  as revealed by EDS analyses. Meanwhile, the boron atoms get adsorbed on to the dangling edges of the newly forming bumps, preventing them from capping (Fig. 4.20b-c). The anchored particles (containing Fe and S), then catalyze the radial growth of the tubular branches while boron continues to adsorb onto the catalyst help to prevent tube closure, and are thus seen at the tips of the tubular branches (Fig.4.20d). The presence of boron atoms at the tips of the branches in the EELS maps shown in the previous section further supports this model. This is also consistent with previous reports on boron enabling the growth of long tubes by preventing tube closure.<sup>327</sup>,

showing that boron atoms tend to be deposited at the tips of CNTs.<sup>327</sup> The growth of the branches stops when the carbon feedstock is no longer available. Thus, both sulfur and boron atoms work synergistically in creating a hierarchical 3D structure composed of branched CNTs during the CVD process.



**Figure 4.20**: (a)-(d) Proposed growth model for growing carbon nanotentacles. The first step involves sulfur atoms inducing "bumps" or regions with positive curvature on the tubes via the formation of heptagons. The catalyst particles are anchored within these bumps and catalyze the growth of branches. The boron atoms help to keep the catalyst active during the growth of the branches.

### 4.6 Conclusions

In summary, the AACVD process was explored for creating covalent 3D network structures with CNTs as the fundamental building blocks. The effect of dopants such as boron and sulfur during CNT growth was investigated. The structure and properties of boron-doped and pristine 3D MWNT sponges were studied thoroughly in order to identify potential avenues for practical applications. To the best of our knowledge, the CVD synthesis of hierarchical structures by co-doping CNTs with boron and sulfur is here reported for the first time. Interestingly, these materials exhibited tentacle-like structure, with conical tubes protruding outwards from a thick CNT stem. A systematic study of their structure and composition shed light on their growth mechanism. These novel materials are promising for various applications such as oil and gas adsorption, biological scaffolds, energy storage, sensors, and catalytic supports because of their multifunctional properties.<sup>72,73,328</sup>

# **5** Conclusions

## 5.1 Summary of contributions

After almost three decades of fullerene research, two decades of carbon nanotube research and a decade of graphene research, we are still posed with a question – "what is next in carbon science?" The driving force for this work has been the conviction that carbon nanoscience has "plenty of room" for problem-solving and innovation. The major findings in this study were the development of novel synthetic approaches that enabled the controlled growth of complex 3D architectures using CNTs. This was achieved for both SWNTs and MWNTs using growth-based and post-growth processing approaches. The structures were synthesized in order to establish covalent junctions between CNTs that result in a 3D network. These covalently interconnected 3D CNT networks helped to take advantage of many of the favorable properties of CNTs such as their lightweight, thermal and chemical stability, electrical and thermal conductivity, as well as mechanical robustness, at a macro-scale.

**Chapter 2** delved into a novel post-growth processing approach that involved two steps for the creation of 3D MWNT networks. A sol-gel process used for coating MWNTs with SiO<sub>x</sub>, followed by SPS at 1800°C and 80MPa, were carried out to create such a SiC-CNT composite material. This was a simple yet efficient way to create covalent junctions among MWNTs; SiO<sub>x</sub> underwent carbothermal reduction during the sintering process (at 1800°C) to form SiC linkers in between tubes. Therefore, lightweight, thermally and electrically conducting composites were fabricated as a result of this novel process. This work was published in *Advanced Functional Materials*.<sup>62</sup> **Figure 6.1**, which shows a graphical illustration of covalently interconnecting CNTs with a "welding" material, was selected as the journal cover.<sup>62</sup>



Figure 6.1: Cover of Adv. Funct. Mater. 25, (2015).

In **Chapters 3** and **4**, the use of dopant-assisted CVD processes to create novel 3D networks of CNTs was discussed. Previous theoretical studies on the doping of SWNTs with Si have indicated the possibility of forming short diameter tubes and inducing electronic structural changes within nanotubes.<sup>240</sup> The present study shed light on the Si doping mechanism by a careful analysis of Si-doped SWNTs using

Raman spectroscopy and electronic transport measurements. Density functional tight-binding (DFTB) calculations of the electronic transport in the Si-doped SWNTs were also performed to elucidate the conduction mechanism that was experimentally observed in Si-SWNTs. Our findings confirmed that the Si doping helped to selectively grow smaller diameter SWNTs during CVD. In addition, the addition of Si resulted in a higher degree of defects on the nanotubes, as observed from Raman spectroscopy and electronic transport measurements. Furthermore, electronic transport calculations revealed an increased coupling and quantum conductance across the tubes within a bundle when doping with Si. This suggested the establishment of covalent interconnections between SWNTs *via* the formation of C-Si-C bridging or a C-Si-Si-C dimer (**Fig. 6.2**). This work was recently submitted to the journal *Carbon* (June 2016) and is currently under review.



**Figure 6.2**: A molecular model of covalently interconnected SWNT tubes within a bundle by the formation of C-Si-Si-C dimers. (*Image Courtesy: Eduardo Cruz-Silva*)

Macro-porous 3D networks of CNTs with many covalent junctions were also synthesized by adding boron and sulfur during CVD growth. Doping with boron resulted in "sponge-like" structures that were highly flexible, robust, and thermally stable when compared to its un-doped counterpart. The study on gas adsorption performance of these 3D CNT sponges yielded novel results, including CO<sub>2</sub> adsorption capacities that reached up to 28 mmol g<sup>-1</sup>. To the best of our knowledge, the effects of hetero-doping with sulfur and boron during CVD growth was examined and reported here for the first time. The hetero-doping resulted in the growth of hierarchical 3D CNT structures resembling "nano-tentacles". A detailed analysis of the structure of these materials was carried out by electron microscopy and state-of-the-art elemental analysis. By comparing these analyses with results from previously reported theory on the effects of boron and sulfur doping, a growth mechanism for the "nanotentacles" was proposed. These materials could also be used in energy storage applications including Li-ion batteries and supercapacitor electrodes.

## 5.2 Future work

This thesis presented pioneering results in novel synthetic methods for creating 3D networks of CNTs. However, further work is still necessary in order to explore practical applications for these materials. Some of the applications that will be explored include energy storage, thermal management, 3D scaffolds for tissue engineering and multi-functional composites. Recently, there have been some reports on creating covalent interconnections between different allotropes of carbon at the nanoscale.<sup>329</sup> However, developing low-cost and reliable methods to scale up the production of these materials are still very challenging. On-going work involves the CVD growth of CNT-graphene hybrid materials with a focus on creating covalent interconnections between and CNTs.

### **5.3** List of publications

#### Journals:

- <u>L. Pulickal Rajukumar</u>, E. Cruz-Silva, A. L. Elías, J. E. Slimak, S. Tarragó,
   A. M. Gómez, J. T. Portas, N. Perea-López, H. Terrones, M. Terrones,
   "Silicon-doped carbon nanotubes: controlling tube diameter and electronic transport", (2016), submitted.
- Z. Guo , Z.-H. Huang, R. Lv, <u>L. Pulickal Rajukumar</u>, N. Perea-Lopez, Y. Yang, M. Terrones & F. Kang, "Buckling and seaming graphene sheets into tubes through confinement reaction of GO/carbon hybrid nanofiber", (2015), submitted.
- W. Zhao, A. L. Elias, <u>L. Pulickal Rajukumar</u>, H. Kim, D. J. O'Brien, B. K. Zimmerman, E. Penev, M. Terrones, B. Yakobson, B. Wei, X. L. Lu, J. Suhr, "Controllable and Predictable Viscoelastic Behaviors of 3D Boron-doped Multiwalled Carbon Nanotube Sponges", Particle & Particle Systems Characterization, 33(1), 21–26 (2016).
- L. Pulickal Rajukumar, M. Belmonte, J. E. Slimak, A. L. Elías, E. Cruz-Silva, N. Perea-López, A. Morelos-Gómez, H. Terrones, M. Endo, P. Miranzo, M. Terrones, "3D nanocomposites of covalently interconnected multi-walled carbon nanotubes with SiC with enhanced thermal and electrical properties", Advanced Functional Materials, 25(31), 4985-4993 (2015).
- R. Lv, H. Terrones, A. L. Elías, N. Perea-López, H. R. Gutiérrez, E. Cruz Silva, L. Pulickal Rajukumar, M. S. Dresselhaus and M. Terrones, "Two-

dimensional transition metal dichalcogenides: Clusters, ribbons, sheets and more", **Nano Today**, 10(5), 559–592 (2015).

- W. Zhao, C. Shan, A. L. Elias, <u>L. Pulickal Rajukumar</u>, D. J. O'Brien, M. Terrones, B. Wei, J. Suhr, and X. Lucas Lu, "Hyperelasticity of Three-Dimensional Carbon Nanotube Sponge Controlled by the Stiffness of Covalent Junctions", Carbon, 95, 640–645 (2015).
- P. A. M. dos Santos, M. R. Gallas, C. Radtke, E. V. Benvenutti, A. L. Elias, <u>L.</u> <u>Pulickal Rajukumar</u>, H. Terrones, M. Endo, M. Terrones, T. M. H. Costa, "Stable and solid pellets of functionalized multi-walled carbon nanotubes produced under high pressure and temperature", Journal of Nanoparticle Research, 17:238 (2015).
- Z. González, P. Álvarez, C. Blanco, S. Vega-Díaz, F. Tristán-López, <u>L.</u> <u>Pulickal Rajukumar</u>, R. Cruz-Silva, A. L. Elías, M. Terrones, R. Menéndez, "The influence of carbon nanotubes characteristics in their performance as positive electrodes in vanadium redox flow batteries." Sustainable Energy Technologies and Assessments, 9, 105-110, (2015).
- R. Cruz-Silva, A. Morelos-Gomez, H. Kim, H. Jang, F. Tristan, S. Vega-Diaz, <u>L. Pulickal Rajukumar</u>, A. L. Elias, N. Perea-Lopez, J. Suhr, M. Endo, M. Terrones, "Super-stretchable graphene oxide macroscopic fibers with outstanding knotability fabricated by dry film scrolling", ACS Nano, 8(6), 5959–5967 (2014).
- M. Crespo, M. González, A. L. Elías, <u>L. Pulickal Rajukumar</u>, J. Baselga, M. Terrones, J. Pozuelo, "Ultra-light carbon nanotube sponge as an efficient

electromagnetic shielding material in the GHz range", **Physica Status Solidi** (**RRL**), (2014).

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#### **Book Chapter:**

 A. L. Elías, N. Perea-López, <u>L. Pulickal Rajukumar</u>, A. McCreary, F. López-Urías, H. Terrones, M. Terrones, "Three-dimensional Nanotube Networks and a New Horizon of Applications", Book Chapter 17, Nanotube Superfiber Materials, 457-493, (2013).

#### Manuscripts under preparation:

- 14. <u>L. Pulickal Rajukumar</u>, J. P. Pedrozo, A. L. Elías, W. Zhao, B. Wei, X. L. Lu, J. Suhr, A. J. Hernández-Maldonado, M. Terrones, "Gas adsorption properties of carbon nanotube sponges".
- 15. <u>L. Pulickal Rajukumar</u>, A. L. Elías, A. McCreary, A. L. M. Reddy, K. Kalaga, N. Perea-López, M. E. Audiffred, D. Swanson, H. R. Gutiérrez, R. Vajtai, V. Meunier, B. G. Sumpter, P. M. Ajayan, H. Terrones, M. Terrones, "Dopants as morphology promoters: a fundamental study of the role of boron and sulfur in the formation of MWNT junctions".
- 16. C. Guerrero-Bermea, <u>L. Pulickal Rajukumar</u>, A. Dasgupta, M. Terrones, S. Sepulveda Guzman, R. Cruz-Silva, "2D and 3D Composites based on graphene oxide and other hexagonal structures: synthesis, morphological haracterization and applications".
- 17. A. Dasgupta, <u>L. Pulickal Rajukumar</u>, C. Rotella, M. Terrones, "Synthesis and environmental applications of 3D carbon structures".

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### APPENDIX



**Figure A.1:** (a) Raman spectra of pristine SWNT (black), and Si-SWNTs synthesized with 0.06 wt% (red) and 0.10 wt% MTMS acquired with 514.5 nm wavelength laser excitation. (b) High resolution RBM spectra of these samples showing a preference for smaller diameter tubes on Si doping.

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