Structure and Morphology Control in Carbon Nanomaterials for Nanoelectronics and

Hydrogen Storage

by

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry in the Graduate School of Duke University

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ABSTRACT

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Abstract

Carbon nanomaterials have a wide range of promising and exciting applications. One of the most heavily investigated carbon nanomaterial in recent history has been the carbon nanotube. The intense interest in carbon nanotubes can be attributed to the many exceptional characteristics which give them great potential to revolutionize modern mechanical, optical and electronic technologies. However, controlling these characteristics in a scalable fashion has been extremely difficult. Although some progress has been made in controlling the quality, diameter distribution and other characteristics of carbon nanotube samples, several issues still remain. The two major challenges which have stood in the way of their mainstream application are controlling their orientation and their electronic characteristics. Developing and understanding a Chemical Vapor Deposition based carbon nanotube synthesis method has been the major focus of the research presented here. Although several methods were investigated, including the so-called “fast-heating, slow-cooling” and large feeding gas flowrate methods, it was ultimately found that high-quality, perfectly aligned carbon nanotubes from a variety of metal catalysts could be grown on quartz substrates. Furthermore, it was found that using MeOH could selectively etch small-diameter metallic carbon nanotubes, which ultimately led to the productions of perfectly aligned single-walled carbon nanotube samples consisting almost entirely of semiconducting carbon nanotubes. Thiophene was utilized to investigate and support the hypothesized role of MeOH in producing these selectively gown semiconducting carbon nanotube samples. Additionally, this sulfur-containing compound was used for the first time to demonstrate a two-fold density enhancement in surface grown carbon nanotube samples. This method for selectively producing perfectly aligned semiconducting carbon
nanotubes represents a major step towards the integration of carbon nanotubes into mainstream applications.

Although extremely useful in a variety of technologies, carbon nanotubes have proven impractical for use in $\text{H}_2$ storage applications. As such, microporous carbons have been heavily investigated for such ends. Microporous carbons have distinguished themselves as excellent candidates for $\text{H}_2$ storage media. They are lightweight and have a net-capacity of almost 100%, meaning that nearly all of the $\text{H}_2$ stored in these materials is easily recoverable for use in devices. However, developing a microporous carbon with the appropriately small pore diameters (~1 nm), large pore volumes (>1 cm$^3$) and large surface areas (>3000 m$^2$/g) has proven exceedingly difficult. Furthermore, maintaining the ideal graphitic pore structure has also been an unresolved issue in many production means. Several microporous carbon synthesis methods were investigated herein, including inorganic and organically templated production schemes. Ultimately, thermally treating poly (etherether ketone) in CO$_2$ and steam environments was found to produce large surface area porous carbons (>3000 m$^2$/g) with the appropriately small pore diameters (<3 nm) and large pore volumes (>1 cm$^3$) necessary for optimized storage of $\text{H}_2$. Furthermore, the surface chemistry of these pores was found to be graphitic. As a result of these ideal conditions, these porous carbons were found to store ~5.3 wt.% $\text{H}_2$ at 77 K and 40 bar. This represents one of the most promising materials presently under investigation by the United States Department of Energy $\text{H}_2$ Sorption Center of Excellence.

The success of both of these materials demonstrates the diversity and promise of carbon nanomaterials. It is hoped that these materials will be further developed and will continue to revolutionize a variety of vital technologies.
Dedication

I would like to dedicate this to my loving family. Without their love and support, I would never have been able to develop into the person that I am today. I am eternally grateful to them.
Contents

Abstract......................................................................................................................................................iv

List of Tables ..................................................................................................................................................xi

List of Figures ...............................................................................................................................................xii

Acknowledgements ........................................................................................................................................xxiv

1. Introduction ...............................................................................................................................................1

1.1 Introduction to Carbon Nanotubes .................................................................................................1

1.1.1 Carbon Nanotube Discovery ........................................................................................................1

1.1.2 Carbon Nanotube Properties (Electronic, Optical, Mechanical Structure) .......................2

1.1.2.1 Carbon Nanotube Structure ..................................................................................................2

1.1.2.2 Carbon Nanotube Band Structure and Electronic Structure ...........................................4

1.1.2.3 Carbon Nanotube Optical Properties ................................................................................10

1.1.2.4 Carbon Nanotube Mechanical Structure ...........................................................................14

1.1.3 Carbon Nanotube Synthesis .......................................................................................................14

1.1.3.1 Arc Discharge ......................................................................................................................15

1.1.3.2 Laser Ablation .....................................................................................................................17

1.1.3.3 Chemical Vapor Deposition (CVD) ..................................................................................17

1.1.4 Carbon Nanotube Applications .................................................................................................21

1.1.4.1 Carbon Nanotube Composites ..........................................................................................21

1.1.4.2 Carbon Nanotube FETs/Sensors ......................................................................................24

1.1.4.3 Carbon Nanotubes in Energy ...........................................................................................31

1.1.5 Carbon Nanotube Challenges ....................................................................................................36

1.2 Introduction to Micro/Mesoporous Carbons .............................................................................37

1.2.1 Alternative Energy and the DOE H₂ Storage Goals ..............................................................37
1.2.2 Materials for H\textsubscript{2} Storage ........................................................................................................... 45
  1.2.2.1 Metal Hydrides ......................................................................................................................... 45
  1.2.2.2 Metal Organic Frameworks (MOFs) ....................................................................................... 47
  1.2.2.3 Porous Carbons ...................................................................................................................... 49
1.2.3 Micro/Mesoporous Carbon (Synthesis Background) ................................................................. 53
  1.2.3.1 Templated Synthesis ................................................................................................................ 53
  1.2.3.2 Carbide-Derived Carbons (CDC) .......................................................................................... 54
  1.2.3.3 Polymer Thermal Treatment/Activation ................................................................................ 58

2. Carbon Nanotube Orientation Control .............................................................................................. 63
  2.1 Introduction ..................................................................................................................................... 63
  2.2 Fast Heating Slow Cooling ............................................................................................................. 65
    2.2.1 Materials/Experimental .......................................................................................................... 65
    2.2.2 Results/Discussion .................................................................................................................. 68
    2.2.3 Summary .................................................................................................................................... 74
  2.3 Horizontally Aligned SWCNT on Quartz from Various Metal Catalysts ........................................ 74
    2.3.1 Materials/Experimental .......................................................................................................... 74
    2.3.2 Results/Discussion .................................................................................................................. 75
    2.3.3 Summary .................................................................................................................................... 84
  2.4 Dense SWNT Arrays and High-Throughput Suspended Nanotube Devices .................................... 85
    2.4.1 Introduction ............................................................................................................................... 85
    2.4.2 Materials/Experimental .......................................................................................................... 86
    2.4.3 Results/Discussion .................................................................................................................. 90
    2.4.4 Summary .................................................................................................................................... 94
  2.5 Size-Enhanced Diffusion in Melting Iron Nanoparticles (Size Dependence) ............................... 95
    2.5.1 Introduction ............................................................................................................................... 95
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5.2 Materials/Experimental</td>
<td>95</td>
</tr>
<tr>
<td>2.5.3 Results/Discussion</td>
<td>96</td>
</tr>
<tr>
<td>2.5.4 Summary</td>
<td>102</td>
</tr>
<tr>
<td>2.6 Summary</td>
<td>102</td>
</tr>
<tr>
<td>3. Carbon Nanotube Electronic Structure Control</td>
<td>104</td>
</tr>
<tr>
<td>3.1 Introduction</td>
<td>104</td>
</tr>
<tr>
<td>3.2 Selective Growth of Aligned Semiconducting-SWCNT on Quartz Substrates</td>
<td>105</td>
</tr>
<tr>
<td>3.2.1 Materials/Experimental</td>
<td>105</td>
</tr>
<tr>
<td>3.2.2 Results/Discussion</td>
<td>107</td>
</tr>
<tr>
<td>3.2.3 Summary</td>
<td>119</td>
</tr>
<tr>
<td>3.3 Sulfur Assisted Density and Quality Enhancement of Aligned Single-Walled Carbon Nanotube Thin Films on Quartz Substrates</td>
<td>119</td>
</tr>
<tr>
<td>3.3.1 Introduction</td>
<td>119</td>
</tr>
<tr>
<td>3.3.2 Materials/Experimental</td>
<td>120</td>
</tr>
<tr>
<td>3.3.3 Results/Discussion</td>
<td>121</td>
</tr>
<tr>
<td>3.3.4 Summary</td>
<td>135</td>
</tr>
<tr>
<td>3.4 Direct Observation of the High Affinity Interaction between Carbon Nanotubes and Quartz</td>
<td>136</td>
</tr>
<tr>
<td>3.4.1 Materials/Experimental</td>
<td>136</td>
</tr>
<tr>
<td>3.4.2 Results and Discussions</td>
<td>137</td>
</tr>
<tr>
<td>3.4.3 Summary</td>
<td>146</td>
</tr>
<tr>
<td>3.4 Summary</td>
<td>147</td>
</tr>
<tr>
<td>4. Micro/Mesoporous Carbon for H₂ Storage</td>
<td>150</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>150</td>
</tr>
<tr>
<td>4.2 Inorganically and Organically Templated Porous Carbons</td>
<td>151</td>
</tr>
<tr>
<td>4.2.1 Inorganically Templated Porous Carbons</td>
<td>151</td>
</tr>
</tbody>
</table>
4.2.1.1 Materials/Experimental ................................................................. 151
4.2.1.2 Results/Discussion ........................................................................ 152
4.2.2 Organically Templated Porous Carbons ........................................... 156
  4.2.2.1 Materials/Experimental ............................................................... 156
  4.2.2.2 Results/Discussion ........................................................................ 157
4.2.3 Summary .......................................................................................... 161
4.3 H₂ Storage in Microporous Carbons from PEEK Precursors .............. 161
  4.3.1 Introduction ....................................................................................... 161
  4.3.2 Materials/Experimental Details ..................................................... 162
    4.3.2.1 CO₂ Thermal Treatment ............................................................. 162
    4.3.2.2 Steam Thermal Treatment .......................................................... 164
    4.3.2.3 Analysis ...................................................................................... 164
  4.3.3 Results/Discussion ........................................................................... 165
  4.3.4 Summary .......................................................................................... 180
4.4 Summary .............................................................................................. 181
5. Summary and Conclusions .................................................................... 182
References .................................................................................................. 186
Biography .................................................................................................... 196
List of Tables

Table 1[59] Porous carbons obtained from chemical activation. It is obvious from this table that activated carbons can be synthesized with large surface areas (>2000 m$^2$/g) and pore volumes (>1.9 cm$^3$/g). .................................................................................................................................................. 62

Table 2 Average length of carbon nanotubes produced from nanoparticles with increasing diameters. It can be seen from this data that, as the nanoparticle diameter increases, the average length of nanotube products per unit time decreases. .................... 99

Table 3 The materials produced by thermally treating PEEK under different chemical environments have impressive H$_2$ gravimetric and volumetric uptakes compared to other pure and doped carbon materials presently being investigated. Materials in blue represent CO$_2$ derived products whereas those in red represent steam treated products. Materials being used for comparison are in black. § Note: All H$_2$ gravimetric uptake measurements were done at 0.2 MPa, 77 K unless otherwise specified. .............................. 178
List of Figures

Figure 1 A) Graphene sheet displaying the rolling vector (Ch), nanotube axis (T) and graphene lattice vectors (a₁ and a₂). The rolling vector is defined as C_h = nα₁ + mα₂ and connects two crystallographically equivalent carbon atoms. Therefore, this vector describes the direction along which a graphene sheet would be rolled to form a carbon nanotube. This determines the helicity and therefore many of the characteristics of the carbon nanotube. Ultimately, this vector is described simply by its (n,m) values. Examples of this rolling are exemplified by the B) tube rolling type and C) scroll type model for graphene rolling originally portrayed in Iijima’s momentous paper.

Figure 2 The Density of States (DOS) of a) metallic and b) semiconducting carbon nanotubes. Metallic nanotubes have a nonzero value everywhere in the DOS whereas semiconducting nanotubes have a band-gap where the DOS = 0. The sharp peaks in the DOS are known as Van Hove Singularities which arise from the circumferential boundary condition of the carbon nanotubes.

Figure 3 The Density of States (DOS) of semiconducting materials: bulk (blue), a 10 nm quantum wells (red), a 10 nm by 10 nm quantum wires (green) and quantum dots (black). The DOS begins as a continuum with 3D materials. As boundary conditions are added, and thus the number of dimensions decreased, so are the number of wavefunctions/wavevectors which are permitted by those boundary conditions. As such, this continuum of available energy states in the DOS of three-dimensional materials transforms to the sharp peaks shown in the DOS of one-dimensional materials, like carbon nanotubes. These peaks are known as Van Hove Singularities.

Figure 4 The DOS of a) metallic and b) semiconducting carbon nanotubes is comprised of sharp peaks known as Van Hove singularities. These singularities occur in both the valence and conduction bands and arise from the circumferential boundary condition which gives carbon nanotubes their one-dimensional status. Note that the DOS of semiconducting nanotubes has no energy states between the c1 and v1 levels (band gap) whereas metallic nanotubes do have energy levels in this region.

Figure 5 The “Kataura Plot” of the calculated transition energy (E_ii) as a function of nanotube diameter (d). Here, E_{11} corresponds to the energy associated with the transition of the first ground state to the first excited state in a semiconducting carbon nanotubes. It is obvious that several different carbon nanotubes can be observed using a single excitation energy and that the diameter and type of each can be identified using this tool.

Figure 6 A typical Raman Spectra of a metallic (top) and semiconducting (bottom) carbon nanotube. The Radial Breathing Mode (RBM) (100-500 cm⁻¹) can be used to determine the diameter of the carbon nanotube, whereas the graphite (G) band (~1590 cm⁻¹) is always present.
cm$^{-1}$) and disorder band (D) (1350 cm$^{-1}$) can be used to determine the number of defects in the nanotube.

Figure 7 a)[23] An example of an apparatus used in the arc discharge method. Here, a DC current is passed through two graphite electrodes separated by approximately 1-2 mm. This current produces a plasma of the inert gas (He) and consumes the graphite anode, forming carbon deposits containing carbon nanotubes on the cathode. b)[24] By adding metal catalyst, it is possible to produce SWNTs in relatively high yield, as depicted in this TEM image. When no catalyst is used, this method produces mostly MWNTs.

Figure 8[23] a) An apparatus used in laser ablation. Here, a high-powered laser is used to vaporize a graphite target in a reactor filled with inert gas heated to 1200 °C. The carbon nanotube “soot” is collected on a cooled collector and harvested for analysis and application. As in the arc discharge method, MWNTs dominate the products when no catalyst is used, whereas SWNTs dominate when metal catalyst is incorporated into the target. In such cases, large amounts of SWNTs (b and c) can be produced at a rate up to 1.5 g/hr.

Figure 9 A) A setup used in the CVD production of carbon nanotubes. Here, catalyst is first deposited on the support of choice. After catalyst deposition, typically reduction of the catalyst is accomplished using H$_2$, followed by raising the temperature to 700-900 °C. After this temperature is reached, carbon-feeding gasses are introduced and allowed to react with the catalyst for a predetermined amount of time, usually lasting from minutes to a few hours. By varying the catalyst and growth conditions, samples dominated by either SWNTs or MWNTs can be achieved. Also, by varying the deposition method and support in addition to the reaction conditions, well dispersed carbon nanotubes (B) and carbon nanotube thin films (C) can be produced.

Figure 10[20] A TEM image of a carbon nanotube-polystyrene composite. As can be seen, the carbon nanotubes are well dispersed and integrated into the polystyrene matrix. The dispersion and integration into the polymer matrix are both crucial for the success of carbon nanotube composites.

Figure 11[33] An example of the pick-up stick transistor. a) A cartoon representation of this device. This basic but useful transistor can be used in a variety of FETs and devices. Often this transistor geometry is used in FET based sensors. b) Such a transistor can be formed by depositing electrodes and then spin coating the patterned wafer with carbon nanotubes suspended in solution. Alternatively, this transistor can be formed by growing a carbon nanotube thin film on a wafer followed by electrode deposition.

Figure 12[35] A single carbon nanotube device formed using a) Pd source and drain electrodes and a p-type doped Si back gate. b) This electrode deposition is followed by placement of a HfO$_2$ layer and Al top gate. The SEM picture in (c) shows the device which results from this process. Because of the sensitivity of single carbon nanotube devices, they are ideal for use in many transistors and sensors.

Figure 13[38] a) A carbon nanotube gas sensor comprised of a p-type semiconducting carbon nanotube. This p-type behavior gives rise to the conductance changes seen when
sensing b) NO₂ and c) NH₃. Using this mechanism, NO₂ and NH₃ can be sensed down to 200 ppm and 1 % respectively due to the sensitivity of the electronic structure of carbon nanotubes.

Figure 14 A) A biological sensor in which a carbon nanotube Field Effect Transistor (FET) is bound to glucose oxidase (GOx) through a 1-pyrenebutanoic acid succimidyl ester linker. Sensing is accomplished by this linking which ultimately causes a change in conductance in this FET. Similarly, in B, polymers which are linked to biotin have been used to coat the carbon nanotubes. This biotin binds preferentially to streptavidin. This binding event ultimately causes a change in conductance similar to the sensor in A.

Figure 15 shows three basic types of solar cells: a) Si-based b) Organic-based and c) Dye-Sensitized. As can be seen in d) the carrier mobility of carbon nanotubes is much higher than that of other materials like Si. Carbon nanotubes are most commonly incorporated into the photoactive material of organic–based solar cells or the electrodes of organic-based and dye sensitized solar cells. Using carbon nanotubes of varying diameters, and thus varying band-gaps, photoactive materials can be formed which can utilize a large range of wavelengths of light to generate excitons. Also, the large carrier mobility of carbon nanotubes makes them useful in photoactive layers and electrodes to facilitate charge separation.

Figure 16 a) H₂ adsorption of Sample 1: as prepared SWNTs, Sample 2: SWNTs purified by soaking in 37 % HCl acid for 48 h, followed by rinsing with deionized water and drying at 423 K and finally Sample 3: SWNTs prepared similar to those in Sample 2, except with vacuum heat-treating for 2 h at 773 K. Sample 3 reaches a H₂ gravimetric uptake of 4 %. b) Hydrogen uptakes of samples prepared from SWNTs. Amazingly, these samples demonstrated a H/C absorption ratio up to 1, which corresponds to a gravimetric H₂ uptake of >8 wt.%.

Figure 17 Percent of net electricity generation from nuclear power. It should be noted that this has increased four-fold over the last three decades, reflecting the viability of nuclear energy as an alternative energy source. (Image from DOE website)

Figure 18 a) A 750 kW NEG Mico Turbine in Moorehead Minnesota. Windmills/turbines like this one can be used to produce electricity cleanly and renewably. b) A table illustrating the power density achievable from wind at various turbine heights and wind speeds. (Image and Table from DOE website)

Figure 19 A photovoltaic solar cell harvesting light energy for the production of electricity. It is apparent from this image that these solar cells can be incorporated into populated areas. (Image from DOE website)

Figure 20 Marketed Production of Natural Gas in the United States and Gulf of Mexico (GOM) in millions of cubic feet. (Image from DOE website) Obviously, the ability to produce large amounts of natural gas within the US makes this an attractive alternative fuel.
Figure 21 The relative volume associated with various storage methods. These volumes are based on the storage capacities of these materials and the DOE system targets. (http://www.afdc.energy.gov/afdc/fuels/hydrogen_alternative.html)..........................44

Figure 22 a) A TEM image of Mg$_2$Ni hydride which displays up to 7 wt.% H$_2$ gravimetric uptake. Mg based metal hydrides are particularly interesting for their H$_2$ storage capacities. b) However, like most metal hydrides, these materials suffer from relatively slow hydrogenation/dehydrogenation cycling and low net capacities. These characteristics result from their high-binding energy to H$_2$. .................................................................46

Figure 23 Examples of various MOF structures, specifically a) MOF-177, ZnO(btb)(btb = benzene-1,3,5-tribenzoate) b) IRMOF-8, Zn$_4$O(ndc)$_3$ (ndc = naphthalene-2,6-dicarboxylate) c) MIL-53 M(OH)(bdc) (M = Al$^{3+}$ or Cr$^{3+}$) and d) Zn$_2$(bdc)$_2$(dabco) (dabco = 1,4-diazabicyclo[2.2.2]octane). (C: black, N: green, O: red, Zn: blue polyhedra, M: green octahedral) The yellow spheres represent the pores in the evacuated crystalline frameworks. d) As can be seen from the table, MOFs can demonstrate high surface areas and impressive H$_2$ uptakes. However more work needs to be done to increase their available net capacity, as the binding energy of MOFs is still generally too high. .............48

Figure 24 a) and b) are TEM images of two microporous carbons derived from the thermal treatment of poly (etherether ketone). Porous carbons with pore diameters ≤2 nm (micropores) are best for H$_2$ storage concerns.........................................................51

Figure 25 Porous carbon have been shown to have impressive a) gravimetric and b) volumetric H$_2$ uptakes. One example of such a porous carbon is AX-21, which has a surface area of 3300 m$^2$/g which translates to a gravimetric uptake of ~3 wt.% and a volumetric uptake of ~almost 30 g/L. These values are impressive among porous carbon materials; as such, AX-21 has become a benchmark for which most other porous carbons are compared. ........................................................................................................................................52

Figure 26 A pictorial representation of the templated synthesis of porous carbons. a) In the beginning, a zeolite with the appropriate structure is chosen. b) Secondly, a carbon precursor infiltrates the zeolite template. c) Lastly, the zeolite template is removed and the carbon cast with higher surface area is formed..............................................................................................................55

Figure 27 A microporous carbon derived from zeolite Y. This microporous carbon displayed long range ordering (d~1.4 nm) identical to that displayed by zeolite Y. The surface area of this microporous carbon was found to be very large at 1910 m$^2$/g. ..........56

Figure 28 CDC’s surface areas generally depend on chlorination temperature. Optimizing this temperature allows for CDCs with very large surface areas to be formed (2000 m$^2$/g). Here, one such CDC formed from the chlorination of B$_4$C is presented.......57

Figure 29 A CDC derived from TiC being chlorinated at a) 400 °C b) 800 °C and c) 1000 °C. It is obvious that the degree of long-range order of the CDC structure seems to increase with chlorination temperature........................................................................................................59
Figure 30[53] a) and b) are TEM images of a porous carbons derived from both chemical and physical activation.................................................................60

Figure 31 Carbon nanotubes aligned by (a) electrophoresis (b) high flow rate and (c) external electric field. As can be seen, the density and length of these aligned samples are not large enough for acceptable application to large scale electronic devices...........64

Figure 32 CVD setup for “Fast-Heating Slow-Cooling” growth of ultra-long carbon nanotubes. The green arrow indicates the direction in which the furnace is moved and the blue arrow indicates the placement of the Si sample.................................................................66

Figure 33 A schematic of the growth mechanism of Fast Heating-Slow Cooling. The so-called “kite” mechanism begins with A) a catalytic nanoparticle deposited on a substrate. B) When the heat is suddenly introduced to the system, a convection current is established which lifts the nanoparticle off the substrate. C) As the nanoparticle is suspended above the substrate, it produces a carbon nanotube. The laminar flow of the feeding gasses carries the nanoparticle downstream while the growing nanotube tethers the nanoparticle to the substrate. This process results in a nanotube aligned parallel to the laminar flow of the reaction gasses........................................................................69

Figure 34 A) An SEM image of the long aligned carbon nanotubes produced by the fast heating-slow cooling growth method. As is evident from this image, many nanotubes produced using this method reach several millimeters to over a centimeter. B) An AFM image of the end of a carbon nanotube grown by this mechanism. This end was furthest away from the catalyst region and indicates that nanotubes grown in this manner grow by tip-growth[74].................................................................69

Figure 35 A) An SEM image indicating a large array of suspended nanotubes achieved using this growth mechanism. As can be seen, a single nanotube can be suspended over several different trenches. It was also shown that this suspension was achievable using trenches etched using both B) E-beam lithography and C) simple photolithography/RIE. It should be noted that the upper limit of this suspension was found to be approximately a 5 µm wide trench. Also using these nanotubes, suspended carbon nanotube devices (D) were achieved. However, producing such suspended nanotube devices was inconsistent often resulting in dirty and un-suspended carbon nanotubes after processing (E)...................................................................................71

Figure 36[78] SEM evidence of carbon nanotubes grown using A)Co B)Ni C)Pt D)Pd E) Mn F)Mo G)Cr H)Sn and I)Au as catalysts. All samples were grown on quartz under identical growth conditions using CH₄ and H₂ as reaction gasses. Although the yield, density and degree of alignment are different between metals, this likely results from the differences in carbon solubility in each metal. The alignment direction in all cases is along the X-direction of the crystalline quartz substrate. ..............................................76

Figure 37[78] SEM images of horizontally aligned SWNTs growth by (A) Mg and (B) Al. These nanotubes are aligned along the X direction on ST-cut quartz..................................................77

Figure 38[78] SEM images of horizontally aligned SWNTs on quartz grown by (A) Fe and (B) Cu. The alignment direction is the X direction on ST-cut quartz.........................79
Figure 39 AFM images and diameter distributions of aligned SWNTs on quartz grown using (A) Co, (B) Au and (C) Cu. The diameters of SWNTs are less than 2 nm and 3 nm for Co and Au, respectively and in most cases are dominated by nanotubes with diameters $\leq 1.5$ nm.

Figure 40 SEM images of random SWNTs on a Si wafer grown by (A) Fe, (B) Cu, (C) Co, (D) Ni, (E) Pt, (F) Pd, (G) Mn, (H) Mo, (I) Cr, (J) Sn, (K) Au, (L) Mg and (M) Al. SWNTs were obtained using each catalytic metal. These samples were grown using identical growth conditions as the samples produced from quartz (Figure 1). As such, the only difference between these samples and those grown on quartz is their lack of alignment.

Figure 41 AFM images of nanoparticles (A) in the absence of a carbon source and (B) after introducing carbon. The insertion is the corresponding SEM image of aligned SWNTs. The particles only move and aggregate significantly after introducing the carbon source at 900 °C.

Figure 42 The SWNT array printing/transfer process is outlined in this section. Here PMMA is used to bind to the carbon nanotube arrays, which is followed by etching the first layer of the quartz substrate with either KOH or BHF. After the PMMA/SWNT sample is released from the quartz, it can be washed and transferred to any substrate. Here, it was transferred to a SiO$_2$ substrate and then the PMMA was dissolved using acetone. The SEM image at the bottom is an example of one such SWNT array transferred to a SiO$_2$ substrate.

Figure 43 In A, the direction of the surface tension is perpendicular to the carbon nanotube alignment and towards the bottom of the trench over which the nanotubes are suspended. This creates many problems upon drying, which often result in the suppression of the carbon nanotube to the bottom of the trench. Alternatively, in B the drying liquid stabilizes the carbon nanotube equally around its circumference while drying. Thus, the only significant surface tension lies along the alignment direction of the carbon nanotubes.

Figure 44 A) Dense arrays of well-aligned SWNTs can be produced on a large scale using this method. B and C further demonstrate the large density and perfect alignment of the nanotube products. Also, after transferring the SWNT arrays, it can be seen in D and E that the alignment is well preserved. In some cases, the density of the transferred arrays was lower than of the SWNT arrays before transferring. However, in many cases this was not so. Also, it should be noted that the suspended portions of the aligned carbon nanotubes appear invisible because of the low number of electrons being deflected back to the electron detector in the SEM. The contrast provided by the substrate, in this case SiO$_2$, allows the portions of the nanotube on the substrate to be imaged more clearly.

Figure 45 As displayed in A, the necessary etching procedure involved RIE etching of the oxide layer (~200 nm). Often, this was followed by a KOH/IPA/NPH$_2$O Si etching which provided an overhang. It should be noted that trenches with widths $\leq 5$ µm were necessary to achieve suspended SWNT samples as seen in B. Finally, it is believed that,
after etching, electrodes could be easily deposited using E-beam metal evaporation and then SWNT arrays placed using the transfer procedure outlined here.

Figure 46 Plot of the calculated diffusion rate of carbon feeding gasses into nanoparticles v. inverse diameter of those nanoparticles at various temperatures. It can be seen that, per unit temperature, the diffusion rate increases with decreasing nanoparticle diameter.

Figure 47 As in Table 1, it is obvious that nanotubes grown from the smaller diameter nanoparticles A) 1.6 nm, are longer than those grown using the larger diameter nanoparticles in B (7.6 nm). This indicates that smaller diameter nanoparticles nucleate and grown nanotubes faster than larger diameter ones. This data indicates that diffusion of carbon feeding gasses into the smaller, and therefore more fluid nanoparticles, occurs more readily than in larger, less fluid nanoparticles.

Figure 48 A plot of the average carbon nanotube diameter v growth time for nanoparticles with diameters ranging from 1-2 nm (blue) and from 2.5-7.6 nm (red). It was found that, as growth time increased, so did the average diameter of carbon nanotubes products. This was true in the case of nanoparticles which produced both SWNTs and MWNTs. Thus, it was confirmed that diffusion of carbon feeding gasses into smaller nanoparticle occurred faster because of their more liquid-like state relative to larger nanoparticles.

Figure 49 Arrays of nearly exclusively semiconducting SWNTs were produced herein. A and B show SEM images of such nanotubes. The bright, parallel horizontal lines visible in the images are catalyst lines. (C) AFM image of these nanotube products. (D) Diameter distribution of 200 SWNTs of an array measured by AFM. (E and F) Raman spectra of SWNTs transferred onto the SiOx/Si substrates. The spectra were obtained using 488- and 633-nm excitation laser lines at 10 different spots over the substrate for each laser line. Each curve in a panel shows spectra at a spot on the substrate. Peaks within the rectangles marked with S correspond to the semiconducting SWNTs. The rectangles marked with M denote the frequency range where RBM peaks of metallic SWNTs are expected.

Figure 50 Raman active G-Band peaks of an array of SWNTs grown using the “selective” growth method. This sample was grown on quartz and was then transferred to a SiOx/Si wafer. These spectra were taken with a) a 633 nm and b) 488 nm excitation laser at 10 different spots over the substrate. Also, all spectra were normalized to the G' peak. It is evident from these spectra that the samples consist almost exclusively of semiconducting SWNTs.

Figure 51 The D and G band of a sample grown using the method outlined here. This investigation was done using a 633 nm excitation wavelength and analyzing 10 different regions on the substrate. This investigation showed that the G-band/D-band average intensity ratio was ~45, indicating a largely defect free SWNT array.

Figure 52 High on/off ratio FETs fabricated with as-grown aligned CNT arrays top-gated by solid electrolyte polymer films. (A) Large magnification view of the set of electrodes of a test device. The widths of the gaps between the 40 nm-thick gold contact
lines correspond to the channel lengths of FETs (from top to bottom): 4 µm, 3 µm, 2 µm, 1 µm, and 5 µm. To break possible current paths through the nanotube array past the transistor channels, the tubes were partially removed by reactive ion etching (RIE) in oxygen plasma. (B) Family of transfer characteristics (drain current, $I_d$, versus top gate voltage, $V_g$) of one of the test devices under a bias voltage $V_{ds} = 80$ mV. The parameter of the family is the transistor channel length $L$. The channel width is 0.5 mm. (Inset) The on/off ratios obtained for the device as a function of the channel length, $L$.

Figure 53[68] SWNTs grown on SiO$_x$/Si substrate. (A) An SEM image of such nanotubes. The bright stripe in (A) corresponds to the catalyst area. (B) Raman spectra of the as-prepared SWNTs. The spectra were obtained using 633-nm excitation laser line at 10 different spots over the substrate. Each curve in a panel shows spectrum at a spot on the substrate. Peaks within the squares marked with S and M correspond to the semiconducting and metallic SWNTs, respectively.

Figure 54[68] A a) SEM image and b) Raman spectra of nanotubes in the catalyst region. The SEM image shows the disorder of the tubes in the catalyst region and the Raman spectra shows the loss of selectivity for semiconducting SWNTs. Raman data was taken from 10 different spots on the substrate using a 633 nm excitation wavelength. The S and M square-labels indicate semiconducting and metallic respectively. The green arrows indicate peaks corresponding to the quartz substrate.

Figure 55[122] Samples grown on quartz using Cu as catalyst and EtOH-MeOH mixtures as carbon feeding gasses. Each sample was grown with A) 0 B) 0.01 C) 0.03 D) 0.05 E) 0.075 and F) 0.1 wt% thiophene. 2X density enhancement was demonstrated over this range, giving an average nanotube density of 2-4 nanotubes/µm and 6-8 nanotubes/µm without and with thiophene respectively. (Scale bar in all pictures is 10 µm)

Figure 56[122] Samples grown on quartz using Fe as catalyst and EtOH-MeOH mixtures as carbon feeding gasses. Each sample was grown with A) 0 B) 0.01 C) 0.03 and D) 0.05 wt% thiophene. 2X density enhancement was demonstrated over this range, giving an average nanotube density of 2-4 nanotubes/µm and 6-8 nanotubes/µm without and with thiophene respectively. (Scale bar in all pictures is 10 µm)

Figure 57[122] Samples A and C were grown on quartz with the previously mentioned EtOH/MeOH growth conditions using Cu as the catalyst and no added thiophene. Samples B and D were grown using the same growth conditions but with 0.075 wt% thiophene. These SEM images indicate that the nanotube samples grown using thiophene are longer than those grown without thiophene. These shorter nanotubes are indicated by darker areas in center of the growth region (between catalyst lines), as designated by the red arrows in Figures A and C. These darker regions indicate low nanotube density in the center of the growth region, thus indicating shorter nanotubes when no thiophene is used. As a corollary, the brighter regions in the center of the growth area of Figures B and D indicate higher nanotube density, and thus longer nanotubes. The scale bars are 1 mm in Figures A and B, and 100 µm in Figures C and D.
Figure 58 AFM comparison of aligned nanotubes grown on quartz using an Fe catalyst. Figures A, B and C are samples grown using the previously mentioned EtOH/MeOH growth conditions with no added thiophene, whereas D, E and F represent samples grown under the same growth conditions but with 0.01 wt.% thiophene added in EtOH. A) 5 μm x 5 μm B) 2 μm x 2 μm C) 1 μm x 1 μm D) 5 μm x 5 μm E) 2 μm x 2 μm F) 1 μm x 1 μm. The height scale is 8 nm.

Figure 59 AFM comparison of aligned nanotubes grown on quartz using a Cu catalyst. Figures A, B and C are samples prepared using the previously mentioned EtOH/MeOH growth methods without thiophene, whereas D, E and F represent samples grown under the same growth conditions but with 0.03 wt.% thiophene added in EtOH. A) 5 μm x 5 μm B) 2 μm x 2 μm C) 1 μm x 1 μm D) 5 μm x 5 μm E) 2 μm x 2 μm F) 1 μm x 1 μm. The height scale is 8 nm.

Figure 60 The growth enhancement demonstrated by thiophene is often evident in the catalyst line region as indicated by the red arrows in Figures A and B. Samples A and B were grown using Fe as catalyst and EtOH-MeOH mixtures as carbon feeding gasses with A) 0 wt% and B) 0.01 wt% thiophene respectively. Figures C and D demonstrate the sulfur induced density enhanced samples grown with C) Fe and D) Cu. 2X density enhancement was demonstrated using both catalysts, raising the average nanotube density of 2-4 nanotubes/μm to 6-8 nanotubes/μm without and with thiophene respectively. (Scale bar in pictures A and B are 20 μm and in C and D are 250 nm and the height scale on C and D are both 8 nm.)

Figure 61 Adding the appropriate amount of thiophene can improve the nanotube density with both Fe (0.05 wt% thiophene) and Cu (0.075 wt% thiophene) catalysts represented by A and C respectively. However, adding more than this optimal amount will cause a dramatic decrease in the density as represented by B) grown using Fe catalyst and 0.2 wt% thiophene and D) grown using Cu catalyst and 0.12 wt% thiophene. All scale bars are 100 μm.

Figure 62 A and B were grown using Cu as catalyst and EtOH = 150 sccm and H₂ = 200 sccm with no added thiophene. C was grown using the same conditions but with 0.01 wt% thiophene. Upon adding thiophene, the density of short nanotubes becomes larger and the sample becomes somewhat cleaner. However, the cleanest and longest nanotubes are achieved using EtOH and MeOH mixtures with thiophene and Cu, as displayed in D. D is grown using Cu and 0.075 wt% thiophene. All scale bars are 10 μm.

Figure 63 AFM images of samples grown using Cu as catalyst and EtOH as the only carbon feeding gas. (EtOH = 150 sccm H₂ = 200 sccm) Samples A and B have no thiophene added, but C and D have 0.01 wt% thiophene in EtOH. A and C are 10 μm x 10 μm images and B and D are 1 μm x 1 μm images. The height scale is 8 nm.

Figure 64 Radial Breathing Mode (RBM) spectra of samples grown using Cu as catalyst and A) 0 and B) 0.075 wt% thiophene; after growth, samples were transferred onto a Si wafer with 1 μm oxide layer for Raman analysis. A 633 nm wavelength excitation laser was used to scan the RBM to investigate the effect of thiophene on the
selective growth of semiconducting SWNT. Comparing A and B illustrates that thiophene does interfere with the selective growth mechanism.

Figure 65 Arrays of high density SWNTs grown on ST-cut single crystal quartz with a large ratio of methanol/ethanol used as carbon precursors. (A, B and C) SEM images of such nanotubes. The bright and parallel horizontal lines visible in (A) are catalyst lines. The magnification is 100x (A), 25,000x (B) and 150,000x (C), respectively. (D) AFM image of the as-grown nanotubes. The scale bar is 500 µm (A), 2 µm (B), 500 nm (C) and 500 nm (D), respectively.

Figure 66 Arrays of long SWNTs grown on ST-cut single crystal quartz with a large ratio of methanol/ethanol used as carbon precursors. (A and B) SEM images of these carbon nanotubes. The black and parallel horizontal lines visible in (A) are two catalyst lines. (B) is the SEM image of the area marked with dotted rectangle in (A). (C) is the length distribution of the SWNTs in the arrays. The scale bars are 500 µm (A), 10 µm (B), respectively.

Figure 67 Raman spectra of the SWNTs grown on ST-cut single crystal quartz with a large ratio of methanol/ethanol used as carbon precursors. (A) RBM spectra of these nanotubes. (B) G-band spectra of these nanotubes. The Raman spectra were recorded with an excitation laser line of 633 nm. Ten different spots of the sample were characterized over the entire surface. Each curve in a panel shows a spectrum at a different spot on the substrate. The sharp peaks at 127 cm\(^{-1}\) and the broad peaks at 205 cm\(^{-1}\), marked with green stars in (A), correspond to the Raman spectra of the quartz.

Figure 68 Arrays of aligned SWNTs transferred onto a SiO\(_x\) substrate. (A and B) SEM images of these nanotubes. The scale bars are 500 µm (A), 20 µm (B), respectively. (C) RBM spectra of these nanotubes. (D) G-band spectra of such nanotubes. The Raman spectra were recorded with an excitation laser line of 633 nm. Ten different spots of the sample were characterized over the entire surface. Each curve in a panel shows a spectrum at a different spot on the substrate.

Figure 69 Raman spectra of the aligned SWNTs transferred onto the trenched ST-cut single crystal quartz. The top left figure is a schematic illustration of the Raman characterization. The orientation of the aligned SWNTs transferred onto the trenched quartz is parallel with the X [100] direction of the lattice. Figures marked with 1 to 5 represent the Raman characterization of the sections of the nanotube in contact with the quartz (position 1, 3, 5 in schematic illustration) and the sections suspended over the trench (position 2, 4 schematic illustration) of the same SWNT. Each of the inserted spectra depicts the RBM of the SWNT measured simultaneously with the G-band. The sharp peaks marked with green stars in RBM spectra correspond to the Raman spectra of the quartz. The RBM and G-band frequencies are 152 cm\(^{-1}\) and 1605 cm\(^{-1}\) (position 1), 153 cm\(^{-1}\) and 1591 cm\(^{-1}\) (position 2), 153 cm\(^{-1}\) and 1605 cm\(^{-1}\) (position 3), 153 cm\(^{-1}\) and 1591 cm\(^{-1}\) (position 4), 152 cm\(^{-1}\) and 1603 cm\(^{-1}\) (position 5), respectively.

Figure 70 The general procedure for producing porous carbons utilizing inorganic templates is illustrated here. First, an appropriate inorganic template is chosen, followed by carbon deposition. Carbon deposition is typically accomplished using a carbon gas or
liquid impregnation of the inorganic/zeolite structure followed by carbonization and 
template removal. After template removal, a carbon cast of the original inorganic 
material is left, which typically has larger surface areas than the original inorganic 
templates. 

Figure 71 TEM images of porous carbon products formed using FAU as a template. a) 
EtOH was first flowed through the FAU structure at elevated temperature, which 
decomposed carbon on the surface of the zeolite. Alternatively, a polymer such as CTAB 
or b) FA was impregnated and polymerized inside the FAU structure. In both cases, the 
resulting porous carbons had low surface areas owing to difficulties in template 
removal. 

Figure 72 TGA analysis of porous carbon products formed by the EtOH casting of FAU 
revealed that significant mass remained at high temperature. It was deduced that this 
resulted from a significant amount of FAU remaining in the products. 

Figure 73 The organically templated synthesis procedure for producing porous 
carbons. Here, di-block copolymer is used to form a micelle in a hydrophilic 
environment. The length of the hydrophobic segment of this copolymer ultimately was 
used to form different diameter micelles in solution, and thus pores of different sizes in 
the resulting porous carbon products. After solvation of the pluronic surfactant, it is H-
bonded to a resol-type polymer forming in solution. After polymerization is complete, 
the surfactant template is removed and the porous carbon is formed. 

Figure 74 Porous carbons with scalable pore diameters were synthesized using the 
organic templates a) P123 b) P103 c) P84. As determined from TEM, these pluronic 
surfactant templates imparted pore diameters of 1-2 nm, 1 nm and 0.6-0.8 nm 
respectively (marked in white in each figure). Despite this scalability of pore size, the H2 
storage properties of these samples were not investigated as a result of their low BET 
surface areas. 

Figure 75 PEEK in an alumina combustions boat A) before and B) after thermal 
treatment under CO2. It should be noted that the products after thermal treatment were 
similar in appearance when treated with steam. C) The chemical structure of one subunit 
of PEEK. D) After thermal treatment, the porous products were analyzed using TEM. 
Here, PEEK-CO2-9-80 is used to display a typical TEM image in which small diameter 
pores are evident. The scale bar in this image is 10 nm. 

Figure 76 XPS of A) PEEK-CO2-9-80 and B) PEEK-ST-9-91. Both spectra show that the 
porous carbon products derived from PEEK are nearly pure carbon materials even after 
extensive thermal treatment and thus extensive burn off. 

Figure 77 A plot showing the evolution of the Brunner-Emmett-Teller (BET) surface area 
with burn off. Large surface area (~≥3000 m2/g) products were achieved using both CO2 
and steam thermal treatments. 

Figure 78 Representative NMR Spectra of samples with BET surface areas of ~3000 m2/g 
produced using CO2 (red) and steam (blue). The spectra of the CO2 product displays the 
distinct peaks corresponding to micropores (green arrow) and larger pores/voids (blue
The peak in the spectra of the steam produced sample has no distinction between these peaks indicating a breakdown of the pore walls. This breakdown allows for a free exchange of H₂ between the micropores and larger pores/voids.

Figure 79 A plot of Differential Pore Volume measurements for several CO₂ and steam derived samples. A) PEEK-CO₂-9-80 has the largest pore volumes and the largest surface area of all the samples whose diameters were analyzed (3103 m²/g). It is evident that all samples have pores with diameters centered around 1.2, 1.35, 1.8 and 2.5 nm. B) and C) show the evolution of the Differential Pore Volumes of CO₂ and steam derived samples, respectively. D) At 1000 m³/g, the volume of all pore diameters is notably larger for the steam treated product as compared to the CO₂ treated product. This difference in pore volumes is even more pronounced when analyzing E) the Differential Pore Volume distributions normalized at 2000 m³/g. Here, it is evident that the pores with diameters of 1.2 and 1.35 nm in steam treated sample have significantly larger volumes than in the CO₂ treated samples. It should be noted that the Density Field Theory analysis of this data below 1 nm is unreliable. As such, interpretation of pore diameters around 1 nm is supported by NMR data.

Figure 80 A plot of Cumulative Pore Volume v BET surface area. Per unit surface area, steam derived samples do have larger cumulative pore volumes than those produced using CO₂. However, because of pore collapse in steam derived samples, the largest cumulative pore volumes were achieved by the high surface area CO₂ derived products (PEEK-CO₂-9-80,85).

Figure 81 A plot of the NMR shift corresponding to H₂ in micro/mesopores v. changing pressure. Shifts that do not change with pressure indicate samples having pores with diameters ≤1.24 nm (as in PEEK-CO₂-9-1, 26 and PEEK-ST-9-20). The positive slope corresponding to PEEK-CO₂-9-59 and PEEK-ST-9-35,47 indicates the presence of pores with diameters >1.24 nm.

Figure 82 H₂ gravimetric uptakes v BET Surface Area at 77 K and 0.2 MPa. The H₂ sorption profiles of materials produced using steam and CO₂ are very similar at surface areas up to approximately 1500 m²/g. However, at ~2000 m²/g, the steam derived product displays an obvious advantage compared to the material produced using CO₂. Ultimately, the best gravimetric uptake is demonstrated by PEEK-CO₂-9-80 which achieves 3.7 wt% at a surface area of 3103 m²/g.

Figure 83 The excess H₂ gravimetric uptake isotherm of PEEK-CO₂-9-80 at 77 K. This large surface area material (3103 m²/g) has impressive pore volumes and mostly micropores. As a result of these favorable characteristics, this material demonstrated an exceptionally large H₂ gravimetric uptake of 5.29 wt%.
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1. Introduction

1.1 Introduction to Carbon Nanotubes

1.1.1 Carbon Nanotube Discovery

Nanotechnology has been an intense area of research, particularly within the last two decades. This intense focus began with the popularization of carbon nanotubes, by Sumio Iijima’s 1991 publication detailing the production of tubular “carbon needles\textsuperscript{[1]}.” The broad promise and versatility of carbon nanotubes has made them one of the most heavily investigated of all materials in recent history. The discovery of carbon nanotubes is most often attributed to Sumio Iijima because of his 1991 publication. In truth, carbon nanotubes have been part of the scientific community for considerably longer. In 1952, L. V. Radushkevich and V. M. Lukyanovich published perhaps the first images of carbon nanotubes in the Soviet Journal of Physical Chemistry\textsuperscript{[2]}. The Transmission Electron Microscopy (TEM) images presented in that work showed clear evidence of 50 nm diameter carbon tubes; these images represented the first direct proof of what we presently refer to as carbon nanotubes. However, because these discoveries were published in Russian during the time of the Cold War, they were not well circulated and largely went un-noticed. In 1976, Oberlin, Endo, and Koyama published a paper displaying hollow carbon fibers with nanometer scale diameters synthesized from a vapor phase growth technique\textsuperscript{[3]}. Also presented in this work was TEM evidence of a carbon fiber consisting of a single layer of graphene. However, it was not until later that this structure was referred to as a single walled carbon nanotube (SWNT) by these authors. In 1981 Russian investigators characterized their “carbon multi-layer tubular crystals\textsuperscript{[2]}.” From this data, they suggested that such structures resulted from the rolling of graphene layers into cylinders. This is significant because they speculated that many different arrangements of “graphene hexagonal nets” were possible. They specifically
enumerate two such arrangements: circular and spiral/helical; these arrangements are known today as armchair and chiral carbon nanotubes (Figure 1). All of these groups presented evidence of multi-walled carbon nanotubes (MWNTs) much before Iijima’s seminal publication in 1991. However unambiguous evidence of SWNTs did not come until later still. In 1993, the June 17th edition of Nature published two articles submitted independently by Iijima and Ichihashi,[4] and also by Bethune et. al[5] which displayed such SWNTs. Indeed, it was the spark provided by early predictions of the amazing electronic conducting properties of SWNTs that gave this area of research the intensely explored and highly touted status that it enjoys today.

1.1.2 Carbon Nanotube Properties (Electronic, Optical, Mechanical Structure)

1.1.2.1 Carbon Nanotube Structure

As was stated above, some of the early works on carbon nanotubes hypothesized that they formed from rolling up graphene, which consists entirely of sp² hybridized carbon. However, it is now known that this is not the mechanism of formation. Despite this mechanism of formation being inaccurate, it has proven a helpful aid in thinking about the electronic and mechanical structure of carbon nanotubes. This model can be used as a means to illustrate the various types of carbon nanotubes. As in Figure 1A, a graphene sheet is initially considered. In order to form a carbon nanotube from this graphene sheet, a “rolling vector” is established to connect two crystallographically equivalent sites. This vector is perpendicular to the nanotube axis or “translation vector” (labeled T in Figure 1A) and represent the direction along which the graphene sheet is rolled. The rolling vector is denoted as \( C_h \) in Figure 1A and is defined as:

\[
C_h = n\mathbf{a}_1 + m\mathbf{a}_2
\]
Figure 1 A) Graphene sheet displaying the rolling vector ($C_h$), nanotube axis ($T$) and graphene lattice vectors ($a_1$ and $a_2$). The rolling vector is defined as $C_h = na_1 + ma_2$ and connects two crystallographically equivalent carbon atoms. Therefore, this vector describes the direction along which a graphene sheet would be rolled to form a carbon nanotube. This determines the helicity and therefore many of the characteristics of the carbon nanotube. Ultimately, this vector is described simply by its $(n,m)$ values. Examples of this rolling are exemplified by the B) tube rolling type and C) scroll type model for graphene rolling originally portrayed in Iijima’s momentous paper[2]. Depending on the helicity and thus the $C_h$, the possible types of carbon nanotube structures are D) Armchair E) Zigzag F) Chiral[3].
where \( n \) and \( m \) are integers and \( a_1 \) and \( a_2 \) are the graphene lattice vectors. The rolling vector determines the “pitch” or “helicity” of the carbon nanotubes and therefore determines the kind of nanotube being described. As such, it is extremely important in describing the properties of carbon nanotubes. In Figure 1D, E and F, three types of nanotubes are illustrates, each characterized by different rolling vectors and pitches. Figure 1D displays an armchair configured carbon nanotube whereas 1E and F display zigzag and chiral carbon nanotubes respectively. As this demonstrates, the structure of the carbon nanotubes differs significantly with differing rolling vectors; because of this fact, these vectors are often used to describe different kinds of carbon nanotubes. The most common way that this is done is by denoting the \( n \) and \( m \) integers which are used to describe the rolling vector. As such, the carbon nanotubes depicted in Figure 1D-F would each be described according to this convention as follows: D) armchair = \((n,n)\), E) zigzag = \((n,0)\) and F) chiral = \((n,m)\). This rolling vector is also useful for describing the diameter of the nanotube. As the magnitude of the rolling vector \( C_h \) grows larger, so does the diameter. Therefore, with increasing values of \( n \) and \( m \), the diameter of the nanotubes being described increases.

1.1.2.2 Carbon Nanotube Band Structure and Electronic Structure

It is evident that the rolling vector defined by \( n \) and \( m \) is extremely important in dictating the structure and therefore the properties of each type of carbon nanotube. In particular, this \((n,m)\) characterization can be used to classify the electronic structure of carbon nanotubes as either metallic or semiconducting. When \((n-m)/3\) is an integer, the carbon nanotube is metallic; every other time, it is semiconducting. This can be seen
The Density of States (DOS) of a) metallic and b) semiconducting carbon nanotubes. Metallic nanotubes have a nonzero value everywhere in the DOS whereas semiconducting nanotubes have a band-gap where the DOS = 0. The sharp peaks in the DOS are known as Van Hove Singularities which arise from the circumferential boundary condition of the carbon nanotubes.

Figure 2[6] The Density of States (DOS) of a) metallic and b) semiconducting carbon nanotubes. Metallic nanotubes have a nonzero value everywhere in the DOS whereas semiconducting nanotubes have a band-gap where the DOS = 0. The sharp peaks in the DOS are known as Van Hove Singularities which arise from the circumferential boundary condition of the carbon nanotubes.
when analyzing Figure 2. Here, Figure 2A represents the calculated example of the density of states of a (12,6) carbon nanotube (bottom) and the experimentally determined density of states (DOS) for the same nanotube (top). The blue arrow in this figure represents the region around the Fermi-Energy (here set to 0 eV). In this example, the DOS of the (12,6) nanotube has a finite, non-zero value inside this region. This connection between the valence band and the conduction band defines the nanotube as metallic, as indicated by the (n-m)/3 rule stated above. On the other hand, Figure 2B represents the DOS of the semiconducting carbon nanotube (10,0). Notice here that no energy states exist within the region between the valence and conduction bands of this nanotube. This gap between the valence and conduction bands defines semiconducting materials and is known as the band-gap.

The DOS shown in this graph displays sharp peaks associated with specific energies. Unlike in the bulk (Figure 3), not all energy levels are observed within carbon nanotubes. As mentioned previously, it is useful to consider carbon nanotubes as rolled-up graphene sheets. If we consider the energy profile of a graphene sheet, which is a two-dimensional “quantum-well”, step-like features evolve within the DOS. In going from a 3-D system (bulk) down to a 2-D system (as in graphene), boundary conditions have been added in one dimension. Hence, the number of wavefunctions which satisfy these boundary conditions are more limited; as such, the number of available energy states is also limited. Ultimately this results in the step-like features displayed in Figure 3. Similarly, when going from a 2-D system, like graphene, down to a 1D system, like carbon nanotubes, an additional boundary condition is added. Specifically, this boundary conditions arises as:

\[ \mathbf{k} \cdot \mathbf{C}_h = 2\pi q \]
The Density of States (DOS) of semiconducting materials: bulk (blue), a 10 nm quantum wells (red), a 10 nm by 10 nm quantum wires (green) and quantum dots (black). The DOS begins as a continuum with 3D materials. As boundary conditions are added, and thus the number of dimensions decreased, so are the number of wavefunctions/wavevectors which are permitted by those boundary conditions. As such, this continuum of available energy states in the DOS of three-dimensional materials transforms to the sharp peaks shown in the DOS of one-dimensional materials, like carbon nanotubes. These peaks are known as Van Hove Singularities. (http://ece.colorado.edu/~bart/book/welcome.htm)
where $k$ is the wavevector, $C_h$ is the rolling vector and $q$ is some integer. Simply put, the wavefunctions (and therefore wavevectors) must satisfy the boundary condition associated with the concentric nature of a nanotube. This boundary conditions further limits the number of viable wavefunctions and thus observable energy states. This ultimately manifests itself in the sharp peaks in the DOS of carbon nanotubes (as seen in Figure 3 and 4) known as Van Hove Singularities. Furthermore, as can be seen in Figure 4, transitions between these singularities in the DOS is bound by symmetry relationships which produce the interesting electronic and optical properties. Electronic transport within carbon nanotubes is dictated by the rules of such transitions. However, a few more general trends are worthy of noting.

Since SWNTs have been so highly touted because of their promise for revolutionizing modern electronics, much investigation on their electronic structure has been done. In particular, it was observed that the band-gap of semiconducting carbon nanotubes was inversely proportional to nanotube diameter. That is to say that as the nanotube diameter increases, the energy of the band-gap decreases\(^8\). Because of this, well-controlled synthesis of small diameter (~1 nm) SWNTs has been highly sought after for many years. These nanotubes are attractive because their relatively large band-gap would allow them to be used in devices with a very small “off-current” and hence very high on/off ratios. Such characteristics are monumentally important to their successful integration into electronic devices. Conversely, metallic nanotubes have extremely impressive current densities, up to $10^9$ A/cm\(^2\), which is significantly higher than most metals\(^9\). It should also be noted that theoretical calculations demonstrate that MWNTs have an increased possibility of being metallic as the number of chances to have even a single metallic nanotube increases within the number of nanotube shells\(^{10}\). Lastly, it
The DOS of a) metallic and b) semiconducting carbon nanotubes is comprised of sharp peaks known as Van Hove singularities. These singularities occur in both the valence and conduction bands and arise from the circumferential boundary condition which gives carbon nanotubes their one-dimensional status. Note that the DOS of semiconducting nanotubes has no energy states between the $c_1$ and $v_1$ levels (band gap) whereas metallic nanotubes do have energy levels in this region.
should be noted that carbon nanotubes exposed to air exhibit p-type doped behavior due to oxygen being absorbed onto their surface\textsuperscript{[12]}. This demonstrates that while carbon nanotubes are chemically robust, their band structure and therefore electronic and optical properties are extremely sensitive to charge transfer and chemical doping.

1.1.2.3 Carbon Nanotube Optical Properties

As was discussed in the previous section, carbon nanotubes have a distinct electronic structure which makes them attractive elements for incorporation into modern electronics and optics. Nanotubes have fascinating optical characteristics including fluorescence\textsuperscript{[13]}, photoconductivity\textsuperscript{[14]} and other interesting absorption phenomenon\textsuperscript{[15],[16]}. Moreover, the electronic structure, and thus optical properties of these nanotubes is heavily dictated by their physical structure. As such, mapping their optical absorption characteristics can give invaluable information about carbon nanotubes. Accordingly, spectroscopy plays a large role in the characterization of carbon nanotubes. Although UV-VIS-NIR spectroscopy is a useful tool for such characterization\textsuperscript{[17]}, Raman spectroscopy is the most abundantly used spectroscopic means by which carbon nanotubes are investigated\textsuperscript{[18]}.

The “Kataura plot” displayed in Figure 5 demonstrates the calculated transition energy ($E_{ii}$) as a function of nanotube diameter ($d_t$) for different nanotubes. This plot is often used to help analyze the results obtained from Raman analysis of nanotube samples. Using a specific excitation energy, which corresponds to a specific $E_{ii}$, it is possible to induce various transitions in nanotubes with differing diameters. As such, it is possible to irradiate several different types of nanotubes using a single excitation wavelength. A more complete picture of nanotube samples often necessitates the use of multiple difference excitation energies. Ultimately, it is obvious that this plot is very
Figure 5\textsuperscript{[18]} The “Kataura Plot” of the calculated transition energy ($E_{11}$) as a function of nanotube diameter ($d_t$). Here, $E_{11}^S$ corresponds to the energy associated with the transition of the first ground state to the first excited state in a semiconducting carbon nanotubes. It is obvious that several different carbon nanotubes can be observed using a single excitation energy and that the diameter and type of each can be identified using this tool.
useful in determining the diameter and the semiconducting/metallic nature of the observed nanotubes. Further analysis of the Raman spectra can give even greater details as to the diameter distribution, quality and electronic structure of carbon nanotube samples. Perhaps the most used and detailed region of typical Raman spectra on carbon nanotubes is the Radial Breathing Mode (RBM) region, which extends from 100-500 cm\(^{-1}\) (Figure 6). This region describes phonons which are concentric vibrations perpendicular to the carbon nanotube axis. From these transitions, details about the carbon nanotube diameter as well as whether it is semiconducting or metallic can be acquired. As with other electronic transitions, the energy at which these transitions are demonstrated scales inversely with the nanotube diameter, as is demonstrated in the Kutaura plot. Therefore, as the frequency of the transition increases, the diameter of the nanotube being investigated will decrease within the RBM region. Also, the conducting nature of these samples can be explored within this region. As an example, when a 633 nm excitation wavelength is used to irradiate the sample, nanotubes having transitions within the region from ~150-170 cm\(^{-1}\) will be semiconducting, whereas those with transitions from 170-225 cm\(^{-1}\) are metallic. It is obvious that this is an extremely telling region of the Raman spectra. More details regarding the conducting nature of carbon nanotubes can be found within their G-band. The G-band arises from the graphitic nature of the carbon nanotubes. Graphite has a Raman active band at about 1582 cm\(^{-1}\). However, because of its differences in structure, carbon nanotubes display this peak between 1565-1590 cm\(^{-1}\). As can be seen in Figure 6, the shape of the G-band differs from semiconducting to metallic nanotubes. Metallic nanotubes tend to have a broader peak with more prominent shoulder towards lower frequencies. On the other hand, semiconducting nanotubes have a sharp distinct peak favoring a slightly higher frequency transition. Lastly, the D-band, or disorder band, ranges from 1350-1370 cm\(^{-1}\).
Figure 6[19] A typical Raman Spectra of a metallic (top) and semiconducting (bottom) carbon nanotube. The Radial Breathing Mode (RBM) (100-500 cm$^{-1}$) can be used to determine the diameter of the carbon nanotube, whereas the graphite (G) band (~1590 cm$^{-1}$) and disorder band (D) (1350 cm$^{-1}$) can be used to determine the number of defects in the nanotube.
This band originates from deviations in the sp² character of the carbon in the nanotube. Thus, the D-band appears when defects, or sp and sp³ hybridized carbon exist in a carbon nanotube sample.

It should be noted that Raman depends heavily on the environment of the carbon nanotubes as well as the orientation of the excitation laser. Nanotubes on different substrates may have slight differences in the Raman spectra, however most of the rules describing nanotube diameter and conducting type still apply regardless of these variations. However, it should be noted that a laser must be polarized along the nanotube axis in order to induce an excitation with an observable intensity.

1.1.2.4 Carbon Nanotube Mechanical Structure

Owing to their robust cylindrical structure and sp² bonding, carbon nanotubes are the strongest material under tension strain known to man. They have a calculated Young’s modulus of 1 TPa and tensile strength of 63 GPa\[^{20}\], which is over twenty times stronger than the strongest steel. Because of these amazing physical properties, carbon nanotubes have been employed in a large variety of composites, including in collagen for tissue engineering\[^{21}\] and a variety of other materials such as polystyrene\[^{22}\] to enhance their mechanical strength. Such composites show impressive enhancement in their tensile strength and Young’s modulus. This will be further discussed in a later section of this work. However, it is apparent that carbon nanotubes are exceptionally strong and can be successfully incorporated into composites to impart remarkable mechanical strength.

1.1.3 Carbon Nanotube Synthesis

The synthesis of carbon nanotubes occurs in three main ways: Arc Discharge, Laser Ablation and Chemical Vapor Deposition (CVD). Each has its own advantages and disadvantages as will be discussed below.
1.1.3.1 Arc Discharge

In 1991, carbon nanotubes were popularized by Iijima, who produced MWNTs using an Arc discharge method. It was notice that carbon nanotubes, or as he termed them “graphite carbon needles,” formed from the soot of this experiment. Because Arc discharge was the method used in the study which popularized carbon nanotube production, it has been the most used method for carbon nanotube synthesis. The stated optimized conditions\(^{[23]}\) for this method necessitate the passage of 80-100 A of direct current through two high-purity graphite electrodes (6-10 mm OD) separated by approximately 1-2 mm. This is done in an inert gaseous environment, such as He, at approximately 500 torr inside a chamber like the one depicted in Figure 7A. During arcing, plasma is formed which consumes the graphite anode and forms a deposit on the cathode at a rate of approximately 1 mm/min. This reaction occurs at very high temperatures, ranging from 3000-4000 K. It should be noted that while MWNTs can be produced using these conditions with no metal catalyst added, SWNTs require the addition of such a catalyst. Gd, Co-Pt, Co-Ru, Co, Ni-Y, Rh-Pt, Co-Ni-Fe-Ce and Ni, Cu, Fe and S mixtures have been used for such growth and in many cases result in an exceptionally high yield of narrow diameter SWNTs. Specifically, Ni-Y has been used to produced SWNTs yields of at least 40 %\(^{[24]}\) and ranging up to almost 90 %\(^{[23]}\). What’s more, this method can be used to produce good quality SWNTs, double-walled carbon nanotubes (DWNTs) and other MWNTs in bulk\(^{[24],[25]}\).

Although the benefits of this method are significant, the sacrificial graphite electrode, use of metal powders and incorporation of high purity Ar or He drives up the cost of this method. As such, it is not well suited for the large-scale production of carbon nanotubes.
Figure 7 a) An example of an apparatus used in the arc discharge method. Here, a DC current is passed through two graphite electrodes separated by approximately 1-2 mm. This current produces a plasma of the inert gas (He) and consumes the graphite anode, forming carbon deposits containing carbon nanotubes on the cathode. b) By adding metal catalyst, it is possible to produce SWNTs in relatively high yield, as depicted in this TEM image. When no catalyst is used, this method produces mostly MWNTs.
1.1.3.2 Laser Ablation

Laser ablation is similar in many ways to the arc discharge method. In a typical laser ablation growth experiment, a high power laser (YAG, CO₂ etc.) is used to vaporize a pure graphite target in a reactor (Figure 8a) filled with inert gas (Ar or N₂) and heated to 1200 °C. As with the arc discharge method, this method produced primarily MWNTs when no metal catalyst is used. In order to achieve SWNT growth using laser ablation, metal-integrated targets such as graphite-Co-Ni targets are employed. These targets can be used to produce SWNT bundles and ropes packed with 100-500 SWNTs. This production method is highly dependent on factors such as laser power and target composition/structure. For example, it was found that that twice as much SWNT material can be produced when a porous target (graphite-Co-Ni(nitrate)) was used. Other experiments showed that increasing the laser power during growth made the diameter distribution narrower. Moreover, it was found that ultrafast laser pulses could be utilized to produce up to 1.5 g of nanotube material per hour.

Despite these impressive growth rates and quality products, laser ablation is cost-ineffective for the same reasons that the arc-discharge method is. In addition, the use of high-powered lasers is also a deterrent for the economical and scalable production of carbon nanotubes using this method.

1.1.3.3 Chemical Vapor Deposition (CVD)

Chemical Vapor Deposition (CVD) is an extremely useful and versatile technique often employed for the synthesis of carbon nanofibers[26] and carbon nanotubes[27]. CVD processes vary depending on several factors including the catalyst, the reaction gasses and the temperature. A range of catalysts can be used including Fe, Co, Ni, CoMo and many other metal nanoparticles. The size of these metal particles largely determines the
Figure 8\textsuperscript{[23]} a) An apparatus used in laser ablation. Here, a high-powered laser is used to vaporize a graphite target in a reactor filled with inert gas heated to 1200 °C. The carbon nanotube “soot” is collected on a cooled collector and harvested for analysis and application. As in the arc discharge method, MWNTs dominate the products when no catalyst is used, whereas SWNTs dominate when metal catalyst is incorporated into the target. In such cases, large amounts of SWNTs (b and c) can be produced at a rate up to 1.5 g/hr.
diameters of the carbon nanotube products. As with the catalysts, a large variety of carbon precursors can be used to produce nanotubes. These include EtOH, CH₄, hexanes and CO among other carbon containing pure gasses and gas mixtures. H₂ is also frequently used in order to help reduce the catalyst, which often initially exists in an oxidized form, as well as to balance the C:H ratio. These factors are extremely important for successful growth of carbon nanotubes. Finally, temperature is also an extremely important factor for the production of carbon nanotubes. Nanotubes have been produced in most cases between 700-900 °C, however nanotubes have been produced at temperatures lower than 500 °C[28]. At lower temperatures, the carbon nanotube products tend to be dirtier, whereas temperatures greater than 1000 °C favor the production of graphene rather than carbon nanotubes.

Typically, CVD synthesis begins with the patterning of the catalyst on whatever catalyst support is desired. This support most often ranges from some porous material, like a zeolite[29], to a flat substrate like sapphire[30] or Si[31]. After patterning, the catalyst and support are placed inside a quartz tube which is in the heating region of a tube furnace (Figure 9A). The system is then heated under H₂ to reduce the metal catalyst before the introduction of any carbon source gasses. After reduction, the carbon sources are introduced and the reaction is allowed to proceed for a finite duration, after which the sample is cooled to room temperature under an inert environment such as Ar or H₂. CVD based carbon nanotube synthesis is incredibly versatile and efficient. By simply varying the growth conditions, it is possible to tune the products from predominantly MWNTs to DWNTs and even SWNTs. Also, this method is relatively cheap and highly scalable. However, most CVD production methods result in a 1:2 ratio of metallic: semiconducting nanotubes. Also, often times purification and support removal are necessary in the case of bulk grown nanotubes produced by CVD. Ultimately, the many
Figure 9 A) A setup used in the CVD production of carbon nanotubes. Here, catalyst is first deposited on the support of choice. After catalyst deposition, typically reduction of the catalyst is accomplished using $\text{H}_2$, followed by raising the temperature to 700-900 °C. After this temperature is reached, carbon-feeding gasses are introduced and allowed to react with the catalyst for a predetermined amount of time, usually lasting from minutes to a few hours. By varying the catalyst and growth conditions, samples dominated by either SWNTs or MWNTs can be achieved. Also, by varying the deposition method and support in addition to the reaction conditions, well dispersed carbon nanotubes (B) and carbon nanotube thin films (C) can be produced.
advantages of CVD growth makes it the most industrially compatible method and thus holds the greatest hope for the integration of carbon nanotubes into mainstream applications.

1.1.4 Carbon Nanotube Applications

Because of their many exceptional properties, carbon nanotubes have been explored in a large variety of potential applications. Their mechanical strength and small size makes carbon nanotube materials of great interest for developing composites. They have perhaps been most heavily investigated in circuitry and sensors as a result of their extraordinary electronic structure. In addition to these interesting properties, their graphite-like composition and packing have made them attractive materials in a variety of energy-related applications.

1.1.4.1 Carbon Nanotube Composites

Their sp² bonding and tubular structure makes carbon nanotubes extremely strong. In fact, carbon nanotubes are the strongest materials known to man under tensile strain, as stated previously. Furthermore, their high aspect ratio, small size, low density and high conductivity all make carbon nanotubes very attractive for use as composites with many different materials including polymers, ceramics and metals. A great deal of focus has been placed on carbon nanotube-polymer composites because of the ease with which they are mixed as well as the impressive results which arise from such products. Figure 10 shows a TEM image of such a carbon nanotube-polystyrene composite material. Good dispersion and binding with the polymer matrix are extremely important for the proper formation of carbon nanotube nanocomposites. This TEM image shows that the carbon nanotubes are well dispersed and embedded into the polystyrene matrix. As such, it was found by Qian et al. that addition of only 1% by
Figure 10[20] A TEM image of a carbon nanotube-polystyrene composite. As can be seen, the carbon nanotubes are well dispersed and integrated into the polystyrene matrix. The dispersion and integration into the polymer matrix are both crucial for the success of carbon nanotube composites.
weight of carbon nanotubes into a polystyrene matrix improved the tensile strength by 25\% and the elastic stiffness by 36-42\%. Using carbon fibers, 10\% by weight would be necessary to produce these same results. Furthermore, it was found by Andrews et al. that incorporation of 5\% purified SWNTs in isotropic petroleum pitch improved the tensile strength, modulus and electronic conductivity by 90\%, 150\% and 340\% respectively\[32]. This combination of strength and flexibility is extremely impressive and displays quite obviously the advantages of adding carbon nanotubes into polymer matrices. In fact the predicted sheer stress and effective modulus of carbon nanotube-polymer composite materials could reach over 500 MPa and 1 TPa respectively. These remarkable predictions and the exceptional results achieved thus far make the investigation of these composites an extremely active area of carbon nanotube application.

Although ceramics are stiff and relatively low in density, their brittleness makes them ineffective as structural materials. As such, carbon nanotube-ceramic composite materials have been investigated in the hopes of producing an exceptionally tough and temperature stable material. Ma and co-workers investigates carbon nanotube/SiC composites and found a 10\% improvement in strength and fracture toughness at 10\% carbon nanotube loading. Although this is a more modest improvement on the existing mechanical structures, this area of research is still being actively investigated. For example, SiO\textsubscript{x} coating of MWNTs has been investigated as a potential means for protecting the oxidation of carbon nanotubes. This oxidation is usually a significant problem in carbon-based materials; as a result, this route of combating such oxidation may prove valuable. Additionally, carbon nanotube-metal composites have been investigated not only for their mechanical improvements, but also for their catalytic ability. As such, electroplating has been utilized to deposit Ni, Ni-P and Co on the
surface of MWNTs. Also, Kuzumaki et al. formed Ti-MWNT, C₆₀-MWNT and Al-MWNT composites which showed marked improvements in the hardness and Young’s modulus as compared with the bulk. Ultimately, it is obvious that carbon nanotubes hold significant promise for application in composites of many different forms.

1.1.4.2 Carbon Nanotube FETs/Sensors

Owing to their unique and impressive electronic characteristics, one of the areas which has been most intensely investigated is the integration of carbon nanotubes in electronics devices and sensors. Indeed, it has been suggested that carbon nanotubes hold enormous potential for revolutionizing electronics. Considerable progress has been made in this area since their popularization. As mechanisms for controlling the alignment and electronic specificity of carbon nanotubes increases, so do the sophistication of the devices in which they are integrated. With this progress, it is hoped that carbon nanotube will realize their potential in these areas and thus help to drastically improve both electronics and sensors.

Because of early predictions as to their unique and applicable electronics structure, carbon nanotubes have been heavily investigated in transistors and other electronic devices. One of the simplest examples of such a transistor is known as “The Pick-Up Stick Transistor[33].” (Figure 11) Here SWNTs suspended in ortho-dichloro benzene (ODCB) are dispersed in a semiconducting organic host (polythiophene) in chloroform. These composites were then spun onto a pre-patterned Si/SiOₓ chip, as shown in Figure 11. Figure 11B specifically shows the random network of carbon nanotubes that is typical for such devices. Often nanotubes are deposited on pre-patterned chips, as described above, or are first grown on a chip with insulating oxide layer followed by electrode deposition[34]. One important feature of this type of transistor
Figure 11[33] An example of the pick-up stick transistor. a) A cartoon representation of this device. This basic but useful transistor can be used in a variety of FETs and devices. Often this transistor geometry is used in FET based sensors. b) Such a transistor can be formed by depositing electrodes and then spin coating the patterned wafer with carbon nanotubes suspended in solution. Alternatively, this transistor can be formed by growing a carbon nanotube thin film on a wafer followed by electrode deposition.
is that increasing the distance between electrodes decreases the off current. Essentially, increasing the distance between the electrodes increases the likelihood that semiconducting nanotubes will dominate the electronic conduction. This results from the fact that most methods for producing carbon nanotubes do so in a 1:2 metallic: semiconducting ratio. Hence, in a random network, increasing the distance between electrodes increases the number of nanotube-nanotube junctions across which electrons must flow in traveling from the source to the drain; this ultimately increases the likelihood that this path will be dominated by semiconducting carbon nanotubes. It should also be noted that mismatching in the work function of the carbon nanotubes and electrode materials creates large Schottky Barriers, which can strongly affect the electronic conductance of such transistors. This is always a concern in any carbon nanotube based transistor. As such, the choice of electrode metal is very important; typically Pt and Au are used because their work functions are close to that of carbon nanotubes. Other transistor networks capable of demonstrating electronic transport through individual carbon nanotubes have also been sought after because of their increased sensitivity. Such a transistor is shown in Figure 12[35]. Here, an individual carbon nanotube is grown on a doped Si wafer with SiO$_2$ insulating layer, followed by electrode deposition (Figure 12a) and then HfO$_2$ and Al gate layers (figure 12b and c). Such a device is both highly sensitive and capable of achieving extremely high on/off ratios (~10$^5$). Also, because of its single carbon nanotube construct, this device is able to probe the electronic characteristics of a single nanotube. Therefore, not only is it possible to learn about the carbon nanotube itself, but it is also highly sensitive to its surroundings, as mentioned previously. Hence, changes in the carbon nanotube surroundings would affect the observable electronic characteristics of this device. This
A single carbon nanotube device formed using a) Pd source and drain electrodes and a p-type doped Si back gate. b) This electrode deposition is followed by placement of a HfO$_2$ layer and Al top gate. The SEM picture in (c) shows the device which results from this process. Because of the sensitivity of single carbon nanotube devices, they are ideal for use in many transistors and sensors.
model has been used extensively for the detection of both chemical and biological analytes with remarkable sensitivity. One such example of a sensor formed from a similar single carbon nanotube transistor setup is shown in Figure 13a. It should be noted that, as was stated previously, most carbon nanotubes are p-type due to absorbed oxygen on their surface. The nanotube transistors used in this study were also p-type; as such, it was found that the conductance could be drastically affected by exposure to NO$_2$ or NH$_3$. As can be seen in Figure 13B, exposure of such a transistor to only 200 ppm of NO$_2$ increased its conductance by about three orders of magnitude. This considerable increase in conductance is explained by the p-type transistor characteristics. This p-type carbon nanotube transistor is dominated by charge carriers known as holes. These holes conduct through the uppermost energy levels of the valence band. Absorbing NO$_2$ onto the surface of the carbon nanotubes creates a charge transfer which effectively lowers the Fermi level closer to the valence band. This ultimately results in an increase in conductance. Conversely, exposure of carbon nanotubes to NH$_3$ transfers negative charge, which effectively raises the Fermi level away from the valence band. This ultimately resulted in a 100 fold drop in conductance when about 1% NH$_3$ was exposed to the carbon nanotube transistor. It is obvious from this work that carbon nanotubes can be effectively used as highly sensitive chemical sensors. A great deal of progress has also been made using carbon nanotube transistors as biological sensors. Figure 14A shows one such biological sensor in which a carbon nanotube Field Effect Transistor (FET) is bound to glucose oxidase (GOx) through a 1-pyrenebutanoic acid succimidyl ester linker. The GOx is covalently bound to the ester linker which, in tern, binds to the carbon nanotube through van der Waals interactions. These van der Waals interactions immobilize the GOx on the carbon nanotube which causes a change in the carbon nanotube conductance depending on the type of carbon nanotube used. This method is
Figure 13\textsuperscript{[36]} a) A carbon nanotube gas sensor comprised of a p-type semiconducting carbon nanotube. This p-type behavior gives rise to the conductance changes seen when sensing b) NO\textsubscript{2} and c) NH\textsubscript{3}. Using this mechanism, NO\textsubscript{2} and NH\textsubscript{3} can be sensed down to 200 ppm and 1 \% respectively due to the sensitivity of the electronic structure of carbon nanotubes.
Figure 14 A) A biological sensor in which a carbon nanotube Field Effect Transistor (FET) is bound to glucose oxidase (GOx) through a 1-pyrenebutanoic acid succimidyil ester linker. Sensing is accomplished by this linking which ultimately causes a change in conductance in this FET. Similarly, in B, polymers which are linked to biotin have been used to coat the carbon nanotubes. This biotin binds preferentially to streptavidin. This binding event ultimately causes a change in conductance similar to the sensor in A.
extremely versatile and can be used to sense virtually any protein which can be attached to a similar linker. In a similar fashion, Figure 14B\textsuperscript{[37]} shows a carbon nanotube transistor much like the one in Figure 14A, except polyethyleneimine (PEI)/polyethylene glycol (PEG) and polyethylene oxide (PEO)-based polymers have been used to coat the carbon nanotubes. Amide linking is then used to bind various proteins or enzymes to these linkers. These proteins act as a receptor to specifically bind whatever protein is desired in sensing. Here, biotin is used for its affinity to bind streptavidin. Hence, when streptavidin is introduced to the system, it will bind the biotin which is linked to the surface of the carbon nanotube, ultimately producing a change in conductance. As a corollary, other proteins will only bind non-specifically, which can therefore be easily washed away. Thus, this is a highly specific biological sensor based on a carbon nanotube FET.

Obviously carbon nanotubes can be used in many electronic devices for a variety of applications. These devices include but are not limited to transistors as well as chemical and biological sensors. It is hoped that the unique electronic properties of carbon nanotubes will continue to be integrated even more successfully in the years to come. However, significant progress has already been made to produce devices with extremely impressive results based on carbon nanotubes.

1.1.4.3 Carbon Nanotubes in Energy

Another area in which carbon nanotubes electronic and physical structure has made them applicable is in energy generation and alternative fuel storage. Specifically, significant focus has been placed on incorporating carbon nanotubes into solar cells and for hydrogen storage. Because of their high carrier mobility and p-type band structure, carbon nanotubes have been paired with electron-donors for use in organic solar cells. Figure 15\textsuperscript{[40]} shows three basic types of solar cells: a) Si-based b) Organic-based and c)
Dye-Sensitized. Often, carbon nanotubes are mixed with organic polymers in organic solar cells to create the photoactive layer shown in Figure 15B. Here, poly(3-octylthiophene)(P3OT), poly(3-hexylthiophene)(P3HT) and carbon nanotubes are combined to form a layer which produces a photocurrent. Because the work function of carbon nanotubes (4.5-5.1 eV) is close to the valence band of P3OT/P3HT, and because of their high carrier mobility (Figure 15D), this carbon nanotube-based organic solar cell is highly efficient at generating and separating the electron-hole pairs produced by incident light. Generating an exciton from incident photons is a fundamental requirement in solar cells. Because carbon nanotubes can be produced with varying diameters, and thus varying band-gaps, incident light with a broad range of wavelengths can be used to generate these excitons. This increases the efficiency of such organic solar cells. Also, charge separation of the exciton is extremely important for efficient photocurrent generation. Unless the carrier mobility facilitates the fast separation of the electron-hole pair, it will recombine and no current will be produced. As mentioned, the high carrier mobility of carbon nanotubes relative to other materials (Figure 15D) allows for highly effective separation of the generated electron-hole pairs.

Alternatively, carbon nanotubes have also been used in organic and dye-sensitized solar cells as electrode materials. When applied as a top-electrode, carbon nanotubes are usually combined with ITO to form such electrodes. Because these composites are transparent, they are ideal for such light harvesting applications. Also, as was previously stated, their high carrier mobility makes them extremely efficient at charge transport, and thus conducive for exciton separation. Essentially, the carbon nanotubes act as an effective three-dimensional hole-collecting network, which promotes this separation and has been shown to improve the photocurrent to twice what is demonstrated by ITO alone. Furthermore, this corresponds to a 2 %
Figure 15 shows three basic types of solar cells: a) Si-based b) Organic-based and c) Dye-Sensitized. As can be seen in d) the carrier mobility of carbon nanotubes is much higher than that of other materials like Si. Carbon nanotubes are most commonly incorporated into the photoactive material of organic–based solar cells or the electrodes of organic-based and dye sensitized solar cells. Using carbon nanotubes of varying diameters, and thus varying band-gaps, photoactive materials can be formed which can utilize a large range of wavelengths of light to generate excitons. Also, the large carrier mobility of carbon nanotubes makes them useful in photoactive layers and electrodes to facilitate charge separation.

<table>
<thead>
<tr>
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<th>CNT</th>
<th>Silicon</th>
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<tr>
<td>Density (g/cm³)</td>
<td>0.8–1.2</td>
<td>2.33</td>
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<tr>
<td>Band gap (eV, 300 K)</td>
<td>0.1–2.0</td>
<td>1.12</td>
</tr>
<tr>
<td>Resistivity (Ω cm, 300 K)</td>
<td>0.1</td>
<td>~100 (impurity density = 10^{12} cm⁻³)</td>
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<tr>
<td>Electron mobility (cm²/V·s, 300 K)</td>
<td>10⁸</td>
<td>&lt;1400</td>
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<tr>
<td>Hole mobility (cm²/V·s, 300 K)</td>
<td>10³</td>
<td>&lt;500</td>
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<tr>
<td>Manufacture</td>
<td>Bottom up</td>
<td>Top down</td>
</tr>
<tr>
<td>Cost</td>
<td>~50 $/g (SWNTs)</td>
<td>~0.2 $/g (MWNTs)</td>
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improvement of the overall efficiency of the solar cell. As such, carbon nanotubes are extremely versatile in light harvesting applications, performing many roles in the production of efficient, novel solar cells.

Additionally, carbon nanotubes have been extensively studied for their abilities to store H₂ for use in fuel cells. H₂ is an extremely important fuel source, as will be discussed in the following sections. Because of its graphitic structure and close packing geometries, it was thought that carbon nanotubes might hold great potential for H₂ storage. Early work with chemical sensors, as was discussed above, suggested that they were proficient gas adsorbers. This work fueled hope for this potential application. Several studies were done investigating carbon nanotube and carbon nanotube-composite materials for such ends. Figure 16a displays the results of some preliminary experiments. Here, H₂ adsorption of as produced SWNTs (Sample 1) and purified SWNTs (Samples 2 and 3) was analyzed. It was found that the purification of SWNT samples improved the gravimetric uptake of H₂ by 2 wt%. Furthermore, impressive gravimetric uptakes of approximately 4 wt.% were achieved at high pressures. It should be noted that the stated 2010 H₂ uptake system target for the Department of Energy (DOE) is approximately 6 wt.% These targets will be discussed further in the coming sections, but it is obvious that carbon nanotubes can demonstrate impressive H₂ gravimetric uptakes. Further preliminary studies indicated that SWNTs could demonstrate even higher gravimetric uptakes up to approximately 8 wt.% in as produced and sonicated SWNT samples at high pressures. Despite these impressive gravimetric uptake values, carbon nanotubes were eventually found to be impractical for H₂ sorption media because of their relative high cost and difficulties in producing SWNTs with the optimum characteristics to efficiently store H₂. However, it is
Figure 16 a) H₂ adsorption of Sample 1: as prepared SWNTs, Sample 2: SWNTs purified by soaking in 37 % HCl acid for 48 h, followed by rinsing with deionized water and drying at 423 K and finally Sample 3: SWNTs prepared similar to those in Sample 2, except with vacuum heat-treating for 2 h at 773 K. Sample 3 reaches a H₂ gravimetric uptake of 4 %. b) Hydrogen uptakes of samples prepared from SWNTs. Amazingly, these samples demonstrated a H/C absorption ratio up to 1, which corresponds to a gravimetric H₂ uptake of >8 wt.%.
obvious that carbon nanotubes have a great deal of potential in a variety of applications related to energy production and fuel storage.

1.1.5 Carbon Nanotube Challenges

The many unique and intriguing characteristics of carbon nanotubes make them useful in a large variety of different applications. These applications span from composites, which utilize the mechanical strength of carbon nanotubes, to electronic FETs, sensors and solar cells, which utilize their exceptional electronic characteristics. As such, carbon nanotubes are extremely versatile and useful materials. Undoubtedly, further investigation of this remarkable material will spawn even more applications which will hopefully lead to the mainstream integration of carbon nanotubes into a variety of technologies. However, several challenges still remain for this mainstream integration to be successful. Firstly, because CVD holds the greatest hope for cost-effective bulk production of carbon nanotubes, progress towards the fabrication of carbon nanotubes with controlled alignment, diameter and electronic structure using CVD needs to be made. Most electronic applications require that carbon nanotubes be well aligned. As will be discussed, current methods for producing aligned carbon nanotube samples lack scalability and consistency. Furthermore, often times the diameter distribution of as produced nanotube samples is relatively wide. Achieving samples with narrow diameter distributions, and thus with well-controlled band-gap, often requires complicated post-synthesis treatment\(^{14}\). Furthermore, as was previously stated, CVD growth tends to produce a mixture of semiconducting and metallic carbon nanotubes. Such mixtures are undesirable for most applications. Controlling the electronic specificity and alignment are perhaps the largest barriers to the success of carbon nanotubes in modern applications. Significant progress needs to be made in both of these areas, as well as to the cost of carbon nanotube productions in order for carbon
nanotubes to realize their full potential to revolutionize modern electronics and other technologies.

### 1.2 Introduction to Micro/Mesoporous Carbons

#### 1.2.1 Alternative Energy and the DOE H₂ Storage Goals

As stated on the DOE website (http://www.energy.gov/), fossil fuels presently provide approximately 85% of all energy consumed in the United States. However, fossil fuels are non-renewable and unclean sources of energy. Society’s dependence on fossil fuels and other non-renewable energy sources is therefore one of the most concerning issues to date. As such, discovering alternatives to such fuels has become a heavily researched topic, especially within the last several years.

Among the alternative fuels and energy sources being investigated, some of the most promising are coal, nuclear, solar, wind, natural gas and hydrogen. Each has many advantages and disadvantages and it is unlikely that a single source will solve this energy crisis. However, it is important to know which have the greatest potential to meet the present energy requirements. Firstly, coal has been used for many years to derive power, particularly within the United States. Today, coal supplies over half of this nation’s electric power. Furthermore, the United States is home to approximately one-quarter of the world’s coal reserves. Understandably, much focus has been placed on this fuel. However, greenhouse gas emission and water pollution are two deeply concerning by-products of coal-fired power plants. This pollution is a major issue presently standing in the way of an increased reliance on coal. The DOE is presently working with the private sector to develop technologies for the development of an emission-free coal-fired power plant for the future. Further investigation into dealing with these issues is being carried out as part of the Clean Coal Power Initiative.
Figure 17 Percent of net electricity generation from nuclear power. It should be noted that this has increased four-fold over the last three decades, reflecting the viability of nuclear energy as an alternative energy source. (Image from DOE website)
Figure 18 a) A 750 kW NEG Mico Turbine in Moorehead Minnesota. Windmills/turbines like this one can be used to produce electricity cleanly and renewably. b) A table illustrating the power density achievable from wind at various turbine heights and wind speeds. (Image and Table from DOE website)
However, coal is not considered a renewable energy source. As such, relying on coal to a significant extent will not be a permanent solution. Nuclear power generates a large fraction of the remaining electric power used by the United States (Figure 17). Over the last several decades, the nation’s reliance on nuclear power has quadrupled, and within the last few years, nuclear energy has provided approximately 70 billion kilowatt-hours of electricity per year. However, pollution with respect to the cooling towers in the nuclear energy plants as well as dispersed placement of these plants makes heavy reliance on this form of energy unrealistic. Solar and wind energy have been highly touted because of their clean and renewable energy generation. Wind power is presently being used to create over 34 billion kilowatt-hours of electricity each year. Furthermore, depending on wind-speed, power densities of up to 2000 W/m$^2$ may be achievable. (Figure 18) Although this is in the case of relatively fast winds, it is non-the-less impressive especially among renewable fuels. However, wind power generation is not compatible with all areas of the United States. As can be seen in Figure 18, the use of large windmills is necessary in such generation, which may prove incompatible with densely populated areas. Solar energy is being harvested through photovoltaic cells, concentrating solar power technologies and low temperature solar collectors. Photovoltaic solar cells are of particular interest because of their ability to be incorporated into populated areas, as can be seen in Figure 19. Furthermore, they are diverse enough to be incorporated for a variety of needs, such as powering small personal electronics as well as large energy requirements such as electric grids. However, the expense and relatively low-efficiencies of solar harvesting technologies have been key issues standing in the way of their more common implementation. These technologies have all proven useful, but all have limitations which stand in the way of their application as robust fossil fuel replacements. This is particularly true when
Figure 19 A photovoltaic solar cell harvesting light energy for the production of electricity. It is apparent from this image that these solar cells can be incorporated into populated areas. (Image from DOE website)
considering power generation for transportation concerns. Two-thirds of the oil consumed daily is for transportation. Because the energy sources discussed in the previous paragraph are mostly incompatible with much of the transportation industry, other fuels have been sought after to meet the need to developing an alternative energy source applicable in industrial, home and automotive settings. Natural gas is one of the most attractive of these investigated fuels. In fact 900 of the next 1000 US power plants will use natural gas. Natural gas is also domestically produced (Figure 20), making it particularly important for US markets. Furthermore, it is relatively clean as compared to fossil fuels when used in automobiles. It can be stored on board a vehicle in tanks as a compressed gas or as a cryogenically cooled liquid. In addition to natural gas, it is believed that hydrogen holds enormous potential as an alternative fuel. Hydrogen can be produced by fossil fuels and biomass and even by electrolyzing water. It is light, abundant and completely emission free upon combustion:

\[ 2H_2 + O_2 \Rightarrow 2H_2O \]

Furthermore, \( H_2 \) is relatively cheap and has an extremely high energy density per unit mass (143 MJ/kg), especially compared to fossil fuels (<70 MJ/kg). As such, it is extremely attractive as an alternative fuel. However, \( H_2 \) has one major drawback: it has a low energy density per unit volume. Because \( H_2 \) is such a light gas, containing and storing \( H_2 \) is a challenge that has yet to be fully overcome. Thus, finding various ways to store \( H_2 \) so as to increase its deliverable energy per unit volume has been a major effort of the DOE. Many methods have been explored to achieve this storage. As shown in Figure 21, most of the methods displayed above have not yet achieved the targets set forth by the DOE. The DOE set these targets based on allowing a light-duty fuel cell
Figure 20 Marketed Production of Natural Gas in the United States and Gulf of Mexico (GOM) in millions of cubic feet. (Image from DOE website) Obviously, the ability to produce large amounts of natural gas within the US makes this an attractive alternative fuel.
Figure 21 The relative volume associated with various storage methods. These volumes are based on the storage capacities of these materials and the DOE system targets. (http://www.afdc.energy.gov/afdc/fuels/hydrogen_alternative.html)
vehicle to travel 300 miles before refueling. One leading area being investigated to accomplish this storage involves the physio/chemiosorption of H\textsubscript{2} onto sorbent materials. Specifically, the revised 2015 DOE targets require a H\textsubscript{2}/sorbent system to have a gravimetric uptake of 5.5 wt.% and a volumetric uptake of 40 g/L. Again, these targets are for a H\textsubscript{2}/sorbent system. It is likely that the material uptake requirements would need to be higher than these numbers in order to meet these system goals. Furthermore, this system should be cost effective ($2/kW) and energy efficient. This means that a binding energy of most sorbent materials should be between 20-30 kJ/mol in order to achieve a large net capacity. That is, in order to obtain a large amount of useable H\textsubscript{2} in an energy efficient and cost effective manner, a H\textsubscript{2} binding energy in this range is necessary for most sorbent materials. As such, the adsorption of H\textsubscript{2} onto many materials has been investigated.

1.2.2 Materials for H\textsubscript{2} Storage

Initially, carbon nanotubes showed a great deal of promise for H\textsubscript{2} storage, as was stated previously. However, they were ultimately found to be unsuitable for such applications as a result of their relatively high cost and an inability to reliably produce them with well-controlled characteristics. As such, many other materials were investigated for their hydrogen sorption abilities. Some of the materials which have demonstrated the most promise are metal hydrides, metal organic frameworks (MOFs) and porous carbons.

1.2.2.1 Metal Hydrides

Materials used for H\textsubscript{2} storage, particularly H\textsubscript{2} sorption, should possess a large H\textsubscript{2} storage capacity, fast kinetics of hydrogenation/dehydrogenation, easy activation and minimal deterioration during hydrogenation cycling\textsuperscript{[45]}. Metal hydrides of the form AB\textsubscript{5}
Figure 22\textsuperscript{[48]} a) A TEM image of Mg\textsubscript{2}Ni hydride which displays up to 7 wt.% H\textsubscript{2} gravimetric uptake. Mg based metal hydrides are particularly interesting for their H\textsubscript{2} storage capacities. b) However, like most metal hydrides, these materials suffer from relatively slow hydrogenation/dehydrogenation cycling and low net capacities. These characteristics result from their high-binding energy to H\textsubscript{2}. 
and AB₂ have historically been most studied. AB₃ metal hydrides have relatively good hydrogenation cycling kinetics, however they have relatively low hydrogen storage capacities (≤1.5 wt.%). Furthermore, they typically suffer from decrepitation and/or disproportionation upon hydrogenation cycling. AB₂ metal hydrides typically do not suffer from such degradation, but still have relatively small hydrogen storage capacities (<1.8 wt.%). On the other hand, it was found that metal hydrides which incorporated Mg, such as Mg₂Ni (Figure 22a), had hydrogen storage capacities scaling to over 7 wt.%. However, the hydrogenation cycling kinetics of such metal hydrides was found to be unacceptably slow (Figure 22b). Furthermore, these slow kinetics occurred even after extensive activation at temperatures up to 400 °C. This has been the major obstacle standing in the way of the success of metal hydrides. They typically display excellent H₂ storage capacities, however they suffer from relatively low net capacities (usable H₂). This low net capacity is related to the adsorption energies of H₂ onto the metal hydride. Because they are very high, it takes extreme conditions such as high temperature activation and low pressures to extract the H₂ for use. These conditions are relatively energy-expensive, resulting in heat management problems in on-board systems. As a result, it is presently inefficient to use metal hydrides for H₂ storage despite their extremely impressive H₂ storage capacities. Also, this example makes the important point that available net capacity of H₂ is more important to H₂ storage than is H₂ storage capacity.

1.2.2.2 Metal Organic Frameworks (MOFs)

Other metal-based materials which have been heavily investigated recently for H₂ storage concerns are metal organic frameworks (MOFs). MOFs are crystalline solids of metal ions or clusters connected by organic based molecular bridges (Figure 23a-d). They can be synthesized with various metals and linkers in order to impart a large array
Examples of various MOF structures, specifically a) MOF-177, Zn(O(btb))(btb = benzene-1,3,5-tribenzoate) b) IRMOF-8, Zn$_3$O(ndc)$_3$ (ndc = naphthalene-2,6-di-carboxylate c) MIL-53 M(OH)(bdc) (M = Al$^{3+}$ or Cr$^{3+}$) and d) Zn$_2$(bdc)$_2$(dabco) (dabco = 1,4-diazabicyclo[2.2.2]octane). (C: black, N: green, O: red, Zn: blue polyhedra, M: green octahedral) The yellow spheres represent the pores in the evacuated crystalline frameworks. d) As can be seen from the table, MOFs can demonstrate high surface areas and impressive H$_2$ uptakes. However more work needs to be done to increase their available net capacity, as the binding energy of MOFs is still generally too high.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Frame size (Å)</th>
<th>Accessible volume fraction (%)</th>
<th>Apparent surface area (m$^2$ g$^{-1}$)</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>H$_2$ uptake (wt%)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn$_2$O(bdc)$_2$. IRMOF-1</td>
<td>7.8/15.2</td>
<td>0.59</td>
<td>3362</td>
<td>1.19</td>
<td>1.32</td>
<td>77 K, 1 atm, 1.0 RT, 20 bar</td>
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<td>Zn$_2$O(ndc)$_3$. IRMOF-8</td>
<td>5.0/11.2</td>
<td>0.50</td>
<td>2630</td>
<td>0.03</td>
<td>1.0</td>
<td>77 K, 1 atm, 1.65 RT, 40 atm</td>
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<tr>
<td>Zn$_2$O(hpd)$_2$. IRMOF-11</td>
<td>6.4/11.4</td>
<td>0.40</td>
<td>1911</td>
<td>0.68</td>
<td>1.62</td>
<td>77 K, 1 atm</td>
</tr>
<tr>
<td>Zn$_2$O(btb)$_2$. MOF-177</td>
<td>5.4/11.8</td>
<td>0.42</td>
<td>1501</td>
<td>0.51</td>
<td>0.99</td>
<td>77 K, 1 atm, 2.0 RT, 10 atm</td>
</tr>
<tr>
<td>Zn$_2$O(ndc)$_3$. MIL-53</td>
<td>6.4/6.4</td>
<td>0.29</td>
<td>1590, 1020</td>
<td>-</td>
<td>-</td>
<td>77 K, 1 atm, 3.8 RT, 10 atm</td>
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<tr>
<td>Cr$_3$(OH)$_4$(bdc)$_2$. MIL-53</td>
<td>6.6/6.6</td>
<td>0.29</td>
<td>1500, 1020</td>
<td>-</td>
<td>-</td>
<td>77 K, 1 atm, 3.1 RT, 10 atm</td>
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<tr>
<td>Mn$_2$(HCO)$_4$.</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>Cu$_2$(hfpbb)$_2$ (H$_2$hfpbb)</td>
<td>3.4/7.1</td>
<td>0.03</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>77 K, 1 atm</td>
</tr>
<tr>
<td>Ni$_2$(cyclam)$_2$(bpy)$_2$.</td>
<td>6.1/7.6</td>
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<td>817</td>
<td>0.17</td>
<td>1.1</td>
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<td>Zn$_2$O(btb)$_2$. (dabco)</td>
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<td>1450</td>
<td>-</td>
<td>-</td>
<td>77 K, 1 atm, 2.0 RT, 40 atm</td>
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<tr>
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<td>0.15</td>
<td>0.6</td>
<td>77 K, 1 atm</td>
</tr>
<tr>
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<td>-</td>
<td>0.14</td>
<td>0.7</td>
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<td>Ni$_2$(bta)$_2$ (3-picol) (pd)$_2$.</td>
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<td>-</td>
<td>0.63</td>
<td>2.1</td>
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<td>502</td>
<td>0.20</td>
<td>1.12</td>
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<tr>
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<td>390</td>
<td>0.13</td>
<td>0.98</td>
<td>Kf, 48 bar</td>
</tr>
<tr>
<td>Cu$_2$(pdac)$_2$(py)$_2$. CPL-1</td>
<td>3.4/5.0</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>89 K, 1 atm</td>
</tr>
<tr>
<td>Cu$_2$(bpta)$_2$. MIL-505</td>
<td>6.7/10.1</td>
<td>0.37</td>
<td>1646</td>
<td>0.63</td>
<td>2.48</td>
<td>77 K, 1 atm</td>
</tr>
</tbody>
</table>
of characteristics such as geometric rigidity, chemical functionality and chirality. Furthermore, they can be scalably synthesized in high yield. Owing to their extremely high surface area, they stirred a great deal of attention for application in H\textsubscript{2} storage. Early results indicated that MOFs could be demonstrated with surface areas up to 4500 m\textsuperscript{2}/g (MOF-177 in Figure 23a). Furthermore, predictions about their H\textsubscript{2} storage capacities have proven extremely impressive. For example, IRMOF-2-60 has been predicted to have a H\textsubscript{2} capacity of 9.7 wt\% at 77 K and 90 bar\textsuperscript{[47]}. Figure 23d shows the experimentally determined H\textsubscript{2} storage capacities of several MOF derivatives. The storage capacities of these MOFs preliminarily ranged up to about 3.8 wt.% at 77 K and 16 bar, which was impressive, but not as much as was expected from their high surface area and tunable structure. Recently, Yaghi et al. achieved a MOF-177 structure having a surface area of over 5000 m\textsuperscript{2}/g and displaying H\textsubscript{2} storage capacities of up to 7.5 wt.% at 70 bar and 77 K\textsuperscript{[48]}. These results were extremely impressive and inspired a great deal of interest in MOFs as potential H\textsubscript{2} storage media. However, few investigations of the kinetics and binding energies of these materials have been rigorously done. In fact, preliminary experiments suggest that, much like in metal hydrides, the binding energy of H\textsubscript{2} to MOFs is very high. This large binding energy results in energy and heat management issues in on board system. Despite these issues, MOFs could prove very attractive materials for use in H\textsubscript{2} storage; however, more work needs to be done to develop these materials\textsuperscript{[49]}.

1.2.2.3 Porous Carbons

A purely organic based physisorption of H\textsubscript{2} can be accomplished using porous carbons. Because they are comprised almost exclusively of carbon, they are lighter than metal hydrides and MOFs. A result of this fact is that porous carbons with very high surface areas can be achieved from a variety of synthesis methods\textsuperscript{[50],[51]} (>3000 m\textsuperscript{2}/g).
Moreover, porous carbons with tailored pore diameters and volumes can be achieved on a large scale, relatively cheaply. The ability to tailor pore diameters has proven especially important, as not all pore diameters are desirable for optimal H₂ storage. In fact, it has been shown that micropores (pores with diameter ≤2 nm) are preferred for significant H₂ sorption[52]. A typical TEM picture of such microporous carbons can be seen in Figure 24. Obtaining such pores is crucial for efficient H₂ storage. Additionally, it was found by Chahine et al. that H₂ adsorption capacities scaled with surface areas[53],[54]. Later, Chahine would assert that for every 500 m²/g of surface area obtained on a porous carbon with graphitic slit pores, approximately 1 wt.% H₂ gravimetric uptake was achievable. This informal rule later became known as the “Chahine Rule.” As such, it is predicted that porous carbons with ~3000 m²/g surface area should have gravimetric H₂ storage capacities at around 6 wt.%, and would thus approach the DOE 2015 system targets for H₂ storage. This rule has been generally proven inaccurate for most experimental observations; nonetheless, the general trend of increased H₂ sorption with increased surface area of porous carbon materials holds true. However, synthesizing a porous carbon with the appropriately large surface area and small diameters for optimal H₂ storage has proven difficult for most methods. Regardless of this fact, large gravimetric and volumetric H₂ uptake values have been demonstrated by several porous carbons (Figure 25a and b). It should be noted that the porous carbon AX-21 has become a standard with which most other porous carbon samples are compared. AX-21 has a measured surface area of up to 3300 m²/g and has displayed 3 wt.% H₂ sorption at 77 K and 2 bar. Even though this material has impressive gravimetric H₂ storage capacities, porous carbon materials have demonstrated uptakes up to ~7 wt.% at 77 K and 20 bar[51]. Such high gravimetric uptakes make these materials good candidates for investigation in
Figure 24 a) and b) are TEM images of two microporous carbons derived from the thermal treatment of poly (etherether ketone). Porous carbons with pore diameters ≤2 nm (micropores) are best for H₂ storage concerns.
Figure 25\textsuperscript{[53]} Porous carbon have been shown to have impressive a) gravimetric and b) volumetric H\textsubscript{2} uptakes. One example of such a porous carbon is AX-21, which has a surface area of 3300 m\textsuperscript{2}/g which translates to a gravimetric uptake of \~3 wt.% and a volumetric uptake of \~almost 30 g/L. These values are impressive among porous carbon materials; as such, AX-21 has become a benchmark for which most other porous carbons are compared.
H₂ storage. What is even more remarkable is that the net capacity for H₂ sorption for most porous carbons is extremely high (~99 %). This means that nearly all of the H₂ stored in the porous carbon templates is recoverable as useable H₂. The large H₂ gravimetric uptake values combine with the large net capacities to make porous carbon an exceptional candidate for applications as H₂ storage media.

1.2.3 Micro/Mesoporous Carbon (Synthesis Background)

Porous carbons have set themselves apart as an excellent candidate for H₂ storage media, in addition to a variety of other applications. Of particular interest in H₂ storage is the area of low diameter mesoporous carbons (diameter = 2-50 nm) and microporous carbons. However, as was stated previously, synthesizing a porous carbon with the appropriately large surface area and the appropriately small pore diameters has been very challenging. Several methods have been employed for achieving such a material with varying degrees of success. Perhaps the most successful have been templated synthesis, carbide-derived carbon synthesis and polymer activation.

1.2.3.1 Templated Synthesis

Using a template to impart structure to a porous carbon is a method frequently employed. In this templated synthesis, finding the correct porous template is a crucial step. Because of their highly porous structure and relatively large surface areas, zeolites are often employed for this templating. Figure 26 shows a typical procedure which utilizes a zeolite and pyrolytic carbon infiltration to form a porous carbon. The resulting carbon is structurally similar to the original zeolite, but will have a larger surface area. The increased surface area comes from two main areas. Firstly, since this is a casting or templating procedure, the area originally occupied by the zeolite will be empty space. Carbon only forms a cast of the original template as shown in Figure 26c, leaving exposed surface area where the zeolite previously occupied. Secondly, zeolites are
aluminosilicate structures. As such, a carbon representation of their structure would be lighter than the original structure which contained aluminum, silicon and oxygen. By decreasing the weight, the surface area is effectively increased, as the units of surface area are normalized per gram of material. An example of one such material synthesized using zeolite Y as a template is shown in Figure 27a. As can be seen, a high surface area porous carbon with long-range order very similar to the zeolite template can be synthesized reliably using such templating. However, this method does have drawbacks. Perhaps most significantly, removal of the zeolite template often requires the use of extensive acid leaching. This often employs HCl and HF among other dangerous acids. Also, this method creates a large amount of waste. As a result, synthesis of porous carbon with this method is hazardous and problematic for industrial scaling.

1.2.3.2 Carbide-Derived Carbons (CDC)

Selective removal of metals from metal-carbides is a controllable and versatile method for producing porous carbons. This process is often carried out using Chlorine gas at high temperatures (>600 °C), as illustrated by the equation\(^{[55]}\):

\[
\text{MeC} + (x/2)\text{Cl}_2 \rightarrow \text{MeCl}_x + \text{C}
\]

Using this reaction, it is possible to achieve microporous carbons with well-controlled diameters and scalable, large surface areas (~2000 m\(^2\)/g)\(^{[56]}\). This high surface area can be seen in CDC made from the chlorination of B\(_4\)C (Figure 28). It is important to note that finding the correct chlorination temperature is essential to achieving such large surface area microporous carbons. Furthermore, it was found that the chlorination temperature had an effect on the pores of the products, as demonstrated by the CDC obtained using TiC (Figure 29). As is evident from this figure, both the pore size and structural regularity of CDC samples is temperature dependent. This means
Figure 26\textsuperscript{[57]} A pictorial representation of the templated synthesis of porous carbons. a) In the beginning, a zeolite with the appropriate structure is chosen. b) Secondly, a carbon precursor infiltrates the zeolite template. c) Lastly, the zeolite template is removed and the carbon cast with higher surface area is formed.
Figure 27[58] A microporous carbon derived from zeolite Y. This microporous carbon displayed long range ordering (d~1.4 nm) identical to that displayed by zeolite Y. The surface area of this microporous carbon was found to be very large at 1910 m²/g.
Figure 28[56] CDC’s surface areas generally depend on chlorination temperature. Optimizing this temperature allows for CDCs with very large surface areas to be formed (2000 m$^2$/g). Here, one such CDC formed from the chlorination of B$_4$C is presented.
that by simply choosing the appropriate metal-carbide and the appropriate reaction conditions, it is possible to tailor the structure of the CDC to whatever ends are desired. Another advantage of this method is that it doesn’t require any post processing, as was necessary in much of the templated work. As such, no significant solid or liquid waste is formed.

However, this will not be the case if the chlorination does not completely remove the metals from the metal-carbide structures. Failure to remove these metals will not only decrease the surface area of the CDC, but will necessitate post processing which will likely involve acid treatment. Furthermore, this process uses chlorine gas, which is dangerous. Both of these issues have limited the large-scale production and engineering of CDCs.

1.2.3.3 Polymer Thermal Treatment/Activation

Chemically or physical activation has been employed to produce porous carbons with high surface areas and pore with a wide range of diameters and volumes. Typically, in chemical activation, KOH or another oxidizer is employed with a carbon source to undergo the following reaction:\[51:\]

\[
6\text{KOH} + 2\text{C} \iff 2\text{K} + 3\text{H}_2 + 2\text{K}_2\text{CO}_3
\]

In chemical activation, a similar oxidation is carried out, except the carbon products are gaseous. This oxidation/gasification occurs when a carbon source, often a polymer, is exposed to a gaseous oxidizer such as CO\(_2\) or steam. This activation ultimately produces CO and CO\(_2\). In both forms, vacancies in the carbon networks of the carbon source are left in place of the extracted carbon. The results from such activation experiments can be seen in the TEM images of Figure 30. The nucleation of such oxidation occurs at the least stable carbon sites; this nucleation often occurs during the entire length of the activation. This nucleation is in equilibrium with pore diameter and volume “etching.” Different
Figure 29 A CDC derived from TiC being chlorinated at a) 400 °C b) 800 °C and c) 1000 °C. It is obvious that the degree of long-range order of the CDC structure seems to increase with chlorination temperature.
Figure 30 a) and b) are TEM images of a porous carbons derived from both chemical and physical activation.
activation agents produce carbons with different ratios of number of pores: pore diameters and pore volumes. Regardless, as is demonstrated in Table 1, porous carbons with large total pore volumes (1.9 cm$^3$/g) and surface areas ($\geq$2000 m$^2$/g) can be consistently achieved over many samples relatively easily. Furthermore, recently activated carbons have been synthesized which demonstrate surface areas $>3000$ m$^2$/g$^{[51]}$. With these exceptionally high surface areas and reasonable pore diameters, activated carbons have been investigated for a variety of applications including H$_2$ storage. Furthermore, this method does not require any post-production processing, nor does it utilize harmful chemicals or produce hazardous waste products. This method is cheap, scalable and safe and produces porous carbons which are utilizable as produced.

The major limitation of these materials, particularly for H$_2$ storage concerns, has been an inability to simultaneously produce samples with large surface areas and pore volumes while maintaining small pore diameters. Achieving such products would represent a major advancement in microporous carbon synthesis and thus in H$_2$ storage.
Table 1 Porous carbons obtained from chemical activation. It is obvious from this table that activated carbons can be synthesized with large surface areas (>2000 m²/g) and pore volumes (>1.9 cm³/g).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>ZnCl₂/Shell Ratio</th>
<th>S\textsubscript{BET} [m²/g]</th>
<th>S\textsubscript{NE} [m²/g]</th>
<th>V\textsubscript{NI} [cm³/g]</th>
<th>V\textsubscript{ET} [cm³/g]</th>
<th>V\textsubscript{NE} [cm³/g]</th>
<th>V\textsubscript{NE}/V\textsubscript{ET} [%]</th>
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<td>Filtrasorb100</td>
<td>--</td>
<td>937</td>
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2. Carbon Nanotube Orientation Control

2.1 Introduction

Since their discovery in 1991 by Iijima\textsuperscript{[1]}, the mechanism of carbon nanotube formation has been intensely investigated\textsuperscript{[60],[61],[62],[63],[64]}. This interested has been generated due to their extremely useful mechanical\textsuperscript{[65],[66]} and optical properties\textsuperscript{[13],[67]}. However, it is their promise for revolutionizing modern electronics that perhaps holds their most exciting potential\textsuperscript{[68],[69],[70]}. Although much progress has been made towards understanding the nanotube growth mechanism, as well as towards overcoming the barriers which have inhibited the realization of their full potential for application in modern devices, there is still much work to be done. Specifically, as has been discussed, there are several major issues which still limit the application of carbon nanotubes to modern electronic devices. Most limiting are the fact that there exists no scalable methods to produce SWNTs with controllable orientation, nor are there any scalable methods to selectively achieve electronically specific carbon nanotubes. These limitations are believed to be the last major issues standing in the way of mainstream carbon nanotube based modern electronics. As such, demonstrating control over the orientation as well as the electronic specificity of carbon nanotubes would represent significant progress towards realizing their considerable promise.

Firstly, controlling the orientation of carbon nanotubes is essential to their application in most electronic devices. However, demonstrating such control in a reliable and up-scalable way has proven extremely difficult. Most existing methods rely on external forces to manipulate the carbon nanotubes, either during or post growth. For example, some progress has been made in post-growth orientation manipulation using methods such as electrophoresis. Electrophoresis utilizes an electric field and liquid
Figure 31 Carbon nanotubes aligned by (a) electrophoresis (b) high flow rate and (c) external electric field. As can be seen, the density and length of these aligned samples are not large enough for acceptable application to large scale electronic devices.
surface tension to form bundles of carbon nanotubes from nanotubes dispersed in liquid (Figure 31a). These tight bundles can then be placed wherever is desired with controllable orientation. However, like most post-growth alignment methods based on solution processing, electrophoresis suffered from an incompatibility with many SWNT based technologies as well as with carbon nanotube purity issues. Also, scalability and efficient engineering concerns limited these as potential solutions to this problem. As such, controlling the orientation of carbon nanotubes during growth became an attractive means for achieving this goal. Of the aligned growth methods, most significant progress was demonstrated using external electric fields\cite{71}, surface modification\cite{72} and lattice guidance\cite{73}. External electric fields (Figure 31c) and high gas flow rates (Figure 31b) both gave very impressive results, resulting in carbon nanotube samples directly applicable in electronic devices. However, the density and length of these nanotubes was still less than was desirable for their appropriate application. As such, increasing the length and density of such well-oriented carbon nanotubes became the focal point of much research, some of which is discussed below.

2.2 Fast Heating Slow Cooling

2.2.1 Materials/Experimental

HiPCO carbon nanotubes rich in Fe cat. were used as received from Rice University. These nanotubes were suspended in nanopure water (NP H$_2$O) filtered from a Barnstead NANOpure water filtration system and using either Triton X-100 purchased from Sigma Aldrich or sodium dodecyl sulfate (SDS) purchased from Fisher Scientific. Si wafers with 1 μm SiO$_x$ were used as received from University Wafer. CVD was done in a Lindberg Blue one-inch tube furnace using a three foot long, one inch diameter quartz tube to house the sample and reaction gasses. All gasses were purchased from National
Figure 32 CVD setup for “Fast-Heating Slow-Cooling” growth of ultra-long carbon nanotubes. The green arrow indicates the direction in which the furnace is moved and the blue arrow indicates the placement of the Si sample.
Welders. All other chemicals were purchased from Fisher Scientific and used as received unless otherwise specified.

 Typically, HiPCO catalyst was patterned on one edge of a 1 cm² Si chip. After patterning, the chips were placed into a quartz tube set in a CVD tube furnace. H₂ was flowed at 200 standard cubic centimeters per minute (sccm) and the system was flushed for 5 min. After flushing, the furnace was heated up to 700 °C under H₂ to reduce the Fe-based catalyst for about 5 min. The system was then allowed to gradually cool to below 200 °C. Following cooling, the furnace was moved such that the patterned Si sample was outside of the heating region, as shown in Figure 32. The furnace was heated to 1000 °C and CO was introduced at a flow rate of approximately 800 sccm. Once this temperature was reached and all gasses were introduced, the furnace was moved so that the sample was in the center of the heating region and the furnace was changed to the reaction temperature of 900 °C. The carbon nanotubes were then allowed to grow for at least one hour before turning off the CO and allowing the system to cool under H₂.

“Trenched” substrates, or substrates with trenches etched into them were prepared using E-beam lithography or basic photolithography and reactive ion etching (RIE). After the pattern was formed using poly (methyl methacrylate) (PMMA) as resist in the case of E-beam lithography, or Shipley-1813 in the case of basic photolithography, RIE was done to etch the exposed region of SiOₓ in the Si/SiOₓ substrate. Typically, this etching was done to a depth of 200 nm. After the trenched samples were prepared, the nanotubes were grown perpendicular to the width of the trenches, thus resulting in suspended nanotube samples.

In the case of suspended nanotube devices, trenches were formed after growing such aligned carbon nanotubes. After growth, Cr (3 nm) and Au (30-50 nm) were deposited on top of these tubes. These metal-coated samples were then coated with
Shipley-1813 resist followed by standard photolithography to expose regions to be etched into trenches. The chips with Shiple-1813 were then “hard-baked” at 120 °C for 15-25 min to insure the integrity of the photoresist as a mask for etching. This was followed by submersion in successive etches of commercial Au and Cr etchants purchased from Transene Inc., and in buffered HF (BHF). These steps etched through the Au, Cr and SiO₂ respectively. In some samples, these steps were followed by a Si etching step (KOH stabilized in isopropanol).

2.2.2 Results/ Discussion

In order to avoid limitations caused by the substrate effects during surface growth, a “kite-mechanism” of carbon nanotube synthesis was developed[74]. This mechanism relies on the strong convection current present at the extremely high temperatures used in typical CVD processes. Because of the strength of the convection current, the catalyst nanoparticles are actually lifted up, off of the substrate during growth. This phenomenon is illustrated in Figure 33. As can be seen in this figure, we begin with a stationary catalyst particle on the substrate surface. (Figure 33A) This particle is patterned and reduced while on this surface; however, with the sudden introduction of the convection current, the catalyst lifts off of the surface and is suspended in the laminar flow of the reaction gasses during growth (Figure 33B). The vector sum of the forces provided by the convection current and the flowing reaction gasses results in an angled vector which is oriented linearly away from the catalyst region towards the opposite end of the chip. Thus, the catalyst should actually be carried parallel to the reaction gas flow. (Figure 33C) While the catalyst is carried by this net force, it produces a carbon nanotube. This nanotubes will keep the nanoparticle tethered to the substrate and become aligned by this entire process. Because there are no longer surface defects or other surface influences which significantly effect carbon nanotube
Figure 33 A schematic of the growth mechanism of Fast Heating-Slow Cooling. The so-called “kite” mechanism begins with A) a catalytic nanoparticle deposited on a substrate. B) When the heat is suddenly introduced to the system, a convection current is established which lifts the nanoparticle off the substrate. C) As the nanoparticle is suspended above the substrate, it produces a carbon nanotube. The laminar flow of the feeding gasses carries the nanoparticle downstream while the growing nanotube tethers the nanoparticle to the substrate. This process results in a nanotube aligned parallel to the laminar flow of the reaction gasses.
growth using this mechanism, nanotubes grown in this manner were shown to be very long; in fact, in many cases these nanotubes had lengths of 1cm or more. (Figure 34A) As such, the aspect ratio of these nanotubes was approximately 10,000,000:1. Additionally, the “tip-growth” based mechanism discussed above was supported by AFM measurements which confirmed the presence of the catalyst nanoparticles on the opposite edge of the Si chip than was originally patterned with catalyst. (Figure 34B[74]) Thus, the proposed kite-growth mechanism was confirmed.

It is obvious from these results that ultra-long arrays of carbon nanotubes can be directly produced in a scalable manner using this “tip-growth” based synthesis mechanism. This method proved both reliable and versatile, being successfully carried out with a variety of catalyst particles and carbon feeding gasses. Also, since it is substrate independent, this method can be applied to any surface, as long as that surface can withstand the growth conditions. This versatility made this method attractive for many applications. One such application was the formation of high-throughput suspended nanotube devices. Because the “kite” mechanism of this growth method suspended a portion of the growing carbon nanotube above the surface, it was not affected by surface defects and was shown to grow over such obstacles[74]. Thus, it was also thought to be particularly applicable to the formation of suspended nanotube devices. Suspended nanotube devices have been particularly sought after because of their sensitivity. If nanotubes rest on a substrate, their electronic band structure is affected by that substrate. Taking away this substrate effect allows for the un-altered band structure of the suspended carbon nanotubes to be more sensitive to analytes. Therefore, this growth mechanism was applied to these ends.

After undergoing the etching procedures outlined above, it was found that nanotubes grew fairly easily over these trenched substrates (Figure 35). This method for
Figure 34 A) An SEM image of the long-aligned carbon nanotubes produced by the fast heating-slow cooling growth method. As is evident from this image, many nanotubes produced using this method reach several millimeters to over a centimeter. B) An AFM image of the end of a carbon nanotube grown by this mechanism. This end was furthest away from the catalyst region and indicates that nanotubes grown in this manner grow by tip-growth\textsuperscript{[74]}. 


Figure 35 A) An SEM image indicating a large array of suspended nanotubes achieved using this growth mechanism. As can be seen, a single nanotube can be suspended over several different trenches. It was also shown that this suspension was achievable using trenches etched using both B) E-beam lithography and C) simple photolithography/RIE. It should be noted that the upper limit of this suspension was found to be approximately a 5 µm wide trench. Also using these nanotubes, suspended carbon nanotube devices (D) were achieved. However, producing such suspended nanotube devices was inconsistent often resulting in dirty and unsuspended carbon nanotubes after processing (E).
suspending nanotubes was found to be extremely versatile and efficient, as shown in Figure 35A. Here, it is obvious that, in a single growth process, one nanotube device could be suspended over several trenches. While some portions of some nanotubes did touch the bottom of the trenches, many potential suspended nanotube were achieved because of the volume of nanotubes produced and the mechanism by which these nanotubes grow. Also, this method for suspending nanotubes was found to be extremely versatile, only showing any real dependence on the trench width and, to a lesser extent, its depth. It was found that suspended nanotubes could remain suspended across trenches with widths ranging from a few nanometers (Figure 35B) to a maximum width of approximately 5 µm (Figure 35B and C). As such, the methods by which these trenches can be produced range from the more expensive E-beam lithography (Figure 5B) to the relatively inexpensive photolithography and RIE (Figure 35C). Thus, this method was found to be a versatile and cost efficient means of producing such suspended nanotubes. However, to produce devices, electrode placement was necessary. Because nanotubes growth conditions would adversely affect electrodes with the necessary aspect ratios and thicknesses, an alternative process was developed. In this process, nanotube growth was carried out first, followed by electrode deposition and etching steps, as outlined in detail above. It was found that creating suspended nanotube devices in such a manner was indeed achievable, as demonstrated in Figure 35D. However, as shown in Figure 35E, this process was not as reliable as would be necessary for industrial scaling. Some devices would be successful, but many would be dirty and/or not have suspended nanotubes. As such, this method was found to be successful on a small scale, but suffered from detrimental limitations in efficient up scaling.
2.2.3 Summary

It was found that the fast heating-slow cooling method of carbon nanotube growth was successful in growing long and well-aligned carbon nanotubes. The origins of their extreme length and alignment came from the “kite” growth mechanism. In this mechanism, a portion of the growing nanotube was suspended above the substrate surface in the laminar flow of the source gasses. By thus eliminating any surface effects which may inhibit nanotube growth, these nanotubes were able to grow very long, in many cases extending more than 1 cm. Also, because the growing nanotube was suspended in the laminar flow of the reaction gasses, they were aligned parallel with these gasses. As such, it was thought that this growth mechanism would be well suited for producing suspended carbon nanotubes and devices. While significant success was demonstrated using this method to produce suspended nanotubes, it was found to be ultimately incompatible with standard methods for producing suspended nanotube devices efficiently.

2.3 Horizontally Aligned SWCNT on Quartz from Various Metal Catalysts

2.3.1 Materials/Experimental

All SWNT’s were grown using CVD as described below. Here, the growth conditions and feeding gasses were held constant to negate any effects other than the catalytic activity of the metals investigated here. Also, all nanotubes were grown on ST-cut quartz substrates purchased from Hoffman Materials Inc. and used as received.

In addition to the more commonly used metal catalysts in the iron-family, such as Fe, Co, and Ni, other less common catalysts like Au, Pt, Pd, and Cu\textsuperscript{[75],[76],[77]} and even less frequently utilized metals such as Mn, Mo, Cr, and Sn were investigated in this study. Most have never been shown to grow lattice guided, horizontally aligned SWNTs
on quartz. Additionally, Mg and Al were chosen because they have never been successfully used as catalysts for producing carbon nanotubes and were generally thought incapable of doing so. Also, to the best of our knowledge, this was the first example of such a large variety of metals catalyzing SWNTs growth under the same growth conditions.

All catalyst solutions were 1 mM metal salts in alcohol. These catalysts were patterned, spin coated, or dip-coated on a quartz substrate which was then treated with oxygen plasma for 15-20 mins and heated at 700 °C in air for 10 mins. Growth was conducted in a one inch Lindberg-Blue tube furnace inside a one inch quartz tube. The system was first flushed with H₂ and then heated to 900 °C. After reaching 900 °C, growth was conducted by introducing H₂ (100 sccm) and CH₄ (800 sccm) for 10 mins. After growth was completed, the system was cooled to room temperature under flowing H₂. The samples were analyzed using a scanning electron microscope (SEM, FEI XL30 SEM-FEG) at an acceleration voltage of 1 kV. Tapping mode atomic force microscopy (AFM, Digital Instruments Nanoscope IIIa, Vecco) and Raman spectroscopy (LabRam ARAMIS, Horiba Jobin Yvon) were also used to characterize these as-grown samples. This work was primarily done by Dr. Dongning Yuan Dr. Lei Ding and myself. The idea to investigate non-traditional metal catalysts originated from Dr. Yuan and myself. Also, the successive growth was done by all three parties.

2.3.2 Results/Discussion

As demonstrated in Figure 1, horizontally aligned SWNTs catalyzed by a variety of catalysts, including Co (Figure 36A), Ni (Figure 36B), Pt (Figure 3C), Pd (Figure 36D), Mn (Figure 36E), Mo (Figure 36F), Cr (Figure 36G), Sn (Figure 36H), and Au (Figure 36I) were achieved herein. Mg and Al were also successfully utilized to achieve aligned nanotubes on quartz. (Figure 37) Additionally, Fe and Cu were also used to produce
Figure 36 SEM evidence of carbon nanotubes grown using A)Co B)Ni C)Pt D)Pd E) Mn F)Mo G)Cr H)Sn and I)Au as catalysts. All samples were grown on quartz under identical growth conditions using CH$_4$ and H$_2$ as reaction gasses. Although the yield, density and degree of alignment are different between metals, this likely results from the differences in carbon solubility in each metal. The alignment direction in all cases is along the X-direction of the crystalline quartz substrate.
Figure 37 SEM images of horizontally aligned SWNTs growth by (A) Mg and (B) Al. These nanotubes are aligned along the X direction on ST-cut quartz.
dense, well-aligned arrays of SWNTs under the same growth conditions, as shown in Figure 38. What was even more interesting was that many of the catalysts produced a large number of SWNT's as determined by AFM measurements. Figure 39 demonstrates three such examples of AFM experiments done on Cu, Co and Au. This data shows that the majority of nanotubes produced in each case was less than 3 nm in diameter. As such, the majority of nanotubes produced by these catalysts should indeed be SWNTs.

Figure 39 also shows the diameter distributions of these samples. It is evident from this data that the bulk of the nanotubes produced by these catalysts have diameters \( \leq 2 \) nm, and in many cases 1 nm. It should be noted that the growth conditions have not been optimized for each catalyst. As such, the degree of alignment and yield between samples varies noticeably. However, it was apparent that, even at un-optimized growth conditions, this large variety of catalysts could produce SWNTs. In order to fully catalogue this versatility, similar experiments were done on Si substrates with a 1 \( \mu \)m thermally grown oxide layer. The results of these experiments are shown in Figure 40. The samples presented in this figure were grown using the same patterning and growth procedures as utilized in the quartz grown samples. Again, these are not the optimized growth conditions for these catalysts, which explains the obvious differences in the growth yields in each case. Regardless of these differences, this figure demonstrates that the growth of carbon nanotubes from each of these catalysts is possible on different substrates. Indeed, it appears that the only real difference between the nanotubes grown on quartz and thermal-SiO\(_x\) is their alignment. Those grown on ST-cut crystalline quartz are aligned along the X direction, and those grown on thermal-SiO\(_x\) are not aligned. It should be noted that, in the case of crystalline quartz, the gas flow rate was found not to affect the alignment direction and that the surface is free of any atomic steps detectible by AFM as demonstrated previously.\(^{79}\)
Figure 38 SEM images of horizontally aligned SWNTs on quartz grown by (A) Fe and (B) Cu. The alignment direction is the X direction on ST-cut quartz.
Figure 39[78] AFM images and diameter distributions of aligned SWNTs on quartz grown using (A) Co, (B) Au and (C) Cu. The diameters of SWNTs are less than 2 nm and 3 nm for Co and Au, respectively and in most cases are dominated by nanotubes with diameters ≤ 1.5 nm.
Figure 40[78] SEM images of random SWNTs on a Si wafer grown by (A) Fe, (B) Cu, (C) Co, (D) Ni, (E) Pt, (F) Pd, (G) Mn, (H) Mo, (I) Cr, (J) Sn, (K) Au, (L) Mg and (M) Al. SWNTs were obtained using each catalytic metal. These samples were grown using identical growth conditions as the samples produced from quartz (Figure 1). As such, the only difference between these samples and those grown on quartz is their lack of alignment.
The origin of this quartz-based alignment is still not thoroughly understood. In previous publications, Rogers et. al. asserted that this alignment resulted from atomic steps formed on ST-cut quartz. In their work, long periods of high temperature thermal annealing of the substrates formed atomic steps. These steps were easily observable under AFM; however, AFM measurements of all samples presented in this study showed no obvious steps, as mentioned previously. In fact, no thermal annealing was performed on the substrates presented in this investigation. Additionally, the degrees of alignment for different growth experiments are different as shown in Figure 36. For example, nanotubes synthesized from Pd, Cr and Sn have relatively poor alignment under the same growth conditions as other metals. This alignment can be improved by optimizing the growth conditions for each metal. Still, if the alignment is indeed caused by the atomic steps, such differences in alignment should not be observed as all experiments were performed on chips cut from the same wafer.

Another possibility is that the lattice of the substrates causes the alignment. From the results presented here, it is obvious that the growing nanotubes/catalyst particles readily move along the X direction on the ST-cut quartz substrates during growth. However, it has been previously reported that different metals interact differently with substrates.[77] The alignment trend of the nanotubes grown in this study seems independent of the metal catalysts used. All of the metals can provide aligned SWNTs in the same direction.

In order to investigate the movement of the catalyst particles, Co nanoparticles formed by the di-block copolymer method[80] were deposited on a quartz substrate. AFM investigations showed no movement of the particles when the substrate was heated to 900 °C without introducing any carbon precursor. However, after performing the same experiment and introducing a carbon precursor, the catalysts was shown to move
Figure 41[78] AFM images of nanoparticles (A) in the absence of a carbon source and (B) after introducing carbon. The insertion is the corresponding SEM image of aligned SWNTs. The particles only move and aggregate significantly after introducing the carbon source at 900 °C.
drastically to form aligned SWNTs. (Figure 41) Thus, the introduction of a carbon source seems to be an important factor for the movement of the metal catalyst as well as to the alignment. As a result, a new hypothesis was proposed to explain this alignment. In this hypothesis, the direction of alignment is ultimately determined by the crystal lattice of the substrate. However, instead of interacting directly with the nanoparticle itself, the lattice of the substrate interacts with the carbon-coated nanoparticle. An interaction with the carbon shell which precipitates on the outer surface of the catalysts would best explain the apparent independence of alignment trends over the multitude of metal catalysts presented herein. This hypothesis also helps explain the differences in the density, yield, and degree of alignment for different metal catalysts. Carbon has a different solubility in different metals under the same temperature and carbon feeding conditions. Because the yield, density and degree of alignment all depend on this carbon solubility, they would likely be different for different catalysts. Thus, this hypothesis can explain the growth of aligned nanotubes from the large variety of metals demonstrated here. However, more work is needed to confirm this hypothesis.

2.3.3 Summary

Growth of carbon nanotubes from a large variety of metal catalysts was successfully demonstrated on multiple substrates. Differences in yield, density and degree of alignment could be attributed to differences in the carbon solubility of the various catalysts. Regardless, all catalysts were shown to be viable catalysts for carbon nanotube growth. Also, the mechanism of carbon nanotube alignment was investigated and a new hypothesis presented. This hypothesis asserts that the lattice of the substrate interacts with the carbon shell of the catalytic nanoparticle rather than the nanoparticle itself. Thus, the alignment is thought to arise from this interaction and the resulting guidance provided by the substrate lattice.
2.4 Dense SWNT Arrays and High-Throughput Suspended Nanotube Devices

2.4.1 Introduction

As was discussed previously, suspended nanotube devices have been highly sought after due to their sensitivity and un-altered band structure. These characteristics make them particularly applicable in electronics and sensors among other technologies. However, to date no method exists to produce suspended nanotube devices in a scalable and cost-effective manner. Because of compatibility issues, previous methods aimed at achieving such ends have met with seemingly insurmountable obstacles. In the case of the “kite” mechanism associated with fast heating-slow cooling nanotube growth method, carbon nanotubes were only suspended a fraction of the time. What’s more, upon introduction of the processes necessary for manufacturing of devices, even fewer nanotubes remained suspended. One of the most daunting challenges in producing such devices is the fact that the surface tension of most liquids is enough to depress nanotubes to the bottom of trenches, or damage them in some way. As such, repeatedly submerging and drying suspended nanotube samples proved detrimental to most devices. Therefore, a process which utilized a limited number of liquid submersion and drying cycles was thought necessary to achieve high-throughput suspended nanotubes and devices. Such a method also needed to be compatible with standard electrode deposition processes. The simultaneous development of a growth method which produced dense arrays of SWNTs and a printing process which allowed for them to be transferred to virtually any substrate provided the tools for what may be a viable solution for such aims.
2.4.2 Materials/Experimental

All chemicals were purchased from Fisher Scientific. Quartz wafers were purchased from University Wafers (supplied by Hoffman Materials Inc.) and used as received. Nanotube growth was conducted in a one inch Lindberg Blue CVD tube furnace at 900 °C using 1 mM of either Fe/PVP or Cu/PVP in EtOH. After patterning the catalyst on the quartz wafers, the patterned wafers were placed in the CVD furnace and burnt in air at 750 °C for approximately 10 min. The system was then cooled to room temperature and flushed with H₂ and EtOH/MeOH to clear the lines of any residual air. The system was then heated to 750 °C under H₂ (450 sccm). The catalyst particles were then reduced under H₂ at that temperature for 10 min. After this reduction step, the system was heated to 900 °C and Ar was introduced flowing through EtOH (150 sccm) and MeOH (600 sccm). Following a 15 min growth period, the Ar was turned off and the system was cooled under flowing H₂. These samples were then characterized by SEM and AFM.

Once the presence of dense arrays of aligned nanotubes was confirmed, a solution of A-8 Poly (methyl methacrylate) (PMMA) was spin coated on top of these arrays at 2000 rpms for 45 sec. The chips were then heated at 170 °C for 10 min to cure the PMMA and promote carbon nanotubes adhesion. After curing, the PMMA was cooled to room temperature and then placed in either a KOH or buffered HF (BHF) solution consisting of 3 g KOH and 40ml NPH₂O or 2-3 ml HF, 5.5 grams of NH₄F and 40 ml nanopure H₂O (NPH₂O), respectively. This solution was boiled for approximately 45 min at which point the PMMA stamp with the aligned nanotubes was peeled off the original quartz substrate. This stamp was washed thoroughly with NPH₂O and then carefully placed on a Si chip (200 nm thermal oxide). This Si chip had trenches that had
Figure 42[68] The SWNT array printing/transfer process is outlined in this section. Here PMMA is used to bind to the carbon nanotube arrays, which is followed by etching the first layer of the quartz substrate with either KOH or BHF. After the PMMA/SWNT sample is released from the quartz, it can be washed and transferred to any substrate. Here, it was transferred to a SiO$_x$ substrate and then the PMMA was dissolved using acetone. The SEM image at the bottom is an example of one such SWNT array transferred to a SiO$_x$ substrate.
been etched to at least 200 nm using standard photolithography and RIE, followed in some cases by a KOH/IPA/NPH\textsubscript{2}O Si etch. It was crucial that the alignment direction of the nanotubes be placed parallel to the width of the trench to achieve the appropriately suspended nanotubes. This PMMA/SWNT film was then blown flat using hand-held canned air (Fisher Scientific). This was essential to remove all remaining liquid which separated the nanotube arrays and the SiO\textsubscript{x} substrate. This PMMA/SWNT/SiO\textsubscript{x} sample was then heated at 160 °C for 12 min and then cooled to room temperature. The PMMA was then dissolved with acetone for 10 min. The sample was then removed from solution and allowed to dry while standing with the direction of the nanotube axis of alignment perpendicular to the bench. (Figure 43B)
Figure 43 In A, the direction of the surface tension is perpendicular to the carbon nanotube alignment and towards the bottom of the trench over which the nanotubes are suspended. This creates many problems upon drying, which often result in the suppression of the carbon nanotube to the bottom of the trench. Alternatively, in B the drying liquid stabilizes the carbon nanotube equally around its circumference while drying. Thus, the only significant surface tension lies along the alignment direction of the carbon nanotubes.
2.4.3 Results/Discussion

By optimizing the growth conditions for catalyst nanoparticles, here Fe and Cu, it was found that dense arrays (2-4 SWNTs/µm) of perfectly aligned SWNTs could be produced. As was mentioned before, the SWNTs were aligned along the X-direction on the surface of the quartz substrate. Along with the impressive density and alignment of these samples (Figure 44A-C), the nanotubes in these arrays were found to be quite long, in many cases growing to lengths ≥1 mm. (Figure 44A) The synthesis of such nanotubes will be discussed in more detail in the following chapter. However, it is obvious that these carbon nanotube arrays posses many impressive characteristics which make them well suited for a variety of applications. In this preliminary work, their application to the manufacturing of high throughput suspended nanotube devices was investigated.

Previous work with suspended carbon nanotube devices made it obvious that liquid submersion and drying cycling of such suspended nanotube samples was detrimental to their integrity. This either resulted in the introduction of contaminants or the suppression of the carbon nanotubes to the bottom of the trenches. Therefore, developing a process which successfully suspended carbon nanotubes and involved a limited number of such cycles was the focus of the research presented here.

Utilizing the transfer/printing process outlined in the experimental section above, a process was developed to achieve such high-throughput suspended nanotubes (Figure 44D and E). It should be note that, many times the suspended portion of carbon nanotubes, particularly SWNTs, cannot be seen in SEM using a low acceleration voltage (1-2 kV). However, this acceleration voltage is necessary when imaging carbon nanotubes so as not to destroy them. This “invisibility” results because too few electrons
Figure 44 A) Dense arrays of well-aligned SWNTs can be produced on a large scale using this method. B and C further demonstrate the large density and perfect alignment of the nanotube products. Also, after transferring the SWNT arrays, it can be seen in D and E that the alignment is well preserved. In some cases, the density of the transferred arrays was lower than of the SWNT arrays before transferring. However, in many cases this was not so. Also, it should be noted that the suspended portions of the aligned carbon nanotubes appear invisible because of the low number of electrons being deflected back to the electron detector in the SEM. The contrast provided by the substrate, in this case SiO₃, allows the portions of the nanotube on the substrate to be imaged more clearly.
are deflected back to the electron detector merely by the suspended carbon nanotube. Alternatively, the portions of the nanotube that remain on the surface have a contrast provided by that surface which allows the carbon nanotubes to be imaged clearer. Thus, portions of the carbon nanotubes which appeared “invisible” were evidence of suspended nanotubes.

It was found that there were several important factors which contribute to the success of this method. Firstly, proper adhesion of the carbon nanotubes to the surface onto which they are being transferred was extremely important. Thus, it was necessary to remove all of the water from under the stamp and bake the PMMA/SWNT/SiO\textsubscript{x} samples thoroughly. Also, the width of the trench was found to be another crucial factor for the success of this method. It was found that trenches with widths $\leq 5$ $\mu$m were necessary to achieve appropriate carbon nanotube suspension. This limit was established for trenches with depths ranging from approximately 200 nm to approximately one micron. Additional etching into the Si below the 200 nm thermal oxide was found to be beneficial, not only because it increased the depth of the trench, but also because it provided an overhang as shown in Figure 45A and B. While it is possible that this 5 $\mu$m width limit may not be accurate outside this depth range, this limitation was found to be quite concrete for efficient production of suspended nanotubes arrays with reasonable depths. It was also found that, after dissolving the PMMA in acetone, drying the samples such that the direction of alignment of the carbon nanotubes was perpendicular to the bench-top was advantageous. Since the surface tension was found to be such a large factor, it is believed that drying the samples so that the surface tension was parallel rather than perpendicular to the alignment direction of the nanotubes helps promote the production of arrays of suspended nanotubes. In fact, preliminary results showed that drying in this manner (Figure 45B) improved the
As displayed in A, the necessary etching procedure involved RIE etching of the oxide layer (~200 nm). Often, this was followed by a KOH/IPA/NPH$_2$O Si etching which provided an overhang. It should be noted that trenches with widths $\leq 5\, \mu$m were necessary to achieve suspended SWNT samples as seen in B. Finally, it is believed that, after etching, electrodes could be easily deposited using E-beam metal evaporation and then SWNT arrays placed using the transfer procedure outlined here.
success rate from approximately 30% to almost 80%. However, further investigation is necessary to support this hypothesis. Lastly, limiting the submersion and drying cycling of unsupported nanotubes to one cycle was key to successfully produce suspended nanotube arrays efficiently and reliably. Since only one step involving liquid processing was done without PMMA supporting the structure/suspension of the nanotube arrays, the effect of surface tension was limited. Also, acetone is a low viscosity liquid, which means that it has a relatively small surface tension. Thus, the effect of surface tension was limited as much as possible in this manufacturing method.

The next step of this research is to extend this process to device manufacturing. This method is compatible with standard metal evaporation techniques as illustrated in Figure 45C. It is thought that first producing the appropriately etched substrates (Figure 45A) followed by electrode deposition by E-beam metal evaporation will produce a substrate which is suitable for the highly efficient transfer/printing process outlined above. Therefore, after successfully transferring these nanotubes, this method would be able to reliably produce high-throughput suspended SWNT devices. (Figure 45C)

2.4.4 Summary

High-throughput suspended carbon nanotube devices have been heavily sought after with only limited success. Herein, a method for achieving such suspended carbon nanotube devices is presented. It was found that a few factors were crucial to the success of such devices. Firstly, the effect of surface tension should be limited. Related to this, the drying process was found to be a crucial point in such manufacturing. Perhaps most importantly, the width (≤5 μm) and depth (≥200 nm) of the trench were found to be extremely important. The procedures outlined here should be compatible with standard electrode deposition methods, which will be the subject of further investigations in the
immediate future. It is hoped that using these methods will lead to the successful production of high throughput suspended carbon nanotube devices.

2.5 Size-Enhanced Diffusion in Melting Iron Nanoparticles (Size Dependence)

2.5.1 Introduction

The discovery of the impressive and versatile method of producing aligned carbon nanotube arrays outlined in the previous section lent itself to many applications in addition to the production of suspended carbon nanotube devices. Many of these applications involved investigations into existing phenomena on which further study was needed. Several such investigations were conducted here. These investigations ranged from those necessary to fully characterizing this growth method, to investigations into sulfur promotion of carbon nanotube growth and size dependent nanoparticle characteristics. The investigations into sulfur’s growth promotion will be discussed later in this work. This section will focus on further characterizing this growth method while investigating the size-enhanced diffusion of carbon feeding gasses into nanoparticles.

2.5.2 Materials/Experimental

All calculations were done using molecular dynamics (MD) simulations carried out in a canonical ensemble using the Verlet algorithm\(^{[81]}\) and Fe as the catalyst nanoparticle (d=1.1-1.8 nm). Two sets of growth experiments were conducted. First, carbon nanotubes were grown using multiple different sized catalytic Fe nanoparticles. This was accomplished by using the same amount of PVP (0.006 g M.W.=55k) and EtOH (15 ml) but with different concentrations of FeCl\(_3\) added. Adding more FeCl\(_3\) produced larger nanoparticles as more Fe was divided into the same number of PVP micelles. After nanoparticle formation, growth was carried out under identical conditions for all
catalyst nanoparticles. The growth conditions were the same as outlined in the previous section. Briefly, EtOH/MeOH (150 sccm/600 sccm) and H\textsubscript{2} (450 sccm) were used to grow nanotube arrays on quartz substrates. Reduction was done at 750 °C for 10 min under flowing H\textsubscript{2} and then growth was carried out at 900 °C for 15 min using EtOH/MeOH/H\textsubscript{2}. Results were characterized and carbon nanotube lengths were measured using SEM. Nanoparticle diameters were measured using Tapping Mode AFM after spin coating quartz wafers at 2000 rpm for 45 seconds and removing the PVP by O\textsubscript{2} plasma treatment for 15 min.

The second batch of experiments was conducted using two Fe catalysts, one with diameter distribution between 1-2 nm and one between 2.5-7.6 nm. The first diameter distribution was used to measure the average diameter of SWNTs produced as growth time increased and the latter was used for the same measurements of MWNTs.

### 2.5.3 Results/Discussion

It is known that the properties of materials, including their melting point, change when those materials cross over from the bulk to the nanoscale\textsuperscript{[82],[83]}. It was proposed here that diffusion of carbon feeding gasses would be accomplished faster in nanoparticles that were liquidus, or more liquid than solid. Theoretical calculations (Figure 46) showed that, at a given temperature, carbon diffusion (D) increases with the inverse of Fe nanoparticle diameter (d). Thus, as Fe nanoparticles get smaller in diameter, the carbon would diffuse into the nanoparticles more easily. If this were true, it would ultimately manifest itself by smaller catalytic nanoparticles producing nanotubes at a faster rate than larger ones. To test these theoretical results, two sets of experiments were conducted.

First, nanoparticles of varying diameter were synthesized and characterized by AFM. After determining the size of these nanoparticles, each was used to grow
Figure 46 Plot of the calculated diffusion rate of carbon feeding gases into nanoparticles v. inverse diameter of those nanoparticles at various temperatures. It can be seen that, per unit temperature, the diffusion rate increases with decreasing nanoparticle diameter.
nanotubes for the same amount of time. By standardizing time, it was believed that the relative growth speed could be determined simply by comparing the average length of nanotubes produced by each nanoparticle. The results of this experiment are as detailed in Table 2. It is obvious from these results that larger diameter nanoparticles did produce shorter nanotubes. Therefore, it was deduced that these nanoparticles produced nanotubes at a slower rate than smaller diameter nanoparticles. This is also obvious when comparing SEM images of carbon nanotubes produced from the smallest and largest nanoparticles used in this study. (Figure 47) Here, the nanotubes produced by the larger nanoparticle are obviously shorter. However, it was noted that many factors which may prevent the nanotubes from growing very long are present during carbon nanotube growth. As such, an experiment was designed which set out to prove the related hypothesis that smaller nanoparticles would nucleate carbon nanotube growth faster than large ones. Therefore, for given nanoparticle size distributions (here ~1-2 nm and ~2.5-7.6 nm), the average carbon nanotube diameter would increase with growth time. Therefore, nanoparticles having the diameter distributions enumerated above were used to catalyze carbon nanotube growth conducted for varying amounts of time. Figure 48 illustrates the results of this experiment. Indeed it is obvious from these results that the average carbon nanotube diameter increases with increasing growth time. This indicates that smaller diameter nanoparticles are nucleated first and produce nanotubes sooner than larger nanoparticles. This was found to be true both in the nanoparticle size regime corresponding to SWNTs as well as MWNTs. Thus, the theoretical predictions which state that diffusion of carbon feeding gasses increases with decreasing nanoparticle size, and therefore with increasing fluidity were confirmed.
Table 2 Average length of carbon nanotubes produced from nanoparticles with increasing diameters. It can be seen from this data that, as the nanoparticle diameter increases, the average length of nanotube products per unit time decreases.

<table>
<thead>
<tr>
<th>Average Nanoparticle Diameter (nm)</th>
<th>Average Carbon Nanotube Length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>838</td>
</tr>
<tr>
<td>2.6</td>
<td>392</td>
</tr>
<tr>
<td>7.6</td>
<td>300</td>
</tr>
</tbody>
</table>
Figure 47 As in Table 1, it is obvious that nanotubes grown from the smaller diameter nanoparticles A) 1.6 nm, are longer than those grown using the larger diameter nanoparticles in B (7.6 nm). This indicates that smaller diameter nanoparticles nucleate and grown nanotubes fast than larger diameter ones. This data indicates that diffusion of carbon feeding gasses into the smaller, and therefore more fluid nanoparticles, occurs more readily than in larger, less fluid nanoparticles.
Figure 48 A plot of the average carbon nanotube diameter v growth time for nanoparticles with diameters ranging from 1-2 nm (blue) and from 2.5-7.6 nm (red). It was found that, as growth time increased, so did the average diameter of carbon nanotubes products. This was true in the case of nanoparticles which produced both SWNTs and MWNTs. Thus, it was confirmed that diffusion of carbon feeding gasses into smaller nanoparticle occurred faster because of their more liquid-like state relative to larger nanoparticles.
2.5.4 Summary

The dense arrays of well aligned carbon nanotubes produced herein have lent
themselves to many applications and investigations. In this work, it was determined that
such arrays could be used to produce films of both SWNTs and MWNTs. In doing this
investigation, the theoretically supported hypothesis which asserted that carbon feeding
gasses would diffuse into and thus grow carbon nanotubes faster in smaller (and thus
more liquid) nanoparticles was confirmed experimentally. It is believed that this size-
enhanced diffusion in smaller nanoparticles results from their more liquid state when
compared to larger nanoparticles. Thus, an increased level of understanding of the
diffusion of gaseous material into nanoparticles was obtained.

2.6 Summary

Paramount to the integration of carbon nanotubes into modern electronics is
control over their alignment. Many methods have been employed to achieve such
alignment with varying degrees of success. It was found that ultra-long (≥1 cm), well-
aligned carbon nanotubes could be produced on any substrate utilizing a “kite”
mechanism as presented in the fast heating-slow cooling work outlined in this chapter.
This work was especially applicable to the development of suspended nanotubes.
However, problems with low densities and an incompatibility with carbon nanotube
device fabrications processes made this a poor choice for the development of high-
throughput suspended nanotube devices. Never the less, it was proven a versatile
method for producing good quality, ultra-long and well aligned carbon nanotubes.

Further experimentation revealed that dense (2-4 nanotubes/µm) arrays of
perfectly aligned carbon nanotubes could be grown directly on quartz surfaces using
EtOH/MeOH as carbon source gasses. Furthermore, it was discovered that these well-
aligned nanotubes could be grown from a large variety of metal catalysts. Carbon
nanotubes had never been produced from several of the metals investigated in this study. These results were combined with the printing/transfer process also outlined here to the ends of efficiently producing dense arrays of suspended carbon nanotubes. Moreover, this process should be compatible with standard electrode deposition processes. Therefore, a possible method of producing high-throughput suspended nanotube devices on virtually any substrate was presented.

In addition to these applications, such dense arrays were used to investigate the correlation between the diffusion rate of carbon feeding gasses into nanoparticles and the state of those nanoparticles. It was found that smaller diameter nanoparticles diffused carbon feeding gasses faster than larger diameter nanoparticles. Since smaller nanoparticles would be more liquid in state than larger nanoparticles at the same temperature, it was asserted that this enhanced liquid state helped the diffusion of carbon into the smaller nanoparticles. This supported theoretical results obtained from our collaborators (Dr. Stefano Curtarolo et al.). Further investigation into this dense, aligned carbon nanotube growth method will be presented in the following section. Regardless, it was proven to be a very useful and important development.
3. Carbon Nanotube Electronic Structure Control

3.1 Introduction

The impressive electronic\cite{84,85,86,87} and optical\cite{88,89} properties of SWNTs combined with their diverse utility\cite{90,91,92,93} and durability\cite{94,95} make them a leading material for the development of nanoelectronic devices. In fact, the device performance was shown to be better than Si-based devices in some applications\cite{88}. Moreover, devices made from single nanotubes have shown outstanding performance\cite{89,90,96}, giving great hope for the realization of “next generation” carbon nanotube based electronics. As such, having a fundamental understanding of their growth mechanism as well as the ability to control the properties of the as produced SWNT products is paramount to their incorporation into mainstream applications. Some of the most critical properties that need to be controlled for this mainstream application are density, length and alignment. Recently, significant progress has been made in the ability control the alignment of SWNTs\cite{95,96}. As such, perhaps the most significant challenge standing in the way of this mainstream application is the fact that, in a typical CVD growth process, mixtures of approximately 1:2 Metallic : Semiconducting SWNTs are produced. Having such a mixture presents application problems, as most applications require either metallic or semiconducting SWNTs.

Over the last decade, significant research efforts have been focused on solving such problems; however, only limited progress has been made. A degree of success in the separation of metallic from semiconducting SWNTs has been demonstrated using electrophoresis\cite{97}, physicochemical modification\cite{98,99}, density gradient induced centrifugation\cite{100}, selective elimination by electrical breakdown\cite{101}, gas-phase plasma etching\cite{102}, and many similar methods\cite{103,104}. However, most approaches use chemical separation methods which introduces defects and contamination to the SWNTs.
Additionally, after separation, the isolated nanotubes still need to be reliably self-assembled onto a substrate for device fabrication, for which there is no method currently available. Therefore the direct growth of metallic and semiconducting SWNTs on suitable substrates would represent a significant advancement towards the integration of carbon nanotubes with existing Si fabrication technology. Directly growing electronically specific carbon nanotubes could also utilize many existing advantages, including the methods of producing highly pure nanotubes as well as to control the alignment of the nanotube during growth. This alignment could be controlled by electric field, laminar gas flow and single crystal substrates. Moreover, compatibility with recently fabricated uniform nanotube arrays on single crystal substrates could allow such samples be used directly as thin films for making a large number of devices, representing a major breakthrough in practical fabrication of nanotube devices.

3.2 Selective Growth of Aligned Semiconducting-SWCNT on Quartz Substrates

3.2.1 Materials/Experimental

A chemical vapor deposition (CVD) approach to selectively grow dense arrays of well-aligned, nearly completely semiconducting SWNTs with a narrow diameter distribution was developed within our lab. It should be noted that Dr. Lei Ding primarily developed this method with the assistance and support of several other lab-members including myself. Specifically, I helped with the growth and transfer of these samples.

The dense arrays of aligned SWNTs are grown on single-crystal ST-cut quartz substrates using an ethanol/methanol mixture as the carbon source. Nanotubes within the arrays reveal a narrow diameter distribution from 1.6 nm to 1.8 nm with more than 95% of tubes being semiconducting. It was found that his selective growth relies on two
crucial factors: the presence of methanol in the CVD process and the strong interaction between SWNTs and the quartz lattice. Given their density and electronic structure, these samples can be used for the direct fabrication of nanotube FETs with good performance; still, more work needs to be done for this to be realized. However, this development represents a hope to solve the last major problem which limits the wide use of nanotubes in nanoelectronics. To the best of our knowledge, this is the first time that horizontally aligned nearly exclusively semiconducting SWNTs were produced. More interestingly, SWNT arrays with a significant amount of metallic SWNTs can be synthesized on the same substrates by simply altering the growth conditions. This method provides us the power to obtain the types of nanotubes we need for different applications.

CuCl$_2$/polyvinylpyrrolidone or FeCl$_3$/polyvinylpyrrolidone alcohol solutions were used as the catalyst solutions. Although the types of nanotubes grown under different ethanol/methanol ratios are not the same, typically a flow of hydrogen (450 sccm) and argon (150 sccm through an ethanol bubbler and 300 sccm through a methanol bubbler) was used for the growth of nearly exclusively semiconducting SWNTs. A mixture of metallic and semiconducting SWNTs can be obtained at different growth conditions on the same substrates.

Raman spectroscopy was used to characterize the samples. The radial breathing mode (RBM) and G-band of Raman spectra can be used to determine the ratio of semiconducting : metallic SWNTs. Also, lasers with different wavelengths can excite different types and diameters of SWNTs. In our experiment, lasers with three different wavelengths, 488-nm, 633-nm and 785-nm, were used to characterize these samples. Raman was used to characterize more than 10 spots on each sample. In order to avoid the influence of the Raman peaks from the quartz substrates at 127 cm$^{-1}$ and 205 cm$^{-1}$, the
SWNTs grown on ST-cut quartz were transferred onto the SiO$_x$/Si for Raman characterization.

This transfer process was based on fairly common poly (methyl methacrylate) (PMMA) stamping procedures. Here, an 8% PMMA (molecular mass = 495k) solution in anisole was spin coated at ~2000 on the as-grown nanotube arrays directly on the quartz substrate. After spin coating, the substrates were placed in an oven at 170 °C to cure for about 10 min-15 min. This hardened the PMMA and adhered it to the nanotube arrays. The substrates were then cooled and then placed in boiling KOH (1 M) for approximately 45 min-1 hr. Alternatively, boiling buffered HF solution was also used for this step. The purpose of this boiling step was to dissolve the top layer of SiO$_2$ from the substrate, thus releasing the nanotube arrays on the PMMA. After releasing, the PMMA/SWNT films were washed with nanopure H$_2$O thoroughly and then placed on the surface of choice. In the case of Raman characterization, this was a Si-wafer with a ~1 μm oxide layer. The new surface with the PMMA/SWNT film was then heated in an oven at 160 °C for another 10-15 min to adhere the film onto the new surface. After this adhering step, the PMMA/SWNT/surfaces were cooled and then the PMMA was dissolved in acetone. Any remaining PMMA was burned away in a CVD oven at approximately 350 °C for 5 min.

3.2.2 Results/Discussion

Figure 49 presents the SEM and AFM images as well as the Raman spectra of the aligned semiconducting SWNTs. These uniform, high-density and perfectly aligned arrays of long nanotubes were found on the entire ST-cut quartz substrate as indicated by SEM. From the AFM images (Figure 49C and D), it was obvious that the nanotubes
Arrays of nearly exclusively semiconducting SWNTs were produced herein. A and B show SEM images of such nanotubes. The bright, parallel horizontal lines visible in the images are catalyst lines. (C) AFM image of these nanotube products. (D) Diameter distribution of 200 SWNTs of an array measured by AFM. (E and F) Raman spectra of SWNTs transferred onto the SiOx/Si substrates. The spectra were obtained using 488- and 633-nm excitation laser lines at 10 different spots over the substrate for each laser line. Each curve in a panel shows spectra at a spot on the substrate. Peaks within the rectangles marked with S correspond to the semiconducting SWNTs. The rectangles marked with M denote the frequency range where RBM peaks of metallic SWNTs are expected.
have relatively uniform diameter and show a narrow distribution from 1.4 nm to 1.8 nm. 200 nanotubes were measured for the calculation of the diameter distribution resulting in an average diameter of 1.65 nm. Also of importance, the samples are very clean, having no amorphous carbon on the surface.

When the excitation laser wavelength is 633-nm is used, the Raman peaks around 135-165 and 180-220 cm\(^{-1}\) are due to semiconducting and metallic SWNTs, respectively.\(^{[105]}\) When using an excitation wavelength of 488 nm, the Raman peaks from 140-223 and 235-280 cm\(^{-1}\) are due to semiconducting and metallic SWNTs, respectively. When using a 785 nm laser, the Raman peaks around 220-250 and 140-170 cm\(^{-1}\) result from semiconducting and metallic SWNTs respectively. From the RBMs (Fig. 49E, F) recorded using 488- and 633-nm lasers, it was evident that the nanotubes showed narrow RBM distributions between 143 cm\(^{-1}\) and 158 cm\(^{-1}\), while no observable peaks could be found in the region for metallic nanotubes. This indicates the presence of nearly exclusively semiconducting SWNTs. It has been experimentally determined that the relationship between the diameter (d in nm) of SWNTs and their RBM shift \(\omega\) (in cm\(^{-1}\)) is \(\omega = 248/d\).\(^{[105]}\) From this relationship, it was determined that the diameters of SWNTs in these arrays ranged from 1.6 nm to 1.8 nm. It should be noted that this is narrower than the diameter distribution determined by AFM. It is likely that deformation of the SWNTs due to the force by the tip in the AFM measurement led to a broadening of the distribution. Additionally, no RBM peaks were found when a 785-nm laser was used for the Raman measurement. This indicates that no, or a very low percentage of, metallic SWNTs with RBMs between 140 and 170 cm\(^{-1}\) exist in the sample. Also, no semiconducting nanotubes can be seen using a 785 nm laser because the diameter of the observable semiconducting nanotubes needs to be smaller (d < 1.13 nm) than exists in these samples. The selectivity of this semiconducting SWNTs growth was also
Figure 50 Raman active G-Band peaks of an array of SWNTs grown using the “selective” growth method. This sample was grown on quartz and was then transferred to a SiO₂/Si wafer. These spectra were taken with a) a 633 nm and b) 488 nm excitation laser at 10 different spots over the substrate. Also, all spectra were normalized to the G’ peak. It is evident from these spectra that the samples consist almost exclusively of semiconducting SWNTs.
supported by the Raman G-band analysis (figs. 50), which indicates G-band shapes most indicative of semiconducting nanotubes. Lastly, it should be noted that the spectroscopic details of the disorder-band (D-band) reveal that the SWNTs in these arrays have very low defect density, making them even more attractive for nanoelectronic applications (Figure 51).

Electrical characterization of FETs fabricated from these as-grown aligned tube arrays was done to confirm the selectivity for semiconducting SWNTs. FETs were fabricated directly on the quartz substrates using a top gate produced by standard e-beam lithography. A solid conducting polymer was used as the top gate in these samples. Each test device consisted of five transistors fabricated along one set of parallel nanotubes with channel length L scaling from 1 µm to 5 µm as illustrated in Figure 52A. The channel width of the FETs was 500 µm. The drain leakage current due to the gate voltage did not exceed 20 nA at Vg = 4.5 V with approximately linear dependence on the gate voltage. Consequently, the contribution of this part of the leakage current in the off-state response of the transistors did not exceed 5 %. The drain leakage current associated with the bias voltage was in the picoampere range and can be ignored in the calculation. Six such five-fold devices were fabricated and measured at different spots across the chip. From these measurements, it was found that the on/off ratio falls in the range between 18 and 32. Figure 52B displays the family of transfer characteristics of one of these devices with the channel length as a parameter. The number of parallel nanotubes in each device is over 500, therefore the on/off ratios measured here represent the average ratio of semiconducting and metallic nanotubes in the sample.
The D and G band of a sample grown using the method outlined here. This investigation was done using a 633 nm excitation wavelength and analyzing 10 different regions on the substrate. This investigation showed that the G-band/D-band average intensity ratio was \(~45\), indicating a largely defect free SWNT array.

Figure 51\cite{68}
Figure 52 High on/off ratio FETs fabricated with as-grown aligned CNT arrays top-gated by solid electrolyte polymer films. (A) Large magnification view of the set of electrodes of a test device. The widths of the gaps between the 40 nm-thick gold contact lines correspond to the channel lengths of FETs (from top to bottom): 4 µm, 3 µm, 2 µm, 1 µm, and 5 µm. To break possible current paths through the nanotube array past the transistor channels, the tubes were partially removed by reactive ion etching (RIE) in oxygen plasma. (B) Family of transfer characteristics (drain current, $I_d$ versus top gate voltage, $V_g$) of one of the test devices under a bias voltage $V_{ds} = 80$ mV. The parameter of the family is the transistor channel length $L$. The channel width is 0.5 mm. (Inset) The on/off ratios obtained for the device as a function of the channel length, $L$. 
The on/off ratios in all the measured devices were significantly larger than 3, which is the expected approximate on/off ratio for SWNT nanotube networks where all chiralities of nanotubes appear with equal probability. This is because, in such networks, about 1/3 of species will be metallic. This clearly indicates that a large fraction the nanotubes in the as-grown array are semiconducting. Specifically, the on/off ratio of 20 is expected if 95 % of tubes are semiconducting. Thus, it was estimated from these measurements that the samples produced with this method consisted of 95 to 98 % semiconducting nanotubes.

This large channel width device was used to estimate the percentage of semiconducting SWNTs. However, the large channel width and conducting polymer gate may limit the performance of the device, because even one metallic nanotube will dramatically degrade the on/off ratio in this set-up. Another top-gate FET with Su-8 as the dielectric layer and shorter channel width (50 µm) was fabricated on the nanotube arrays. From such a FET, it was found that the on/off ratio can be up to 5000, which further proved the nearly completely semiconducting SWNTs in the arrays. The improvement in performance for these shorter channel width devices can be explained by the fact that there are smaller numbers of nanotubes in each of the devices and therefore a smaller possibility that metallic nanotubes are present in the devices. Assuming that 98 % of the nanotubes are semiconducting, if each device consists of 5 aligned nanotubes, 90 % of the devices will have only semiconducting nanotubes in them and thus show very low off current.

Two factors were found to be essential to the selective growth of almost exclusively semiconducting nanotube arrays. The first important factor is the presence of methanol. Previous work showed that, using only ethanol, SWNTs arrays having an average diameter of 1.2 nm[95] and consisting of approximately 1/3 metallic nanotubes
were produced on ST-cut quartz\textsuperscript{[106]}. Obviously introducing methanol changes the diameters and the semiconducting/metallic ratio of the SWNT products. Also, when only methanol was used as the carbon feeding gas, no SWNTs were synthesized on the surface. It was postulated that this resulted from the high decomposition temperature of methanol. Previous work has shown that the carbonization temperature increases with the increasing hydrogen-to-carbon ratio in hydrocarbon CVD processes\textsuperscript{[107]}. Thus, a much higher temperature should be used to decompose methanol than for ethanol in the growth of SWNTs. Although methanol does not decompose during growth at 900 °C, it is thought that OH radicals from methanol can selectively etch metallic SWNTs because of their smaller ionization potential as compared to semiconducting SWNTs \textsuperscript{[108]}. This selective etching would result in the enrichment of semiconducting SWNTs which is seen in our samples. Also, this etching effect would help prevent the formation of amorphous carbon on the surface, making the surface very clean. The cleanliness of these samples is confirmed by AFM images and gives support to this hypothesis.

The second important factor for the selective growth of semiconducting SWNTs is the ST-cut quartz substrate. Under the same growth conditions on non-crystalline substrates a mixture of metallic and semiconducting nanotubes was prepared with no indication of selective growth of semiconducting nanotubes. This is demonstrated in Figure 53 which shows SEM and Raman data of the SWNTs grown on a SiO\textsubscript{x}/Si substrate. It is evident from Figure 53A that the nanotubes produced on this substrate were poorly aligned and relatively short. Moreover, from Fig. 53B it was found that both metallic and semiconducting SWNTs are grown on the SiO\textsubscript{x}/Si substrate. Also, the RBM peaks of SWNTs show a wide diameter distribution. Based on these observations, it is evident that the ST-cut quartz lattice on the surface is critical for the enrichment of well-aligned, long and semiconducting SWNTs. Previous work suggests that SWNTs stick to
Figure 53 SWNTs grown on SiO$_x$/Si substrate. (A) An SEM image of such nanotubes. The bright stripe in (A) corresponds to the catalyst area. (B) Raman spectra of the as-prepared SWNTs. The spectra were obtained using 633-nm excitation laser line at 10 different spots over the substrate. Each curve in a panel shows spectrum at a spot on the substrate. Peaks within the squares marked with S and M correspond to the semiconducting and metallic SWNTs, respectively.
the quartz surface during tip growth\textsuperscript{[95]} and that the affinity force between the lattice of Si atoms and the SWNTs guides the alignment of SWNTs on the surface \textsuperscript{[106]}. Also, the RBM peaks of SWNTs grown within the catalyst regions show a relatively wide diameter distribution, worse alignment and the existence of metallic nanotubes (Figure. 54). These observations indicate that the selective growth only applies to the aligned nanotubes with a very narrow diameter range. This analysis indicates that the single crystal quartz substrate is critical for the growth of aligned nanotubes with narrow diameter distribution; together with the right growth conditions, these factors are crucial for achieving the selective growth of semiconducting nanotubes. It should be noted that other factors, such as the ratio between the ethanol and methanol, the hydrogen concentration, the growth temperature etc., also play noticeably important roles and that the full optimization of growth conditions is an ongoing process.
Figure 54 A a) SEM image and b) Raman spectra of nanotubes in the catalyst region. The SEM image shows the disorder of the tubes in the catalyst region and the Raman spectra shows the loss of selectivity for semiconducting SWNTs. Raman data was taken from 10 different spots on the substrate using a 633 nm excitation wavelength. The S and M square-labels indicate semiconducting and metallic respectively. The green arrows indicate peaks corresponding to the quartz substrate.
3.2.3 Summary

In summary, we have discovered a method to grow high-density, perfectly aligned and nearly exclusively semiconducting SWNT arrays on ST-cut quartz using an ethanol/methanol mixture. AFM, Raman and testing of FETs fabricated from these samples showed the high uniformity of SWNTs in alignment, diameter and electronic properties. It is also evident that this selectivity can be attributed to the combination of using methanol in the growth process and the use of ST-cut quartz as a substrate. These nanotube samples can be directly used for the fabrication of a large number of FETs using standard photolithography or e-beam lithography. They can also be easily adapted by the current Si fabrication technology due to their uniformity and perfect alignment. Therefore these results represent important progress towards the ability to control the types of nanotubes produced as well as their alignment, which represent the last major problems for the wide integration of carbon nanotubes into electronics.

3.3 Sulfur Assisted Density and Quality Enhancement of Aligned Single-Walled Carbon Nanotube Thin Films on Quartz Substrates

3.3.1 Introduction

Recently, our group found a method to selectively produce perfectly aligned samples of almost exclusively semiconducting SWNTs (95-98 %)[68]. The selective production of these clean, aligned semiconducting samples represented a significant step in the integration of SWNTs into nanoelectronic devices and mainstream technology. However, further investigation into the mechanism of this growth was necessary to fully understand and therefore utilize the factors which lead to this selectivity.
Previous work has demonstrated that sulfur containing compounds can be used to control the diameter as well as the number of shells of carbon nanotube products\cite{112}. However, perhaps the most investigated effect of sulfur is that sulfur based growth promoters such as thiophene can be utilized to increase the yield and quality of bulk produced SWNTs\cite{113,114,115,116}, typically by approximately 30\%\cite{117}. It is said that sulfur can influence SWNT growth by blocking active sites on the catalyst particle, lowering the melting point of the catalyst or interacting with the growing nanotube\cite{118}. It has also been suggested that the appropriate amount of sulfur can help prevent the buildup of amorphous carbon and thus the poisoning of the catalyst particles\cite{119,120}. However, it is still unclear whether these are the factors which contribute to sulfur’s SWNT growth promotion, and which among these possible factors plays the most significant role during growth.

In our previous work, we found that the combination of the appropriate quartz substrate, catalyst size and amount of MeOH all played significant roles in the selective production of semiconducting SWNT (s-SWNT). Notably, we hypothesized that OH radicals from the MeOH selectively etched the metallic nanotubes because of their lower ionization potential. Also, MeOH may raise the carbonization temperature of the system, which may also contribute to the selective production/nucleation of such small diameter s-SWNT\cite{121}. However, further work was necessary to investigate and clarify these hypotheses. Below, we analyzed the effect of sulfur on the EtOH/MeOH system in order to help elucidate the mechanism of this selective growth as well as the origin of the sulfur growth promotion.

\textbf{3.3.2 Materials/Experimental}

All samples were grown on 36 ° Y-cut single crystal quartz substrates and using 1 mM Fe(NO$_3$)$_2$•9(H$_2$O) or FeCl$_3$ and CuCl$_2$ as catalysts. Catalyst solutions were made in
200 proof EtOH and stabilized by poly(vinyl pyrrolidinone) (PVP). The catalyst diameters ranged from approximately 0.7-2.5 nm, with an average diameter of 1.6 nm as determined by Atomic Force Microscopy (AFM). Detailed synthesis procedures have been described previously\textsuperscript{[68]}. Briefly, after the catalyst was patterned, the substrates were annealed in air at 750 °C for 5 min, then reduced under H\textsubscript{2} at 750 °C for 10 min. After this reduction, samples were raised to 900 °C and grown under EtOH/MeOH/H\textsubscript{2} or EtOH/H\textsubscript{2} for 15 min and then cooled under H\textsubscript{2}. Analysis of the as prepared samples was done using Scanning Electron Microscopy (SEM) and AFM. Using a transfer method described elsewhere\textsuperscript{[68]}, samples were transferred to Si wafers with a 1 µm SiO\textsubscript{2} insulating layer for Raman analysis. Raman was used to analyze the Radial Breathing Mode (RBM) of the dense, aligned samples using a 633 nm laser in order to determine the selectivity of each growth method.

3.3.3 Results/Discussion

Typically, to promote bulk SWNTs growth, a thiophene concentration in the carbon precursor between 0.5-5 wt%\textsuperscript{[113]} is often used with Fe catalysts. However, it was found that in surface growth, the best enhancement was observed at much lower concentrations, specifically from 0.01 wt%\textsuperscript{-}0.1 wt%. Also, these enhancements were seen at different concentrations depending on the type and size of catalyst as well as the source gases. When EtOH/MeOH mixtures were used, density enhancements of up to 2X were seen at 0.075-0.1 wt% thiophene in EtOH for Cu catalyst (Figure 55) and as low as 0.03-0.05 wt% for Fe catalyst (Figure 56) as determined by SEM and AFM. The difference in these optimum conditions is likely a result of their differing catalytic activities. However obvious density and length enhancements can be seen at thiophene concentrations as low as 0.01 and 0.03 wt% (Figure 57, 58 and 59). In both cases, the density of aligned nanotubes was improved from ~2-4 SWNTs/µm to at least 6-8
Figure 55\textsuperscript{122} Samples grown on quartz using Cu as catalyst and EtOH-MeOH mixtures as carbon feeding gasses. Each sample was grown with A) 0 B) 0.01 C) 0.03 D) 0.05 E) 0.075 and F) 0.1 wt% thiophene. 2X density enhancement was demonstrated over this range, giving an average nanotube density of 2-4 nanotubes/µm and 6-8 nanotubes/µm without and with thiophene respectively. (Scale bar in all pictures is 10 µm)
Figure 56\textsuperscript{[122]} Samples grown on quartz using Fe as catalyst and EtOH-MeOH mixtures as carbon feeding gases. Each sample was grown with A) 0 B) 0.01 C) 0.03 and D) 0.05 wt\% thiophene. 2X density enhancement was demonstrated over this range, giving an average nanotube density of 2-4 nanotubes/µm and 6-8 nanotubes/µm without and with thiophene respectively. (Scale bar in all pictures is 10 µm)
Figure 57 Samples A and C were grown on quartz with the previously mentioned EtOH/MeOH growth conditions using Cu as the catalyst and no added thiophene. Samples B and D were grown using the same growth conditions but with 0.075 wt% thiophene. These SEM images indicate that the nanotube samples grown using thiophene are longer than those grown without thiophene. These shorter nanotubes are indicated by darker areas in center of the growth region (between catalyst lines), as designated by the red arrows in Figures A and C. These darker regions indicate low nanotube density in the center of the growth region, thus indicating shorter nanotubes when no thiophene is used. As a corollary, the brighter regions in the center of the growth area of Figures B and D indicate higher nanotube density, and thus longer nanotubes. The scale bars are 1 mm in Figures A and B, and 100 µm in Figures C and D.
SWNTs/µm by the addition of the appropriate amount of thiophene (Figure 60 C and D). These nanotubes were perfectly aligned and of high quality, with no noticeable amorphous carbon contamination; however, this enhancement was also evident in the catalyst regions as shown in Figure 60A and B. Additionally, the aligned nanotubes were noticeably long, mostly stopping only when encountering a physical barrier on the surface (Figure 61A and C). When only EtOH was used as the carbon source, the improvement was demonstrated at much lower thiophene concentrations (0.005-0.01 wt% in EtOH). The enhancement was also less dramatic, displaying only approximately a 30-50% density increase. Most nanotubes were very short and all samples without thiophene were dirty as indicated by SEM and AFM (Figure 62 and 63). Although the addition of thiophene helped to clean samples produced using EtOH, they were still noticeably dirtier than those produced with EtOH and MeOH, and the density of longer nanotubes was still lower. However, it was obvious from these results that adding the optimal amount of thiophene can improve the density of aligned surface grown SWNTs. It should be noted that, as with the enhancement of bulk samples, adding more thiophene than the optimal amount causes a dramatic decrease in the density of SWNT products (Figure 61). To our knowledge, this is the first time a sulfur source has been used to demonstrate such a density enhancement for surface grown SWNTs.

The effect of thiophene can be seen to manifest itself in the diameter distribution of the as produced nanotubes. This is particularly evident in the Raman spectra of these samples (Figure 4). Without thiophene, the diameter of the nanotubes as determined by AFM and Raman \((\omega=248/d)^{[18]}\), displayed a narrow diameter distribution from 1.5-1.8 nm centered around 1.6nm. However, a broadening of this diameter distribution is seen when thiophene is added, extending from 1.2-1.8 and centered around 1.4 nm. This decrease in average nanotube diameter agrees well with the literature regarding
Figure 58[122] AFM comparison of aligned nanotubes grown on quartz using an Fe catalyst. Figures A, B and C are samples grown using the previously mentioned EtOH/MeOH growth conditions with no added thiophene, whereas D, E and F represent samples grown under the same growth conditions but with 0.01 wt.% thiophene added in EtOH. A) 5 µm x 5 µm B) 2 µm x 2 µm C) 1 µm x 1 µm D) 5 µm x 5 µm E) 2 µm x 2 µm F) 1 µm x 1 µm. The height scale is 8 nm.
Figure 59[122] AFM comparison of aligned nanotubes grown on quartz using a Cu catalyst. Figures A, B and C are samples prepared using the previously mentioned EtOH/MeOH growth methods without thiophene, whereas D, E and F represent samples grown under the same growth conditions but with 0.03 wt.% thiophene added in EtOH. A) 5 µm x 5 µm B) 2 µm x 2 µm C) 1 µm x 1 µm D) 5 µm x 5 µm E) 2 µm x 2 µm F) 1 µm x 1 µm. The height scale is 8 nm.
The growth enhancement demonstrated by thiophene is often evident in the catalyst line region as indicated by the red arrows in Figures A and B. Samples A and B were grown using Fe as catalyst and EtOH-MeOH mixtures as carbon feeding gasses with A) 0 wt% and B) 0.01 wt.% thiophene respectively. Figures C and D demonstrate the sulfur induced density enhanced samples grown with C) Fe and D) Cu. 2X density enhancement was demonstrated using both catalysts, raising the average nanotube density of 2-4 nanotubes/µm to 6-8 nanotubes/µm without and with thiophene respectively. (Scale bar in pictures A and B are 20 µm and in C and D are 250 nm and the height scale on C and D are both 8 nm.)
Adding the appropriate amount of thiophene can improve the nanotube density with both Fe (0.05 wt% thiophene) and Cu (0.075 wt% thiophene) catalysts represented by A and C respectively. However, adding more than this optimal amount will cause a dramatic decrease in the density as represented by B) grown using Fe catalyst and 0.2 wt% thiophene and D) grown using Cu catalyst and 0.12 wt% thiophene. All scale bars are 100 µm.
Figure 62\textsuperscript{[122]} A and B were grown using Cu as catalyst and EtOH = 150 sccm and H\textsubscript{2} = 200 sccm with no added thiophene. C was grown using the same conditions but with 0.01 wt\% thiophene. Upon adding thiophene, the density of short nanotubes becomes larger and the sample becomes somewhat cleaner. However, the cleanest and longest nanotubes are achieved using EtOH and MeOH mixtures with thiophene and Cu, as displayed in D. D is grown using Cu and 0.075 wt\% thiophene. All scale bars are 10 \(\mu\text{m}\).
thiophene’s effect on carbon nanotubes and nanofibers. The origin of this decrease in average diameter has been hypothesized to result from sulfur induced localized liquid zones in larger catalyst particles as well as from the prevention of catalyst poisoning of smaller catalytic nanoparticle.\textsuperscript{[120],[123]} Ultimately, this broadening results in a loss of the s-SWNT selectivity previously provided by MeOH during growth, as can be seen in Figure 64. It was determined from this Raman spectra and AFM measurements that metallic nanotubes with diameters ranging from 1.1-1.4 nm are present after the addition of thiophene. Therefore, thiophene must interfere with the forces which provide the selectivity. As was previously stated, we believe that the selectivity results from selective etching of the metallic nanotubes and possibly also from the increase in the carbonization temperature. Also as previously stated, it is generally believed that thiophene effects nanotube growth by coating the catalytic nanoparticles to prevent poisoning, interacting with and helping to stabilize the growing nanotube, blocking active sites on the catalyst or lowering the eutectic point (melting point) of the catalyst. These two sets of theories overlap in two key areas. Firstly, if thiophene interacts with the growing nanotube, by coating or otherwise stabilizing it, this may prevent the MeOH from etching the metallic nanotubes. If this is true, the sulfur coating the nanotubes may be etched in place of the metallic nanotubes. This would essentially require a constant repletion of the sulfur coating to continually protect the nanotube throughout the entire duration of growth. Since thiophene is continually being added to the system as EtOH is added, this is a possibility. Alternatively, the OH radicals from the MeOH may simply not have enough potential to interact with the sulfur-stabilized metallic nanotubes. In essence, this would increase the ionization energy of the metallic nanotubes, preventing them from being etched. It is also likely that, if the sulfur interacts with the growing nanotubes, it will also interact with the catalyst to prevent poisoning.
Figure 63[122] AFM images of samples grown using Cu as catalyst and EtOH as the only carbon feeding gas. (EtOH = 150 sccm H2 = 200 sccm) Samples A and B have no thiophene added, but C and D have 0.01 wt% thiophene in EtOH. A and C are 10 µm x 10 µm images and B and D are 1 µm x 1 µm images. The height scale is 8 nm.
Figure 64[122] Radial Breathing Mode (RBM) spectra of samples grown using Cu as catalyst and A) 0 and B) 0.075 wt% thiophene; after growth, samples were transferred onto a Si wafer with 1 µm oxide layer for Raman analysis. A 633 nm wavelength excitation laser was used to scan the RBM to investigate the effect of thiophene on the selective growth of semiconducting SWNT. Comparing A and B illustrates that thiophene does interfere with the selective growth mechanism.
as previously claimed\cite{124}. If this interaction occurs, the smaller catalyst particles that may have previously been poisoned would be kept active by the sulfur. This would help explain the broadening of the nanotube diameter range observed here. The broadening occurs on the lower end of the diameter range, indicating the presence of small diameter metallic nanotubes. Either because of catalyst poisoning or because of the etching of the small diameter nanotubes by OH radicals, these small diameter metallic nanotubes are not seen without the presence of thiophene. Secondly, if thiophene interacts with catalyst nanoparticles to decrease the eutectic point of the catalyst, this may offset the increase in the carbonization temperature caused by the MeOH. This would result in more catalyst particles being active for nanotube nucleation. As a result, this eutectic point lowering would expand the window of the viable catalyst particles, which would result in a broadening of the diameter distribution. Lastly, thiophene may interact with the MeOH during growth, preventing it from contributing to the reaction of the EtOH and the catalyst particle. However, if this was the case, the density, quality and length of samples with MeOH and thiophene would likely match up well with samples produced using only EtOH, which they do not. Samples produced with just EtOH are, on average, denser, but dirtier and shorter than those produced here using EtOH, MeOH and thiophene. (Figure 62 and 63) Therefore, the most probable explanation is that sulfur does help prevent the selective etching of metallic SWNTs and that perhaps it also helps prevent the poisoning of the catalyst particles. The sulfur may still affect the eutectic point of the catalyst particles as well.

As a corollary, these results and analysis help to support our hypothesis that MeOH selectively etches the metallic SWNTs during growth. By determining that the most likely effect of sulfur is to interact with the catalytic nanoparticle and growing nanotubes, it is reasonable to conclude that the interaction of MeOH during growth
must be with one of or both of these factors. The broadening of the nanotube diameter range occurs to incorporate smaller diameter metallic nanotubes, which are less stable than larger diameter nanotubes. Therefore, because they are less stable, they would be more likely to be etched than would nanotubes with larger diameters. This fact supports our hypothesis that the primary role of MeOH is to selectively etch the less stable metallic nanotubes.

### 3.3.4 Summary

Through this work, we have successfully demonstrated the density enhancement of perfectly aligned SWNTs on quartz substrates using thiophene. To our knowledge, this is the first example of a sulfur based growth promoter being utilized on surface grown nanotube samples. Using SEM and AFM, it was evident that a 2 times density increase of these high-quality, long, aligned SWNTs grown from EtOH/MeOH mixtures was achievable. Although less dramatic, a 30-50% increase of nanotube density was demonstrated when only EtOH was used as the carbon feeding gas. These nanotubes were also shorter and of poorer quality than those produced using EtOH and MeOH as determined by SEM and AFM. By utilizing theories discussed in previous work done on bulk nanotube growth using sulfur based components, we were able to further support our previous hypothesis that the role of MeOH in the selective production of s-SWNTs was to selectively etch the less stable metallic SWNTs. Also, these results help to further clarify the role of sulfur during the growth of SWNTs, indicating that it helps to stabilize the growing nanotubes as well as prevent catalyst poisoning.
3.4 Direct Observation of the High Affinity Interaction between Carbon Nanotubes and Quartz

3.4.1 Materials/Experimental

The substrates used in the CVD approach were ST-cut single-crystal quartz wafer (36 ° Y-cut) obtained from Hoffman Materials Inc. without any further treatment. 200 proof (99.5 %) ethanol was purchased from Fisher Scientific and used for the catalyst solutions and carbon precursor. 99.9 % pure methanol was purchased from Fisher Scientific and used for the carbon precursor. The polyvinylpyrrolidone (PVP) with an average Mw Ca. 55000 and 99 % pure anhydrous CuCl$_2$ were purchased from Aldrich Chemical Company, Inc. and Acros Organics, respectively. A CuCl$_2$ (1.0 mM)/PVP (10 mM) alcohol solution was used to deposit catalyst on to the substrate. The growth experiments were performed in a one inch tube furnace at 900 °C. The catalyst patterning and growth processes were similar to the method reported previously. Typically, the substrate with catalyst precursor deposited on it was annealed in the air at 750 °C for 10 min to remove the PVP in the catalyst precursor. Then the substrate was heated up to 800 °C and kept for 15 min with a flow of hydrogen (750 sccm), followed by CVD growth of SWNTs at 900 °C with a flow of hydrogen (750 sccm) and argon (600 sccm, through a methanol bubbler and 150 sccm, through an ethanol bubbler). After 15 min growth, the sample was cooled to room temperature and inspected with scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectrometer.

Similar processes were performed for the growth of cardiogram shaped SWNTs on quartz. A flow of hydrogen (750 sccm) and argon (150 sccm through the ethanol bubbler, 300 sccm through the methanol bubbler and 500 sccm directly into the growth system) was used in the growth.
The transfer process of the SWNTs from quartz to Si, SiO\(_x\)/Si and quartz wafers was similar to the method reported previously with only minor differences. Briefly, a drop of 8 % PMMA solution (A4) was spin casted on SWNTs/quartz with 2000 revolutions per minute (RPM) to form a PMMA layer. After this, the PMMA/SWNTs/quartz substrate was baked at 160 °C for 10 min and immersed in boiling KOH (1 mol/L) aqueous solution for 40 min. The PMMA/SWNTs film was then peeled off from the quartz, as made possible by the quartz etched by KOH in the previous step. Then the PMMA/SWNTs film was washed with nano-pure water and carefully picked up with the other substrates. The angel between the aligned SWNTs and X [100] lattice direction can be tuned accurately in the pick-up process. Lastly, the PMMA/SWNTs/substrate was baked at 160 °C for 30 min and then washed with acetone and water. The SWNTs transferred onto the trenched quartz were parallel with X [100] direction of the lattice.

SEM images were taken on a FEI XL30 SEM-FEG instrument with 1 kV acceleration voltage. AFM images are taking on a Nanoscope IIIa instrument from Vecco Inc. under the tapping mode (TM). The Raman instrument used is a LabRam ARAMIS from Horiba Jobin Yvon with an excitation laser line of 633 nm. The excitation radiation was polarized parallel to the aligned SWNTs during the Raman measurements. The laser power was carefully controlled to avoid any heating effects.

3.4.2 Results and Discussions

Herein, our lab developed a CVD method which uses a high ratio of methanol/ethanol (600 sccm of Ar through a methanol bubbler and 150 sccm through an ethanol bubbler) as the carbon feeding gasses during growth. Using these conditions, it was found that high-density and uniform SWNT arrays can be grown on ST-cut single crystal quartz substrates. Figure 65 displays the SEM and AFM images of SWNT arrays
Figure 65 Arrays of high density SWNTs grown on ST-cut single crystal quartz with a large ratio of methanol/ethanol used as carbon precursors. (A, B and C) SEM images of such nanotubes. The bright and parallel horizontal lines visible in (A) are catalyst lines. The magnification is 100x (A), 25,000x (B) and 150,000x (C), respectively. (D) AFM image of the as-grown nanotubes. The scale bar is 500 µm (A), 2 µm (B), 500 nm (C) and 500 nm (D), respectively.
Figure 66 Arrays of long SWNTs grown on ST-cut single crystal quartz with a large ratio of methanol/ethanol used as carbon precursors. (A and B) SEM images of these carbon nanotubes. The black and parallel horizontal lines visible in (A) are two catalyst lines. (B) is the SEM image of the area marked with dotted rectangle in (A). (C) is the length distribution of the SWNTs in the arrays. The scale bars are 500 µm (A), 10 µm (B), respectively.
grown on the ST-cut quartz. The nanotubes were distribute uniformly along the X [100] direction over the entire surface with density as high as ~20 SWNTs/µm. The density of the aligned SWNTs is so high that it is difficult to distinguish individual SWNTs when a magnification above 150,000x is used during SEM characterization. As previously stated, during such growth we believe that the OH radicals from methanol can etch amorphous carbon and keep the catalyst nanoparticles from being poisoned. This would result in more catalyst nanoparticles being kept active during growth, which increases the density dramatically. Such dense and uniform SWNT arrays can be used as anisotropic thin-film conductors directly. This work was primarily developed by Dr. Lei Ding, Dr. Wei Wei Zhou and myself.

Earlier research showed that the aligned SWNTs grown using only methane or ethanol with Fe as catalyst have an average length of ~200 µm. However, it was found that the length of the SWNTs can be dramatically improved using a large ratio of methanol/ethanol as carbon precursors. Figure 66a shows the SEM images of such dense and long arrays of SWNTs on ST-cut quartz. The uniform arrays of long SWNTs were found everywhere on the quartz wafer. Also, the density of the SWNTs even in the middle of the arrays is still very high as shown in Figure 66b. Figure 66c shows the length distribution of the aligned SWNTs in the arrays. As is evident, most of the nanotubes have approximate lengths ≥1 millimeter. It was thought the long and well aligned SWNTs originate from the large-ratio of methanol/ethanol used during the growth. It is known that the growth of carbon nanotubes can be terminated if the catalyst nanoparticles become coated with amorphous carbon during growth. As was mentioned above, at high temperatures, the OH radical from methanol can etch amorphous carbon on the catalyst and thus keep it active during SWNT growth. Thus, because the particles were kept active, the SWNT’s produced during growth should be
significantly longer. However, it should be noted that the length of the SWNT from surface guided growth was not as long as that from flow directed growth; this is because surface defects, un-reacted nanoparticles and as-grown SWNTs can all terminate the growth of aligned SWNTs grown on surfaces, whereas surface properties don't significantly impact flow directed growth. Nevertheless, the fabrication of millimeter long SWNT arrays was demonstrated using this method, thus expanding the potential applications of aligned SWNTs to include radio frequency analog electronics.

Resonant Raman spectroscopy (RRS) has been shown to be a powerful tool for revealing the remarkable structural, electronic and phonon properties of SWNTs. RRS was used herein to characterize the SWNT arrays grown on ST-cut quartz using a large ratio of methanol/ethanol as carbon precursors. The spectra in Figure 67 were obtained using a 633 nm excitation laser line and sampling from 10 different spots over the substrate. Figure 67a shows the radial breathing mode (RBM) of the as-grown SWNT arrays on a quartz substrate. From this data, it is evident that only a narrow distribution of RBM frequencies exists between 143 cm$^{-1}$ and 151 cm$^{-1}$; these RBM peaks correspond to semiconducting nanotubes as predicted from the so-called Kataura plot. Figure 67b shows the G-band features of the SWNTs in the arrays on quartz. Interestingly, an obvious “up-shift” of the G-bands with G+ frequencies between 1605 cm$^{-1}$ and 1615 cm$^{-1}$ can be found in these spectra. Such obvious up-shifts of G-band frequencies have never been reported before. Also, no up-shifts of G-bands were found on SWNTs/SiOx samples grown side-by-side with the SWNTs/quartz samples. This seemed to indicate that the strong SWNT/quartz interaction is likely one of the main causes of this observed up-shift.

In order to study the mechanism of this observed up-shift, the aligned SWNT arrays were transferred onto SiOx wafers and characterized using RRS. Figure 68a and b
Figure 67 Raman spectra of the SWNTs grown on ST-cut single crystal quartz with a large ratio of methanol/ethanol used as carbon precursors. (A) RBM spectra of these nanotubes. (B) G-band spectra of these nanotubes. The Raman spectra were recorded with an excitation laser line of 633 nm. Ten different spots of the sample were characterized over the entire surface. Each curve in a panel shows a spectrum at a different spot on the substrate. The sharp peaks at 127 cm\(^{-1}\) and the broad peaks at 205 cm\(^{-1}\), marked with green stars in (A), correspond to the Raman spectra of the quartz.
Figure 68 Arrays of aligned SWNTs transferred onto a SiOx substrate. (A and B) SEM images of these nanotubes. The scale bars are 500 µm (A), 20 µm (B), respectively. (C) RBM spectra of these nanotubes. (D) G-band spectra of such nanotubes. The Raman spectra were recorded with an excitation laser line of 633 nm. Ten different spots of the sample were characterized over the entire surface. Each curve in a panel shows a spectrum at a different spot on the substrate.
present the SEM images of the aligned SWNTs on SiOx wafers. It should be noted that no changes in structure or alignment occurred during the transfer of the SWNT arrays. Figure 68c shows the RBMs of the aligned SWNTs from ten different spots of the SiOx substrate. The distribution of the RBM frequencies is between 143 cm$^{-1}$ and 156 cm$^{-1}$, which is similar with that of the samples characterized in Figure 67a. As is shown in Figure 68b, the aligned SWNTs transferred onto SiO$_x$ have G-band frequencies between 1589 cm$^{-1}$ and 1593 cm$^{-1}$, which was also observed from SWNTs grown on SiO$_x$ surfaces. It was obvious that the “up-shift” of the G-bands disappeared after the SWNTs were transferred onto the SiO$_x$ substrate. This same phenomena was found when the aligned SWNTs were transferred onto a Si substrate. Therefore, it seems evident that the “up-shift” of the G-band frequencies results from a high affinity interaction between the SWNTs and quartz substrate. Once the aligned SWNTs were transferred onto the SiO$_x$ substrate, this high affinity interaction no longer existed and the aligned SWNTs reverted to demonstrating G-bands around 1590 cm$^{-1}$ as they usually do.

In order to further investigate this high affinity force, as-grown SWNTs were transferred across a trench etched into a ST-cut single crystal quartz wafer. The orientation of the aligned SWNTs transferred onto the trenched quartz was parallel with the X direction of the lattice as shown in Figure 69. After transferring, RRS was used to characterize the portions of the nanotubes in contact with the quartz (position 1, 3, 5 in Figure 69) as well as those portions suspended over the trench (position 2 and 4 in Figure 69) of the same SWNT. Each of the inserted spectra is the RBM of the SWNT measured simultaneously with the G-band. As shown in Figure 69, the inserted spectra of RBMs display frequencies between 152 cm$^{-1}$ and 153 cm$^{-1}$ and with no obviously difference between the contacted parts and the suspended parts. It was postulated that the similarity of the RBM frequencies results from either the accuracy of the RRS or the
Figure 69 Raman spectra of the aligned SWNTs transferred onto the trenched ST-cut single crystal quartz. The top left figure is a schematic illustration of the Raman characterization. The orientation of the aligned SWNTs transferred onto the trenched quartz is parallel with the X [100] direction of the lattice. Figures marked with 1 to 5 represent the Raman characterization of the sections of the nanotube in contact with the quartz (position 1, 3, 5 in schematic illustration) and the sections suspended over the trench (position 2, 4 schematic illustration) of the same SWNT. Each of the inserted spectra depicts the RBM of the SWNT measured simultaneously with the G-band. The sharp peaks marked with green stars in RBM spectra correspond to the Raman spectra of the quartz. The RBM and G-band frequencies are 152 cm\(^{-1}\) and 1605 cm\(^{-1}\) (position 1), 153 cm\(^{-1}\) and 1591 cm\(^{-1}\) (position 2), 153 cm\(^{-1}\) and 1605 cm\(^{-1}\) (position 3), 153 cm\(^{-1}\) and 1591 cm\(^{-1}\) (position 4), 152 cm\(^{-1}\) and 1603 cm\(^{-1}\) (position 5), respectively.
weak substrate effect, or both. However, it was interesting to note that the G-bands of the contact parts, which all display frequencies at around 1605 cm$^{-1}$, are quite different from those of the suspended parts which demonstrate frequencies at 1591 cm$^{-1}$. Thus, this experiment further suggests the existence of a high affinity interaction between the aligned SWNTs and the quartz substrate.

The mechanism of this G-band “up-shift” is not fully understood, however the following hypothesis was presented. The G-band of SWNTs consists of two main components, one centered at 1590 cm$^{-1}$ (G+, associated with carbon atom vibrations along the nanotube axis) and the other centered at about 1570 cm$^{-1}$ (G-, associated with vibrations of carbon atoms along the circumferential direction). As is known, the $\omega_{cc}$ is directly correlated to $k_{cc}^{0.5}$ (k, the force constant). It is possible that the high affinity interaction between the SWNT and quartz substrate deforms the SWNT on quartz. This deformation of the SWNTs would result in a warping of the C-C bonds, which may in turn increase the $k_{cc}$. This deformation would be most prominent at the edges, which may cause the observed up-shift of the G-band. Also, the bottom layer of the deformed SWNT would be similar in structure to a monolayer graphene on this substrate. It has been observed that a monolayer of graphene always has a peak at ~1615 cm$^{-1}$ which results from its affinity for the substrate.

### 3.4.3 Summary

It was obvious from this investigation that there does exist a high affinity interaction between the SWNTs and the quartz substrate. This was perhaps most evident when seeing that the G-band shift disappeared when the SWNTs were transferred onto SiO$_x$ or were suspended over a trench. In these situations, the affinity force between the SWNTs and the quartz lattice disappeared and so therefore did the asserted structural deformations which are believed to be the route of this G-band shift.
Regardless, it is apparent that the methods developed here can be used to produce uniform, dense arrays of very long SWNTs. This will help to expand the potential applications of aligned SWNTs to include a variety of other technologies including radio frequency analog electronics.

### 3.4 Summary

Carbon nanotubes hold great promise for revolutionizing electronics and various technologies. However, the means with which they are produced produces mixtures of semiconducting and metallic nanotubes. This presents a major problem for their application to most technologies, as devices usually require only semiconducting or metallic nanotubes. As was mentioned previously, orientation control has been successfully demonstrated using various methods such as ultra high flow rate growth, fast heating growth and lattice aligned growth. Thus, the selective growth of electronically specific carbon nanotubes remains the last major hurdle standing in the way of the mainstream application of carbon nanotubes in modern electronics.

The existing methods of achieving electronically specific nanotube samples all rely on chemical agents to separate such nanotubes; however these methods often modify the carbon nanotube structure by introducing defects or contaminants. Also, no reliable method exists for orienting these nanotubes after separations for use in electronics. Through this work, a scalable method for producing perfectly aligned SWNT samples consisting of almost exclusively semiconducting nanotubes was developed using EtOH/MeOH as carbon feeding gasses and the appropriate Fe and Cu catalysts and quartz substrates. Moreover, it was found that simple manipulation of the EtOH/MeOH flow rates could produce very long (≥1 mm) perfectly aligned SWNT samples. These well-aligned samples can be directly applied to electronic devices, representing a major step forward in nanoelectronic applications.
Investigations into the two major factors contributing to this selective growth were undertaken in a systematic manner. First, thiophene was introduced into the growth system in order to study the effect of MeOH on this selective growth as well as the role of sulfur in nanotube growth promotion. These hypotheses for both overlapped in a few key areas. Mainly this overlap proved that the role of sulfur in growth promotion was to help stabilize the growing nanotubes as well as to prevent catalyst poisoning. By stabilizing these growing tubes, sulfur could counteract the effect of MeOH. It was proposed that MeOH etched the smaller diameter metallic nanotubes, which had smaller ionization potentials. Thus, by stabilizing these nanotubes, their ionization potentials were increased and thus protected from etching. This resulted in a density increase of the SWNT arrays as well as the broadening of the diameter distributions to include smaller diameter metallic carbon nanotubes. Thus, strong evidence indicates that the role of MeOH is indeed to etch these smaller diameter metallic nanotubes.

Secondly, the proposed “affinity” between the SWNTs and the quartz substrate was investigated by transferring the SWNT arrays onto SiO$_2$/Si and “trenched” quartz substrates followed by RRS analyzation. It was found that no RBM or G-band evidence of any affinity existed when the samples were transferred onto the SiO$_2$/Si substrate or over a trench. However, direct evidence of this affinity-force did exist on the portions of the nanotubes that were in contact with the quartz substrate. This manifested itself by and up-shift in the G-band to approximately 1605 cm$^{-1}$ from ~1590 cm$^{-1}$ in these regions. The exact nature of this interaction is still unclear, and the subject of ongoing work. However, it is obvious that a strong affinity interaction does exists.

Thus, the hypothesis linked to the two major contributions to the selective growth of these perfectly aligned arrays of almost exclusively semiconducting SWNTs
were investigated and supported. These investigations confirmed that both the addition of MeOH and the affinity between the SWNTs and the quartz substrate had large roles in this selective growth of these samples. Furthermore, the mechanism of both the MeOH and substrate’s promotion of these selectively grown samples were investigated thus lending experimental supported to the previously asserted hypotheses.
4. Micro/Mesoporous Carbon for H\textsubscript{2} Storage

4.1 Introduction

Recent increases in gas and oil prices are reminders of the need to develop cleaner, more reliable and renewable fuels with which to power our society. Of the alternative energy sources under development, perhaps the most promising is H\textsubscript{2}.\textsuperscript{[125]} It is abundant, easy to handle, and creates only harmless by-products upon combustion. Also, H\textsubscript{2} is the lightest molecule, and thus has a profound advantage over other fuel sources, having approximately three times the gravimetric energy density of petrol.\textsuperscript{[47]} As a result, much interest has been focused on the development of efficient and applicable H\textsubscript{2} powered devices. However, many problems have inhibited their development. Presently, the biggest problem standing in the way of H\textsubscript{2} as a fuel in mainstream applications is its storage. A great deal of effort has been focused on meeting the current Department of Energy (DOE) 2015 goals for system H\textsubscript{2} storage capacities of 5.5 wt.% (40 g/L). Several methods/materials have shown varying degrees of promise for meeting these goals; among these are metal hydrides, compression cylinders and porous materials. However, each has their own limitations. Metal hydrides store H\textsubscript{2} well, but run into problems with heat management and low net H\textsubscript{2} capacities in on-board systems. In essence, desorbing H\textsubscript{2} for use as fuel requires large amounts of energy and is not an efficient process. Compression cylinders and similar storage media are dangerous and difficult to transport. Lastly, both doped and undoped porous materials, such as metal organic frameworks (MOF) and porous carbons, have encountered problems of small surface areas and unstable or inaccessible pores, all of which limit the amount of H\textsubscript{2} able to be stored in such media. However, recent improvements in the production of porous carbons have helped to distinguish them as a leading candidate for investigation as potential H\textsubscript{2} storage media. Among this class of
materials, it is thought that nano/microporous carbon materials have the pore diameters best suited for H₂ storage\textsuperscript{[126]}. However, it has proven non-trivial to achieve both the large surface area and the nano/micropore diameters necessary for optimized H₂ storage\textsuperscript{[50]}. In this chapter, several methods of producing a porous carbon with such features optimized for H₂ storage are discussed.

4.2 Inorganically and Organically Templated Porous Carbons

4.2.1 Inorganically Templated Porous Carbons

4.2.1.1 Materials/Experimental

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<tbody>
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<td>Faujasite (FAU) was purchased from Zeolyst as CBV 780 (SiO₂:Al₂O₃ = 80:1 mol ratio, surface area = 780 m²/g). 52 % wt. HF was purchased from EM Science. Phenol, cetyltrimethylammonium Bromide (CTAB), furfuryl alcohol (FA) and 37 % formaldehyde were purchased from Acros. 1 N NaOH was purchased from Fisher Scientific. An Ace Glass hotplate/stirrer was used during this synthesis. CTAB was encapsulated in FAU and heated at 800 °C and ~1 Torr for 5 hrs. For FA encapsulation, 3 g FAU was placed into a 500 ml round-bottom flask with 120 ml FA and 30 ml benzene. This mixture was gently stirred for 3 days. After 3 days, this solution is filtered and dried. Polymerization of the FA was accomplished by heating the sample under N₂ flow at 80 °C for 24 hrs and then at 150 °C for 6 hrs. Carbonization was then accomplished by heating at 700 °C for 3 hrs under N₂ flow.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4.2.1.1.2 EtOH Impregnation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH was purchased from Fisher scientific and used without further treatment. In this nanocasting procedure, the system was pumped down to ~1 Torr and the temperature was raised to the reaction temperature (800 °C). After reaction temperature was reached, the EtOH was opened to the evacuated system and pumped on for the set reaction period. All samples were processed by mixing approximately 100 mg with 2 ml</td>
</tr>
</tbody>
</table>
diluted HF solution and allowing the mixture to react for 24 hrs. After dissolving the template, the solution was neutralized with 30 ml 1 M NaOH and then diluted with ~20 ml nanopure water, again sitting for 24 hrs. Centrifugation was then used to collect all carbon material. The liquid remaining on the top of the samples was decanted off, and the sample was collected by vacuum filtration using a micro filtration system.

### 4.2.1.3 Analysis

TEM was done using a Phillips 301 using Lacey TEM grates. XRD data was taken on a Philips XPert PRO MRD HR X-Ray Diffraction System. Thermo-Gravimetric Analysis (TGA) data was taken from a SDT Simultaneous DTA-TGA. Surface area measurements were taken with a Micrometrics Tristar.

### 4.2.1.2 Results/Discussion

Figure 70 displays the general procedure used in all templated porous carbon synthesis using zeolites and other inorganic templates. As can be seen, the zeolite was first chosen to be FAU because of its availability and relatively high surface area (~780 m$^2$/g). In the case of EtOH-based carbon casting, EtOH was flowed over and through the FAU framework at a reaction temperature of 800 °C. This temperature allows for the EtOH to be deposited as a cast on the FAU framework. After removal of the FAU, a porous carbon like the one shown in Figure 71a was formed. This method was found to be a simple and easy way to achieve porous carbons with what appeared to be a structure similar to that of FAU under TEM analysis. However, further investigation revealed that, while this method could form carbon casts relatively well, removing the FAU template was difficult even after extensive acid treatment. This is evident in the TGA displayed in Figure 72. Here, all carbon products should burn away at a relatively low temperature when exposed to air (<500 °C). However, the TGA indicates that significant mass still remains at temperatures up to 900 °C. Since no carbon products should survive at this temperature, it was deduced that significant amounts of FAU
The general procedure for producing porous carbons utilizing inorganic templates is illustrated here. First, an appropriate inorganic template is chosen, followed by carbon deposition. Carbon deposition is typically accomplished using a carbon gas or liquid impregnation of the inorganic/zeolite structure followed by carbonization and template removal. After template removal, a carbon cast of the original inorganic material is left, which typically has larger surface areas than the original inorganic templates.
Figure 71 TEM images of porous carbon products formed using FAU as a template. a) EtOH was first flowed through the FAU structure at elevated temperature, which decomposed carbon on the surface of the zeolite. Alternatively, a polymer such as CTAB or b) FA was impregnated and polymerized inside the FAU structure. In both cases, the resulting porous carbons had low surface areas owing to difficulties in template removal.
Figure 72 TGA analysis of porous carbon products formed by the EtOH casting of FAU revealed that significant mass remained at high temperature. It was deduced that this resulted from a significant amount of FAU remaining in the products.
remained, as FAU is stable at this temperature. This was even true for porous carbon products subjected to several acid treatment cycles. It was hypothesized that the FAU structure was extensively coated by carbon, which protected it from the acid treatment. As a result of this inability to remove the inorganic template, only small surface area products were formed. These small surface areas can be attributed to the presence of aluminum and other heavy elements in FAU. The presence of FAU increases the weight of these products, which drives down the surface areas (<200 m²/g). Such products are unsuitable for H₂ storage applications. Further inorganic templating was investigating using polymer impregnation of FAU. Here, FA was incorporated into FAU and polymerized within its framework. An example of such a porous carbon product can be seen in Figure 71b. While this method also appeared to produce porous carbon materials having many of the characteristics of FAU under TEM analysis, these products suffered from the same problems as the EtOH casting. BET analysis indicated the presence of a small surface area product. Further investigations using TGA revealed that a significant amount of FAU appeared to remain. Ultimately, the small surface area of these inorganically templated products combined with the danger of working with HF to dissolve the FAU template to make this approach undesirable and ultimately impractical.

4.2.2 Organically Templated Porous Carbons

4.2.2.1 Materials/Experimental

Pluronic surfactants were supplied by BASF. N₂ was purchased from National Welders. All other materials were purchased from Fisher Scientific and used without further manipulation. In a typical synthesis procedure, 2.0 g phenol, resorcinol or floroglucinol and 5.0 g of 38 wt% formaldehyde solution were added to 50 g of 0.1 M NaOH solution. The mixture was then heated at 72 °C for 30 min. After heating, this
solution was then mixed well with a clear solution composed of 4.8 g pluronic surfactant (P123, P103 or P84) and 50 g nanopure water. This mixture was then stirred at room temperature (20 °C) for 3 h. The temperature was then raised to 64 °C and continued to stir for 120 h. The temperature was then raised to 72 °C and continued to stir for an additional 48 h. After this polymerization procedure was complete, the products were dried in air and heated at 350 °C for 2 h after rising at a rate of 5 °C/min in N₂ flow to remove the pluronic polymer template. After template removal, samples were cooled under N₂ and then categorized by Brunner-Emmett-Teller (BET) surface area analysis and Transmission Electron Microscopy (TEM). The surface area of the samples was analyzed using a 5pt. N₂-BET Analysis using a Micrometrics Gemini 2360 Instrument (Material Synergy). TEM images were taken on a FEI Tecnai G² Twin Microscope with an acceleration voltage of 200 kV.

4.2.2.2 Results/Discussion

Recent developments have produced mesoporous carbons without the use of inorganic templates. Instead, these syntheses utilize organic templates in order to impart structure to porous carbon products. This is extremely beneficial, as it forgoes the use of the dangerous acid treatments necessary to remove most inorganic templates. In one such synthesis, a resol is formed from the reaction of phenol with formaldehyde. After addition of the pluronic copolymer, the resol interacts with the hydrophilic portion of pluronic surfactant. Once the copolymer has been surrounded by the forming resol, polymerization is completed. It is important that the pH remains between 8-9 during this process to retain the H-bonding which links the resol and the structure imparting surfactants. After polymerization is complete, the pluronic surfactant, which provides the porous structure, is removed by simple heat treatment. This process is summarized in Figure 73. The mesoporous carbon produced by carbonizing these products is FDU-
14. It has been reported that FDU-14 can be engineered with a range of pore diameters which includes the microporous range thought to be optimal for H₂ storage. Additionally, it was reported that this material displays a very high BET surface (1150 m²/g). Both factors indicated that porous carbons produced using these organic templates could be extremely interesting for H₂ storage applications. As such, porous carbons synthesized using a variety of pluronic surfactants were produced following the procedure outline in Figure 73. Specifically, P84, P103 and P123 were chosen as pluronic surfactants. These di-block surfactants were utilized because their structure only differed in the length of the hydrophobic segment. Because the length of this segment was different, these copolymers formed different sized micelles in the hydrophilic environment in which the polymerization took place. Ultimately, these differing micelles imparted pores of different diameters in the resulting porous carbon products. The TEM data in Figures 74A-C demonstrate that regular, porous structures with varying pore diameters were successfully synthesized. Here, porous carbons with pore diameters of 1-2 nm, 1 nm and 0.6-0.8 nm were formed using P123, P103 and P84, respectively. The scalability of pore sizes and safe manufacturing conditions made this method very attractive for producing materials for applications in H₂ storage. However, BET surface area measurements indicated that materials produced using this method had very small surface areas (<250 m²/g). It is thought that these small surface areas resulted from extensive pore collapse during the relatively high temperature template removal step. This combined with the relatively narrow production window ultimately made this method impractical for such applications.
Figure 73\textsuperscript{[127]} The organically templated synthesis procedure for producing porous carbons. Here, di-block copolymer is used to form a micelle in a hydrophilic environment. The length of the hydrophobic segment of this copolymer ultimately was used to form different diameter micelles in solution, and thus pores of different sizes in the resulting porous carbon products. After solvation of the pluronic surfactant, it is H-bonded to a resol-type polymer forming in solution. After polymerization is complete, the surfactant template is removed and the porous carbon is formed.
Figure 74 Porous carbons with scalable pore diameters were synthesized using the organic templates a) P123 b) P103 c) P84. As determined from TEM, these pluronic surfactant templates imparted pore diameters of 1-2 nm, 1 nm and 0.6-0.8 nm respectively (marked in white in each figure). Despite this scalability of pore size, the \( \text{H}_2 \) storage properties of these samples were not investigated as a result of their low BET surface areas.
4.2.3 Summary

Inorganic templating was utilized to produce porous carbon materials using a variety of carbon precursors and conditions. However, problems with template removal and dangerous experimental conditions ultimately shifted the focus of such templated porous carbon production to organically templated porous carbons. The experimental conditions used in this synthesis were safer and able to produce porous carbons with scalable pore sizes. However, small surface areas and narrow growth conditions ultimately made this method impractical. Overall, templated porous carbon synthesis was shown to be successful in producing porous carbon products. However the limitations of each method proved significant, resulting in a redirection of porous carbon synthesis efforts in this research.

4.3 H₂ Storage in Microporous Carbons from PEEK Precursors

4.3.1 Introduction

Many methods such as activation\cite{128} and inorganic\cite{129} or organic\cite{130} templating have been utilized to achieve large surface area nano/microporous carbons; however, no material has mastered both a large surface area and small pore diameter. Additionally, most of the templating procedures suffer from dangerous template removal conditions\cite{129} and very narrow production conditions, making large scale production impractical\cite{130,127}. Initial results indicated that CO₂ treatments of poly(etherether ketone), or PEEK (Figure 75), may be very interesting to investigate for the production of porous carbons\cite{131}. This method is both simple and robust, and does not require the removal of any template or the use of any dangerous chemicals. It relies on oxidization of the PEEK structure to create well defined pores. However, more work needed to be done to appropriately characterize this method and explore its versatility.
Most significantly, the H₂ storage capabilities of its porous carbon products needed to be investigated. 

Here, we describe two methods of producing large surface area porous carbons and explore the impressive H₂ storage capabilities of these products. Using these scalable production methods, we were able to produce samples with large surface areas (>3000 m²/g), small pore diameter distributions (≤3 nm) and large cumulative pore volumes (~1.7 cm³/g). Thus, these samples can be used to tailor a porous carbon with the optimal balance of surface area and microporosity for the storage of H₂. If these materials are ultimately successful, the methods outlined herein will aid in the production of tailored porous carbon materials for H₂ storage purposes, and ultimately aid in the replacement of conventional non-renewable fuel sources with H₂.

4.3.2 Materials/Experimental Details

PEEK was used as received from Vitrex Inc. UHP Ar and Research Grade CO₂ were purchased from National Welders. A moisture trap was purchased from Alltech and attached to the Ar line into the one inch Lindberg Blue Chemical Vapor Deposition (CVD) oven reactor. Nanopure water from a Barnstead Nanopure water filtration system was used for steam treatments.

4.3.2.1 CO₂ Thermal Treatment

Typically, five grams of PEEK were placed in an alumina combustion boat from Fisher Scientific (Figure 75A), which was then placed inside the one inch quartz reaction tube. UHP Ar was flowed through the tube at about 700 sccm as the temperature was slowly raised (10 °C/min) from room temperature (25 °C) to 900 °C and maintained there for 30 min. After this carbonization step, Ar flow was stopped and CO₂ was introduced at 100 sccm for the pre-determined reaction time. After the reaction was
Figure 75 PEEK in an alumina combustions boat A) before and B) after thermal treatment under CO$_2$. It should be noted that the products after thermal treatment were similar in appearance when treated with steam. C) The chemical structure of one subunit of PEEK. D) After thermal treatment, the porous products were analyzed using TEM. Here, PEEK-CO$_2$-9-80 is used to display a typical TEM image in which small diameter pores are evident. The scale bar in this image is 10 nm.
complete, Ar was re-introduced and the CO$_2$ stopped as the reaction tube was allowed to cool to room temperature (Figure 75B). After collection, the Burn Off (BO) was calculated assuming that the carbonization yield was 51%$^{[127]}$. The burn offs were then reported relative to the remaining sample after carbonization. After the BO was calculated, the samples were stored under vacuum desiccation until further analysis. These samples were named PEEK-CO2-9-BO. Here, the CO$_2$ and number nine respectively refer to the gas and temperature (divided by 100) used in the reaction.

4.3.2.2 Steam Thermal Treatment

The amount of PEEK and steps taken to carbonize the steam treated samples was the same as for those treated with CO$_2$. After carbonization, Ar was allowed to flow at 700 sccm through a 16 oz. bubbler filled with nanopure water (NP H$_2$O) at room temperature. After being allowed to react for the predetermined reaction time, the pure Ar was re-introduced to the reaction tube as it cooled to room temperature. The BO was calculated the same way as with the CO$_2$ treated samples and stored under vacuum desiccation. These samples were named PEEK-ST-9-BO. Here, the ST and number nine respectively refer to the gas and temperature (divided by 100) used in the reaction.

4.3.2.3 Analysis

Samples were analyzed with a 5pt. BET Analysis using a Micrometrics Gemini 2360 Instrument (Material Synergy). H$_2$-NMR was done using a basic free induction decay pulse sequence in a 4.7 T superconducting magnet at pressures ranging from 100 Pa to 10 MPa, at both room temperature (RT, ~290 K) and 100 K (UNC-CH). Absorption isotherms were taken on a Quantachrome Autosorb-1 by our partners at the National and Renewable Energy Laboratory (NREL). Transmission Electron Microscopy (TEM) images were taken on a FEI Tecnai G$^2$ Twin Microscope with an acceleration voltage of 200 kV.
4.3.3 Results/Discussion

After thermally treating PEEK under different environments, a blackened and highly porous powder product was formed. TEM analysis shows that these porous products have a relatively narrow distribution of small pores at low percent burn off (BO), while higher BO products have a slightly broader diameter range. Figure 75D displays one such example of a high BO product (PEEK-CO$_2$-9-80). It is evident that there is a significant portion of pores with diameter at and around 1 nm; however, it is also apparent that larger diameter pores are present throughout the structure. It is generally thought that steam provides a gentler oxidation environment than CO$_2$. Thus, in this study, steam was used to limit pore diameter widening and thus investigate the relative importance of the diameter distribution and pore volume to H$_2$ storage in microporous carbons. Thus characterization of the pore diameter distributions as well as pore volume distributions was integral. Perhaps most importantly, an understanding of the evolutions of each was paramount to appropriately categorize these methods. Such an understanding is necessary for the successful application of these methods and their tailored porous carbon products, specifically here to H$_2$ storage aims.

One of the most important factors to the H$_2$ storage capabilities of porous materials is surface area. The so called “Chahine Rule” states that, assuming ideal graphitic slit pores, for every 500 m$^2$/g surface area, 1 wt.% H$_2$ gravimetric uptake is achieved by porous carbons.$^{[132]}$ Despite this rule being inaccurate in many cases, it nonetheless emphasizes the importance of surface area to the H$_2$ storage capabilities of these materials. As such, achieving a large surface area is extremely important. Here, we have demonstrated that both CO$_2$ and steam (ST) can be utilized to produce porous carbons with very large surface areas, in both cases reaching ~3000 m$^2$/g or more. It is critical to note that the samples consisting almost entirely of pure carbon, as determined
by X-Ray Photoelectron Spectrometry (XPS). This data indicated that the surface chemistries of the pores was largely graphitic. This was true even after extended treatment, and thus at large surface areas. (Figure 76) Therefore, direct comparison of these CO$_2$ and steam derived products can be utilized not only to compare these products, but also the importance of pore diameter and volume to H$_2$ sorption. Figure 77 shows the evolution of the Brunner-Emmett-Teller (BET) surface area with BO and demonstrates the large surface area (~≥3000 m$^2$/g) achievable using both methods. It is evident that the surface area increases with increasing BO in both cases. This is in line with the proposed pore formation mechanism in which pores are oxidatively etched from the carbonized PEEK structure. However, CO$_2$ produces a much more regular and linear increase in BET surface area with BO. Steam produced samples appear to suffer from a significant amount of pore collapse. This could be due to differences in the mechanism of oxidation by CO$_2$ as compared to steam. If steam did conserve the pore diameter distribution better and increase the pore volume with surface area more than CO$_2$, this could cause structural collapse at certain periods during the extended thermal treatment process. Essentially, the etching would eventually cause the pore walls that separate individual pores to break down. This fact is supported by NMR investigations of steam products. These investigations show that the peaks of H$_2$ in micro/mesopores become indistinguishable from those of H$_2$ in large voids at very high BO. This indicates that most of the pores are connected to each other and to the voids, allowing free exchange of H$_2$. (Figure 78) Thus, steam derived samples reaching 3000 m$^2$/g are not ideal for H$_2$ storage, and therefore were not analyzed beyond surface area measurements in this work. Therefore, CO$_2$ is better for achieving stable, large surface area products.
Figure 76 XPS of A) PEEK-CO$_2$-9-80 and B) PEEK-ST-9-91. Both spectra show that the porous carbon products derived from PEEK are nearly pure carbon materials even after extensive thermal treatment and thus extensive burn off.
Figure 77 A plot showing the evolution of the Brunner-Emmett-Teller (BET) surface area with burn off. Large surface area (≥3000 m²/g) products were achieved using both CO₂ and steam thermal treatments.
Figure 78 Representative NMR Spectra of samples with BET surface areas of ~3000 m$^2$/g produced using CO$_2$ (red) and steam (blue). The spectra of the CO$_2$ product displays the distinct peaks corresponding to micropores (green arrow) and larger pores/voids (blue arrow). The peak in the spectra of the steam produced sample has no distinction between these peaks indicating a breakdown of the pore walls. This breakdown allows for a free exchange of H$_2$ between the micropores and larger pores/voids.
However, which method produced the samples with the smallest pore diameters and largest pore volumes? Also, how important are these factors to storing H\(_2\)?

To determine this, Differential Pore Volume measurements were taken to analyze and compare the products of each method. Figure 79A shows that the sample with the largest pore volume is PEEK-CO\(_2\)-9-80, which has the largest surface area of all the samples whose diameters were analyzed (3103 m\(^2\)/g). However, along with the large surface area and pore volumes, the diameter distribution is evidently higher than the other samples with smaller surface areas. This sample has pores of approximately 1.2, 1.35, 1.8 and 2.5 nm with the largest pore volume (0.1 cm\(^3\)/Å/g) at a diameter of 1.35 nm. However, the pores at 1.8 nm and 2.5 nm also have relatively large pore volumes of approximately 0.06-0.07 cm\(^3\)/Å/g. While the volume of all pores increases with increasing BO, it is apparent from Figure 79B and C that the larger pores develop “later” than smaller pores. Again, this agrees well with the theory of pore formation, since the etching of the pore walls would continue the entire duration of the treatment, as would pore nucleation. Thus, pores would both widen in diameter and increase in volume as BO progresses. Figure 79B displays this evolution for samples produced using CO\(_2\). From Figure 79B, it is evident that PEEK-CO\(_2\)-9-26 is dominated by pores with diameters <1.5 nm. Also, as BO continues, the volume of pores with diameters ~1.35-2.5 nm increase most noticeably, as demonstrated in PEEK-CO\(_2\)-9-59. This represents an increase in BET surface area from ~1000 m\(^2\)/g to 2000 m\(^2\)/g respectively between the samples. Increasing the BET SA further to ~3000 m\(^2\)/g in PEEK-CO\(_2\)-9-80 demonstrates a drastic increase in all pore volumes, with the largest increase in pores with diameters 1.2 and 1.35 nm. Figure 79C shows the evolution of steam derived samples. This graph shows that, unlike the CO\(_2\) derived samples, increasing the surface area from
Figure 79 A plot of Differential Pore Volume measurements for several CO$_2$ and steam derived samples. A) PEEK-CO$_2$-9-80 has the largest pore volumes and the largest surface area of all the samples whose diameters were analyzed (3103 m$^2$/g). It is evident that all samples have pores with diameters centered around 1.2, 1.35, 1.8 and 2.5 nm. B) and C) show the evolution of the Differential Pore Volumes of CO$_2$ and steam derived samples, respectively. D) At 1000 m$^2$/g, the volume of all pore diameters is notably larger for the steam treated product as compared to the CO$_2$ treated product. This difference in pore volumes is even more pronounced when analyzing E) the Differential Pore Volume distributions normalized at 2000 m$^2$/g. Here, it is evident that the pores with diameters of 1.2 and 1.35 nm in steam treated sample have significantly larger volumes than in the CO$_2$ treated samples. It should be noted that the Density Field Theory analysis of this data below 1 nm is unreliable. As such, interpretation of pore diameters around 1 nm is supported by NMR data.
~1000 m²/g to 2000 m²/g in steam treated samples (PEEK-ST-9-35 and PEEK-ST-9-70 respectively) causes the most dramatic pore volume increase in pores with diameter ~1.2 nm. The second most dramatic increase is in pores of diameter ~2.5 nm; however, the pore volume of the 1.2 nm pores increases approximately twice as much as the pore diameter at ~2.5 nm. This seems to indicate that steam treatment may indeed help conserve the pore diameters while successfully expanding the pore volumes, particularly of the crucial pores with diameters around 1 nm. If steam is favorable to CO₂ in this regard, this should be reflected in a comparison of the Differential Pore Volume distributions of steam and CO₂ derived samples normalized to BET surface area. Figures 79D and E displays these comparisons between steam and CO₂ derived samples. Figure 79D displays that, at 1000 m²/g, the volume of all pore diameters is notably larger for the steam treated product as compared to the CO₂ treated product. The pore with the largest volume for this steam sample has a diameter of ~1.35 nm, indicating a predominantly microporous product. The difference in pore volumes is even more pronounced when analyzing the Differential Pore Volume distributions normalized at 2000 m²/g. (Figure 79E) Here, it is evident that the pores with diameters of 1.2 and 1.35 nm in steam treated sample have significantly larger volumes than in the CO₂ treated samples. This does support that steam can be utilized to help conserve small pore diameters while increasing the pore volumes of porous carbon products.

If indeed steam is favorable to CO₂ in maintaining small pore diameters while increasing pore volume, this would indicate that as steam samples increased in surface area, so would their total pore volume as compared to CO₂ derived samples. In essence, per unit surface area, steam produced samples would have larger cumulative pore volumes than samples produced using CO₂. Such a comparison is made in Figure 80. It is clear from this data that, per unit surface area, steam derived samples do have larger
cumulative pore volumes than those produced using CO$_2$. This fact only becomes more pronounced as the surface area increases; however, as was mentioned previously, steam derived samples with very large surface areas (~3000 m$^2$/g) suffer from pore breakdown and were therefore not analyzed further. As such, the largest cumulative pore volumes (~1.7 cm$^3$/g) were achieved by the high surface area CO$_2$ derived products (PEEK-CO$_2$-9-80,85). Still, it is apparent that steam is favorable compared to CO$_2$ with regard to maintaining small diameter pores.

However, it should also be noted that in all samples, the major pore population was below a diameter of ~3 nm. Furthermore, several samples even have significant pore populations dominated by pores with diameters ≤1.5 nm, which is well within the ideal microporous diameter range so crucial for optimized H$_2$ storage. This is further supported in Figure 81, which represents a graph mapping the NMR shift corresponding to H$_2$ in micro/mesopores v changing pressure. From previous work$^{[133]}$, we know that a shift that does not change with evolving pressure indicates pores with diameters ≤1.24 nm. Such shifts can be seen in PEEK-CO$_2$-9-1, 26 and PEEK-ST-9-20. (Figure 81) This means that the pore diameters of these samples are primarily at or below ~1.24 nm. This is supported by the fact that, as was previously stated, steam appears to conserve smaller pore diameters than CO$_2$ at higher BO. Again, this likely results from the differences in the mechanism of pore formation between these two methods. Regardless, both methods are able to produce large surface area samples with pore diameters at or below 1.24 nm.
Figure 80 A plot of Cumulative Pore Volume v BET surface area. Per unit surface area, steam derived samples do have larger cumulative pore volumes than those produced using CO$_2$. However, because of pore collapse in steam derived samples, the largest cumulative pore volumes were achieved by the high surface area CO$_2$ derived products (PEEK-CO$_2$-9-80,85).
Figure 81 A plot of the NMR shift corresponding to H₂ in micro/mesopores v. changing pressure. Shifts that do not change with pressure indicate samples having pores with diameters ≤1.24 nm (as in PEEK-CO₂-9-1, 26 and PEEK-ST-9-20). The positive slope corresponding to PEEK-CO₂-9-59 and PEEK–ST-9-35,47 indicates the presence of pores with diameters >1.24 nm.
Figure 82 H₂ gravimetric uptakes v BET Surface Area at 77 K and 0.2 MPa. The H₂ sorption profiles of materials produced using steam and CO₂ are very similar at surface areas up to approximately 1500 m²/g. However, at ~2000 m²/g, the steam derived product displays an obvious advantage compared to the material produced using CO₂. Ultimately, the best gravimetric uptake is demonstrated by PEEK-CO₂-9-80 which achieves 3.7 wt% at a surface area of 3103 m²/g.
The small diameters, large pore volumes and large surface areas of these samples are very impressive among porous carbon materials. Additionally, having both small pores and large surface areas is extremely beneficial for H$_2$ storage applications. Figure 82 shows the H$_2$ gravimetric uptake at 77 K and 0.2 Mpa as it evolves with surface area for samples produced using both steam and CO$_2$. The H$_2$ sorption profiles of these materials are very similar at surface areas up to approximately 1500 m$^2$/g. However, at ~2000 m$^2$/g, the steam derived product displays an obvious advantage compared to the material produced using CO$_2$. As was discussed previously, the main difference between these two samples is that the pore volumes of the smaller diameter pores (1.2, 1.35 nm) are notably larger for steam products as compared to CO$_2$ products. The larger pore volumes, particularly of these smaller diameter pores, seems to play a noteworthy role in the H$_2$ storage capabilities of these materials. However, the ability of CO$_2$ to produce stable samples with large surface areas ultimately overshadows this fact in these samples. Here, these large surface areas (>3000 m$^2$/g) and relatively large pore volumes and small pore diameters combine to produce a sample that has very impressive H$_2$ sorption capabilities; specifically, PEEK-CO$_2$-9-80 which achieves 3.7 wt% at 77 K and 0.2 MPa. Table 3 compares the materials produced here with several other doped and undoped porous carbon products presently being investigated within and outside of the DOE Hydrogen Sorption Center of Excellence. It is apparent from this comparison that the materials investigated in this work are among the most impressive and exciting candidates for H$_2$ storage media. One trend that is particularly interesting is that the gravimetric uptake of these materials outperforms other materials with larger surface areas in many cases. Surface area is a key factor involved with H$_2$ storage, however in the case of these PEEK derived materials it is obvious that other factors are contributing significantly to their H$_2$ sorption profiles. For example, PEEK-CO$_2$-9-80 has a larger H$_2$
Table 3 The materials produced by thermally treating PEEK under different chemical environments have impressive \( \text{H}_2 \) gravimetric and volumetric uptakes compared to other pure and doped carbon materials presently begin investigated. Materials in blue represent \( \text{CO}_2 \) derived products whereas those in red represent steam treated products. Materials being used for comparison are in black. § Note: All \( \text{H}_2 \) gravimetric uptake measurements were done at 0.2 MPa, 77 K unless otherwise specified.

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<tr>
<td>PEEK-CO2-9-80</td>
<td>3103</td>
<td>3.7</td>
<td>26</td>
<td>1.7</td>
</tr>
<tr>
<td>Corncob(^{[136]})</td>
<td>3500</td>
<td>~5 (at 77 K, 20 bar)</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>
| PEEK-CO2-9-59       | 1986                | ~5 (at 77 K, 20 bar)    | >6 (at 100 K, 80 bar)     | NA                                  | 0.94
Figure 83 The excess $H_2$ gravimetric uptake isotherm of PEEK-CO$_2$-9-80 at 77 K. This large surface area material (3103 m$^2$/g) has impressive pore volumes and mostly micropores. As a result of these favorable characteristics, this material demonstrated an exceptionally large $H_2$ gravimetric uptake of 5.29 wt.%. 
gravimetric uptake compared to AX-21 at the same temperature and pressure despite having a smaller surface area by almost 200 m$^2$/g.

Further H$_2$ gravimetric uptake measurements were performed using NMR. Additionally, high-pressure isotherms were achieved for PEEK-CO$_2$-9-80. Figure 83 displays this H$_2$ gravimetric uptake isotherms taken at 77 K. As has been stated previously, this material has an extremely large surface area (3103 m$^2$/g), which is particularly beneficial for achieving large excess H$_2$ gravimetric uptake values. Furthermore, this material has a large cumulative pore volume (>1 cm$^3$) and small pore diameters (≤3 nm). Both of these characteristics are ideal for creating a material optimized for H$_2$ storage. As such, and as is displayed in Figure 83, this material demonstrates an exceptionally large gravimetric uptake, ranging to ~5.3 wt.% at 77 K and 40 bar. This large gravimetric uptake is one of the best of any material presently under investigation by the DOE HSCoE.

It is evident that many factors are very important to the H$_2$ storage capabilities of these materials. In particular, it appears that a balance between surface area, pore volume and pore diameter must be optimized to achieve ideal H$_2$ storage conditions in porous carbon materials.

4.3.4 Summary

Both steam and CO$_2$ treatments were used herein to produce several materials with impressive H$_2$ uptakes, up to ~5.3 wt%. It was discovered that a balance between large surface area (~2000-3000 m$^2$/g), large cumulative pore volume (>1 cm$^3$/g) and small pore diameter (≤3 nm) must be struck in order to achieve the ideal conditions for H$_2$ storage in porous carbon materials. It is hoped that these methods will aid in the directed manufacturing of tailored porous carbon materials for H$_2$ storage applications.
Successfully engineering such materials would represent a major step in the effort to replace conventional non-renewable fuel sources with H₂.

4.4 Summary

After extensive investigation, it was found that most templating procedures were impractical for producing microporous carbons for H₂ storage applications. The synthesis of porous carbons using inorganic templating suffers from dangerous template removal conditions and small surface areas. Organic templating requires relatively narrow growth conditions and also suffers from small surface areas. These limitations resulted in a shift in porous carbon synthesis towards thermal treatment using polymer precursors. The polymer PEEK was shown to produce large surface area products when thermally treated under both CO₂ and steam environments. Also, this process was used to show the differences between these two oxidizers often implemented in carbon activation. Ultimately, it was found that the milder oxidation conditions provided by steam allowed the surface area of the porous carbon products to increase while maintaining the small pore diameters better than CO₂. This is accomplished by increasing the pore volumes as compared to the pore diameters. However, this led to pore wall breakdown at large surface areas. Ultimately, CO₂ was found to produce microporous carbons with large surface areas (>3000 m²/g) and pore volumes (>1 cm³/g). Furthermore, it was found that these samples could be produced while maintaining a relatively small average pore diameter (≤3 nm). Because these characteristics are highly desired for H₂ storage applications, the H₂ storage capacities of these samples were analyzed. It was found that gravimetric H₂ sorption of ~5.3 wt.% was achievable by these large surface area porous carbons. This represents one of the highest H₂ uptakes demonstrated by any carbon to date. As such, this method represents noteworthy progress towards incorporating H₂ into mainstream applications.
5. Summary and Conclusions

The discovery of carbon nanotubes galvanized nanotechnology. With the promise of a new generation of electronics and optics, carbon nanotubes were highly touted and carried a heavy burden. However, in order to realize this potential, several major hurdles in carbon nanotubes synthesis needed to be scaled. Perhaps the two greatest hurdles which stood in the way of their widespread mainstream application were a lack of alignment and a lack of electronic specificity. Controlling the alignment of carbon nanotubes represented the first challenge investigated in this research. In the beginning, high-flowrate carbon nanotube synthesis was conducted with the “fast-heating slow-cooling” method. This method used a convection current to lift the carbon nanotubes off of the surface and suspend them in the laminar flow of the source gasses. Using this method, long (≥1 cm) aligned carbon nanotubes were able to be grown on a variety of substrates. However, these carbon nanotubes were not perfectly aligned, nor was their density very high. Investigation into other methods of producing such aligned carbon nanotubes resulted in two major discoveries. Firstly, aligned carbon nanotubes could be produced from a variety of metal catalysts, as opposed to the short list (Fe, Co, Ni) of metals commonly implemented. Secondly, perfectly aligned carbon nanotubes could be produced on ST-cut quartz. As investigations into this method progressed, it was also discovered that perfectly aligned and very dense (~3-4 SWNT/µm) arrays of carbon nanotubes could be reliably produced. Furthermore, by controlling the size of the metal catalyst, as well as the ratio of EtOH/MeOH/H₂ during synthesis, carbon nanotube arrays comprised almost entirely of semiconducting nanotubes could be produced. It was hypothesized that the MeOH selectively etched the small diameter metallic carbon nanotubes, thus leaving nearly 100% semiconducting carbon nanotubes in these arrays as confirmed by Raman and electronic measurements. The lack of
electronic specificity between semiconducting or metallic carbon nanotubes during synthesis represented the last critical challenge standing in the way of carbon nanotube integration into mainstream technologies. This growth specificity for semiconducting SWNTs has been heavily investigated for many years. Thus, this production method represented a major breakthrough in carbon nanotube synthesis. Additionally, these samples were perfectly aligned, and could therefore be used directly for electronic applications. Further investigation into this selective growth mechanism was needed. In order to investigate the MeOH hypothesis, thiophene was implemented in this growth. The role of the sulfur growth enhancement previously demonstrated in bulk samples involved several theories; however, the true mechanism of this growth enhancement was unclear. Ultimately, it was found that addition of sulfur negated the specificity of this growth mechanism. As such, it was deduced that sulfur helped to stabilize the lower diameter metallic nanotubes which were previously etched by MeOH during growth. This confirmed one of the leading hypotheses involving the origins of sulfur’s growth enhancement as well as confirmed the selective growth mechanism previously stated.

These advancements represented significant progress towards fully realizing the exceptional promise of carbon nanotubes. However, one area in which carbon nanotubes proved impractical for application despite considerable interest was the area of H₂ storage. The present fuel economy stresses an urgent need for alternative fuels, of which H₂ is a leading candidate. After deciding to shift research efforts away from carbon nanotube based H₂ storage, the direction which appeared most promising was the area of microporous carbons. As such, microporous carbon production was attempted with a variety of methods. Initially, inorganic templates were implemented to impart microporous structure to carbon materials. However, removal of this template proved
exceedingly challenging as indicated by surface area measurements and TGA. As such, organically templated porous carbons were investigated. Although scalability of pore diameters was demonstrated using these organic templates, low surface areas and narrow growth conditions led to redirection of efforts away from templated porous carbon synthesis. Ultimately, thermal treatment of the polymer PEEK under CO$_2$ and steam environments allowed for the production of high surface area (>3000 m$^2$/g) porous carbon products with the appropriately small pore diameters (<3 nm) and large pore volumes (>1 cm$^3$/g) necessary for optimal H$_2$ storage in porous carbons. Additionally, this study allowed for the systematic investigation of the roles of CO$_2$ and steam in microporous carbon development. It was found that steam was better at increasing the pore volume and maintaining small pore diameters (≤2 nm) with increasing surface area than was CO$_2$. However, pore wall breakdown at high surface areas in samples produced using steam indicated that it was unfavorable for H$_2$ storage concerns. Ultimately, the sample which displayed the best H$_2$ storage was produced using CO$_2$. This sample had a surface area of ~3103 m$^2$/g and a gravimetric H$_2$ uptake of ~5.3 wt.% at 77 K and 40 bar. This represents one of the largest gravimetric uptakes displayed by any porous carbon to date.

More work needs to be done on both carbon nanotubes and microporous carbons. However, carbon nanotube synthesis has made large strides recently. The advancements achieved during this period has re-ignited the excitement surrounding carbon nanotubes, as the hope for realizing their amazing potential is now significantly closer to a reality than ever before. Furthermore, although carbon nanotubes were not found to be the best materials for H$_2$ storage applications, microporous carbons have demonstrated extraordinary H$_2$ gravimetric uptakes. As such, microporous carbons have distinguished themselves as leading materials for H$_2$ storage applications. Although
further development of these materials is necessary, it is obvious from these results that carbon nanomaterials have enormous potential for revolutionizing a variety of applications and technologies.


Biography

Born:
    July 1st 1981   West Chester, PA

Mother: Marie T. McNicholas
Father: Thomas P. McNicholas Sr.
Sister: Celine M. McNicholas J.D.

2004-2009
Ph.D. Duke University
Major: Chemistry (Nanoscience Certificate)
Advisor: Dr. Jie Liu
Thesis: Directed Synthesis of Carbon Nanomaterials for
        Nanoelectronics and Hydrogen Storage Applications

2000-2004
B.S. Haverford College
Chemistry Major, Mathematics Minor

Research/Teaching Experience

2004-2009
Research Assistant Duke University
Carbon nanotube synthesis and application, including in biosensors, FET’s and other
electronic devices. (E-Beam and Photolithography, Metal Evaporation, CVD, RIE, Critical
Point Drying, SEM, AFM, Raman Spectroscopy, general MEMS/NEMS and
Cleanroom Experience)

Synthesis and characterization of micro/mesoporous carbons for H₂ storage as part of
the DOE Hydrogen Sorption Center of Excellence. (Polymer Synthesis and Activation,
TEM, BET Analysis, UV- VIS-IR Spectroscopy)

2004-2005
Teaching Assistant Duke University
Laboratory Instructor and Recitation Lecturer General Chemistry

2003
Research Assistant Haverford College
Biophysical Research in DNA/RNA templated nanotube/nanostructure synthesis for biocompatible nanodevices. *(AFM, UV-VIS-IR Spectroscopy, Biocompatible Materials Processing)*

**2002**  
Research Assistant NASA’s Jet Propulsion Laboratory  
CO₂ Spectroscopy for the Orbiting Carbon Observatory. *(UV-VIS-IR Spectroscopy)*

**Honors and Awards**

**2006**  
President Phi Lambda Upsilon Chemistry Honors Society Alpha Phi Chapter  
Graduate and Professional Nanoscience Fellowship  

**2005**  
Vice-President Phi Lambda Upsilon Chemistry Honors Society Alpha Phi Chapter  
Graduate and Professional Nanoscience Fellowship

**Publications**


**Representative Presentations**

**December 2009**

**June 2008**

**October 2007**
Oral Presentation “Folic Acid ‘Trojan Horse’ Transport Kinetics and Nanoparticle Surface Plasmon Resonance in Cancerous Cells” PLU Student Lecture Series, Duke University, Durham, NC.

**March 2006**
Oral Presentation “DNA Wrapped Nanotubes for Biosensor Applications” PLU Student Lecture Series, Duke University, Durham, NC.