Date: 6/15/2015

I, Ruitao Su, hereby submit this original work as part of the requirements for the degree of Master of Science in Mechanical Engineering.

It is entitled:
Multi-Field Physics for the Synthesis of Carbon Nanotube Yarn and Sheet

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Multi-Field Physics for the Synthesis of Carbon Nanotube Yarn and Sheet

A Thesis Submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of Master of Science

by

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Abstract

Synthesis of high performance carbon nanotube (CNT) yarn and sheet is a goal for researchers from around the world. A lot of progress has been made in both substrate based and floating catalyst CVD method over past few years. However, no method has produced yarn or sheet that can exceed the properties of carbon fiber materials. Defects reduce the properties of long nanotubes, whereas the short high quality nanotubes are not long enough to produce yarn and sheet with high strength, which limits their practical applications. There is no method to rapidly manufacture cm long high quality nanotubes and form yarn and sheet, and there is a need to more rapidly synthesize nanotubes in the current length ranges of 1-5 mm. The inability to mass-produce at high growth rates and reasonable cost yarn and sheet based on long nanotubes has limited the commercial applications of nanotubes.

Compared to the substrate based growth method, the floating catalyst method for CNT synthesis has a larger yield and the cost is lower. The product of floating catalyst method is usually a CNT cylindrical assembly or sock that can be easily spun into yarns and wrapped to form sheets. However, the length of individual carbon nanotube produced by the floating catalyst method ranges from the micro scale to 1-2 mm, which means a relatively weak inter-molecular interaction has limited the CNT yarn’s strength. Impurities and defects are obvious, which affect the yarn and sheet mechanical and electrical properties. New methods are in demand to produce longer and stronger carbon nanotubes at a high rate at low cost.

Possible solutions to the above issues are investigated in this thesis. One concept is that multi-field physics (using multiple physical fields to control the synthesis process) may allow the catalyst particles to be stabilized or slowed down in the high temperature growth zone in the floating catalyst method. A longer dwell time for the catalyst particles in the growth zone might increase the length of individual carbon nanotubes. An electromagnetic field is an option for the manipulation of the catalyst particles since Fe nanoparticles are magnetic. For example, a magnetic bottle can be employed to trap charged particles in the reactor while carbon precursors are fed into the reaction zone. The catalyst-CNT assembly can be released and collected when long enough carbon nanotubes are synthesized. With an alternating electromagnetic field, the catalyst particles/nanotubes might be oscillated at a resonant frequency so that the amorphous carbon would be prevented from coating and deactivating the catalyst. During the experiments, a 100 V-60 Hertz AC voltage was measured on the CNT sock assembly. The voltage is believed to come from the electromagnetic induction between the magnetic field generated by the furnace used for the synthesis and the conductive CNT assembly. The voltage indicates the feasibility of magnetic manipulation of the charged particles and sock in the reactor. Moreover, an electrostatic spray system was developed and installed on the reactor to generate better spray patterns and electrically charge catalyst particles, which are expected to be controlled by an electric or magnetic field for purer, straighter and long CNT growth. In addition to physical methods, new chemical recipes play a critical role in high
quality CNT synthesis. For example, water and gadolinium salts are being tested for purification and increased CNT length. The concept of multi-field synthesis and initial experimental work to produce the multi-physics reactor are the main contributions of this thesis. This thesis has been an interdisciplinary effort that lays the path for possibly producing high performance carbon nanotube materials using the gas phase pyrolysis method.
Acknowledgement

Most of the work described in this thesis was conducted together with graduate student Guangfeng Hou, Anli Wang, Lab director Dr. Schulz and post doctor Weifeng Li. Guangfeng did a simulation of gas flow pattern inside the reaction tube which agreed well with video recorded during experiments. He also contributed creative ideas in the design of stable fuel sprayers. Anli did most of the mechanical and electric characterization of the CNT yarns and sheets. The multi-field physics floating catalyst CVD reactor with electrostatic spray and RF manipulating coils were designed and built up by professors and graduate students in Nanoworld Lab. A lot of guidance regarding reactor design and chemical recipe was received from Nanoworld Lab co-director Dr. Shanov. Dr. David Lashmore of the University of New Hampshire provided much advice and guidance on developing and tuning the floating catalyst reactor including important guidance on designing the reactor for safety. Dr. Mast from Physics Department in UC provide very helpful guidance regarding magnetic field control and RF integration with CVD process. Graduate student Rachit in Nanoworld Lab helped with the TGA characterization of the CNT products from this reactor. Post Doctor Albert Song’s test with carbon nanotube sheet was helpful for the firefighter apparel application.

I would like to thank all the people mentioned above for their help and encouragement during this research. Multi-field physics approach for carbon nanotube growth is a very inter-disciplinary and cooperative research. Experimental and theoretical exploration described in this thesis could not have been done so well without a good teamwork. A special gratitude should be given to Guangfeng and Dr. Schulz. They showed me the importance of patience, hardworking and taking the details serious in a scientific research. What I have learned from them is not only how to conduct a high quality research, but also how to take care my teammates and create a motivating atmosphere in the team.

I would also like to thank my families and friends who have always been encouraging me to pursuit what I am interested in doing. All the support I receive from them is the most valuable gift I could ever have.
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Chapter 1 Introduction to Carbon Nanotube Synthesis

The motivation for human beings to look for stronger and more versatile carbon materials has been around for a few hundred years. The first synthesis of carbon filament for practical purpose is by Edison in 1892, when he invented a carbon coil from pyrolysis of bamboo fibers that was used in one of his incandescent light bulbs [1], [2]. Graphite whiskers synthesized by the National Carbon Company research lab was great progress in controlled structural carbon material synthesis [3]. The chemical vapor deposition (CVD) method was proposed as a vapor phase synthesis method for carbon filaments in the 1960’s [4]. During these early attempts at carbon fiber/filaments synthesis, some micro-sized tubules were observed. The discovery of C_{60} led to the hypothesis that there might be a one dimensional structure of carbon atoms at the nano scale as well. It is the experimental discovery of carbon nanotube (CNT) Iijima in 1991 that confirmed this hypothesis and gave rise to huge research interest in CNT thereafter [5]. So far, the synthesis methods of carbon nanotubes mainly include arc discharge, laser ablation, floating catalyst (also called gas phase pyrolysis) and chemical vapor deposition (CVD) [6]–[9]. The gas phase pyrolysis or floating catalyst method is reported in this thesis.

1.1 The Chemical Vapor Deposition (CVD) Method

Researchers had been using vapor for growing carbon fibers (VGCFs) for quite a while before it evolved into the so-called CVD method today. [10] VGCF usually uses hydrocarbons as carbon atom suppliers and catalyst as well as reaction promoter suppliers. It was usually conducted under a temperature range of 800-1200°C. VGCF was widely commercialized because of its mass-production capability. In the CVD method, the basic concept of vapor phase growth was adopted. There are many different types of CVD methods for CNT synthesis, including thermal CVD, laser-assisted CVD and plasma-assisted CVD [11]–[13]. Different CVD methods are identified by the energy sources for the decomposition of precursors and how the catalyst particles are provided. If the hydrocarbon precursors are decomposed under a high temperature condition, the reaction is called thermal CVD; if a laser is used to help decompose and enable the reaction, it is called laser-assisted CVD; if plasma is used to decompose the carbon hydrates and enable the reaction, it is called plasma-assisted CVD [14]–[17].

Other variations of the CVD method can also be proposed by adjusting other synthesis conditions. For example, water-assisted thermal CVD was tried in the Nanoworld Lab and a 21.7 mm vertical aligned CNT array was grown in 2007. Water was reported to play a role of extending the lifetime of active catalyst particles [18].
In a common CVD process, carbon atoms containing precursors, which are hydrocarbons in most cases, are introduced into the reaction zone, where these hydrocarbons will decompose into carbon atoms caused by various conditions, as noted above. The free carbon atoms will combine with the local catalyst particles, iron or nickel typically, and grow into carbon nanotubes. The role of catalyst particles is to stabilize carbon atoms and accumulate enough of them for crystalline growth.

In the substrate-based CVD method, the catalyst particles are generated on a silicon substrate that is prepared by the photolithography method [19]. The pre-deposited catalyst layer will melt and shrink into nano-scale particles during the reaction. Under the high temperature reaction condition or other high-energy fields induced by laser or plasma, the carbon precursors introduced into the furnace will decompose into carbon species, which will then be absorbed onto the catalyst surface/volume. With the accumulation of carbon in the catalyst particles, carbon nanotubes start growing out of the substrate. Shown in Fig. 1.1 is a CNT array synthesized in the Nanoworld Lab in 2006 by the thermal substrate based CVD method [20]. Currently, carbon nanotube researchers have a general idea of the CNT growth process but not a clear and verified schematic plot yet which explains the whole CNT growth process. Most of the research is based on a trial-explanation-modification model.

![Fig. 1.1. The CNT forest synthesized in Nanoworld Lab. left, CNT forest with a length of 4mm; right, SEM image (scale bar length is 200 nm) [20].](image)

The growth process of carbon nanotubes in the substrate-based thermal CVD method has been simulated numerically and good understanding of the growing process has been achieved [21]. According to the research of Dr. Maschmann, individually grown CNTs are bonded together by Van de Wall’s force into a CNT forest. By finite element method (FEM) simulation, as shown in Fig. 1.2, the Van der Wall’s interaction between the tubes was found to decrease with the distance from the substrate and to be proportional to the bending rigidity of the CNT.
1.2 The Floating Catalyst Method

The first employment of floating catalyst method in CNT synthesis was by researchers from Tsinghua University while trying to grow carbon nanofibers using the floating catalyst method [22]. Several important parameters of floating catalyst methods were discussed in this research. In the floating catalyst CVD method, catalyst is provided by metal atoms within chemicals that decompose in the reaction zone. The catalyst atoms produced during this process self-assemble into nano-scale particles that travel through the reactor and have carbon nanotubes nucleate on them with the deposition of carbon atoms from hydrocarbon precursors [23]. Ferrocene is usually used as the chemical to provide iron catalyst particles and sulfur as the reaction promoter [24], [25].

Compared to the substrate CVD method, the floating catalyst method has the advantage of high yield and material efficiency, and continuous production. It inherits the advantage of the VGCF method. Therefore the floating catalyst method has a better chance for industrialization. However, the individual carbon nanotubes synthesized by the floating catalyst method are not very long, with a maximum length of 2 mm so far reported by Nano Comp. [26] This is probably due to the short growth time and more turbulent growth environment caused by complex flow field.

The floating catalyst CVD method for the production of carbon nanotubes is currently being investigated by several groups in the world. A group led by Dr. Koziol from the University of Cambridge made spinnable CNT products that came out of the reactor as a continuous hollow CNT cylinder. The CNT cylinder can be shrunk into threads/wires that have a high Raman G/D ratio, as high as 33. [27] The spun CNT thread has potential application as a new material for electrical conduction because of its high conductivity and low crystal defects. It is claimed to be employed for the next generation of super conductive wires.
Another group led by Dr. Wang that focuses on the floating catalyst method from Huadong University of Science and Technology in Shanghai made a record for the strength and conductivity of CNT thread. A similar CNT hollow cylinder was synthesized from the floating catalyst method. The fiber spun from the CNT cylinder has a tensile strength of 4-5 GPa and electricity conductivity at the order of $10^3$ S/cm. A good practical application prospect of CNT thread made from the floating catalyst method is demonstrated. [28]

Nanoworld lab in the University of Cincinnati started the research in floating catalyst method in August of 2014, and quick progress was made in September 2014 when a continuous CNT cylinder was produced from a reactor that was custom designed and assembled by professors and students in the lab. The production of a spinnable CNT cylinder was stably repeated. Different recipes and parameters have been tested for the production of optimized CNT thread. Effort and time were devoted to improve the reactor for better observation, operation, security and efficiency. For example, a glove box was installed to make the synthesis safe and easy to observe, a variation of fuel injection method are being test for more efficient fuel spray. There is still a lot of room for improvement of the product properties. Other physical methods, such as electromagnetic fields, are being applied to the reactor for improved properties. This thesis is basically based on the work done with this reactor, including mainly the hardware design and assembly, chemical recipes tests and multi field physical implementation. This work is done together with another graduate student in Nanoworld Lab, Guangfeng Hou. A lot of help was received from lab director Dr. Mark Schulz and Dr. Vesselin Shanov, post Doctor Weifeng Li and Professor Mast from Physics Department of the University of Cincinnati.

From a material science perspective, to improve the tensile strength and electrical conductivity of CNT thread, there are two directions to go. The first one is to increase the length of individual CNT because the covalent bonding between carbon atoms is much stronger than van der Wall’s interaction between CNT molecules. Longer individual carbon nanotubes mean that there is a significant increase in the force holding bundles of nanotubes together. This will be reflected as super strong CNT yarn and sheet at the macro scale. In addition, longer individual carbon nanotubes also enhance the yarn and sheets’ electrical and thermal conductivity by reducing the electrons’ transport resistance [29]. The second direction is to improve the purity of the CNT crystal structure, which means to reduce the defects in the structure and reduce the electrical conduction band gap. The impurities of carbon nanotubes include the remnant iron particles, sulfur concentration, amorphous carbon accumulation, and crystalline defects. Addition of other chemicals such as water and gadolinium salt, and tuning the reaction parameters such as temperature and carrier gas flow rate can help reduce the impurities.

Since the first successful synthesis of CNT aerogel sock-like material at the University of Cincinnati (UC), with ferrocene being the catalyst provider and thiophene being the reaction promoter, different
carbon precursors have been tried. Contrary to what other groups have reported, ethanol, butanol and toluene didn’t produce continuous CNT assemblies. A combination of methanol (90% by volume) and hexane (10% by volume) was discovered as the fundamental fuel recipe for producing continuous CNT assemblies. The reaction parameters, including argon flow rate, temperature, fuel injection location and rate, are being tuned to generate the optimized synthesis result. Besides the chemical recipes and reactor parameters being tested for the CNT synthesis, a multi-physics method is also being tried to control the reaction process directly. Electromagnetic levitation of catalysts particles, RF heating, and multi-field holding of catalysts particles are being added to the reactor to gain closer control over the synthesis process.

1.3 Patent Survey

Patents related to nanotechnology are classified as class 977 in the United States of which carbon nanotube related patents are one major section. Patents relevant to carbon nanotubes can be categorized into three major groups: synthesis patents, post processing patents, and application patents [30]. Application related patents account for the majority of the carbon nanotube patents. Below the synthesis related patents are investigated.

The first carbon nanotube synthesis invention was a patent by Iijima from NEC in 1991 for discovering and synthesizing multiwall carbon nanotubes (MWCNT) [31]. In his patent, he claimed the discovery of a graphite filament that has similar structure to graphite except that the filament has a tubular structure. The filament has a maximum outer diameter of 30 nm and inter-wall interval of 0.34 nm. The method used to produce the filament is arc discharge. Two carbon electrodes were employed and placed under a low-pressure inert gas environment. A DC current was conducted through the electrodes for a certain period of time and the MWCNT/tubular carbon filaments were produced. Then in 1993, some researchers from IBM patented the technique of producing SWCNT. [32] They claimed the discovery and synthesis method of a tubular carbon fiber consisting of a single layer of carbon atoms (namely SWCNT). The fiber has a length over 100 nm and was produced by the arc discharge method too. Carbon precursors and catalyst cobalt were vaporized by electric arc heating under an inert gas condition and carbon fibers formed by attaching to the wall of the reaction chamber. The carbon nanotube was found to have a diameter ranging from 1.5 nm to 3.5 nm.

There has also been an attempt to grow carbon nanotubes with the assistance of an electric field. Stebbins et al tried to integrate circuitry into the substrate on which the CNT grow [33]. The substrate is made of a wafer embedded with a CNT catalyst sites matrix. This catalyst matrix was configured with the mentioned circuitry in such a manner that each site is charged electrically. Combined with a set of temperature, pressure and environmental gas parameters, the static charge on the site, later transferred to the carbon
nanotubes grown on the site, can help reduce the bending of the CNT arrays and keep the CNT straight. A multi-physical field integration, electromagnetic field and acoustic field, is also proposed in this thesis and some preliminary experiments were conducted, as described in Chapter 3 and Chapter 7.

The method of introducing fuel and catalysts into the reactor is always a key factor in the floating catalyst method. An interesting method was patented in 2012 by Khodadadi et al [34]. The working mechanism is described in Fig. 1.3. Ferrocene is sublimed and introduced into the reactor through a pipe kept at 400 °C. An annular tube was used to mix the sublimed catalyst and fuel more homogeneously. Fe and MgO were used together as the catalysts and methane as the carbon precursor. The well-mixed reaction agents went through the reaction zone and a continuous CNT product was collected from the bottom of the reaction tube. Under a reaction temperature of 900 °C, both SWCNT and MWCNT were detected in the product. From the Raman spectrum, the SWCNT has a diameter around 1 nm and the MWCNT has a maximum diameter of 20 nm. The G/D ratio can be as high as 10.2. This proved that a better fuel-catalyst introduction and mixture method is vital for the production of high quality and quantity carbon nanotubes.
A patent published in 2014 tried to solve the problem of coking of Fe catalyst particles during the reaction with hydrocarbons[35]. A two tube furnace was employed to conduct the synthesis. Fe and Al catalyst precursors were introduced into the first reaction tube and formed an alloy particle aerosol. The function of metal Fe is to act as a catalyst and crack hydrocarbons for the growth of carbon nanotubes. Even though metal Al doesn’t play any catalytic role during the synthesis, its existence was proven to be able to save Fe from being choked by carbon atoms from the hydrocarbons. Possibly, Al plays this role by dividing the Fe domain into smaller domains. Mixed with H₂, this alloy particle aerosol was then introduced into the second reaction tube where it was mixed with hydrocarbons. It was in the second reaction tube that the carbon nanotubes were grown. The alloy-CNT structure then was washed by acid, such as nitric acid, to release CNT from the alloy particles. Fig. 1.4 shows the SEM image of the carbon nanotube grown from the free floating alloy particles.
Another key technique in the floating catalyst method is the method for fuel introduction. The simplest one can be to use a metal needle to deliver the fuel into the reaction zone. However, the needle can be easily clogged by the precipitated catalyst precursors and carbon atoms from hydrocarbon decomposition. In addition, this delivery method is very sensitive to the needle tip location as described in Chapter 5 and Chapter 6. An ideal fuel introduction method is one that can spray the fuel into the reaction tube in a fine mist format so that the fuel can evaporate immediately as it enters the high temperature zone. This requires the sprayer to be located at a relatively cool spot and spray the fuel with a low carrier gas flow rate. A patent by Dr. Lashmore et al published in 2009 reported a sophisticated sprayer that achieved fine spray and chemical reaction process control [36]. The sprayer basically was made up of two parts. One is a nebulizer that sprays out the fuel together with H₂ or N₂ gas. The design of the nebulizer is a venturi structure that sprays the fuel into a fine mist based on fluid dynamics principles. The second part is a temperature control tube that is surrounded by heating elements and thermal insulation. The constant temperature environment within the tube ensured the evaporation and decomposition of carbon precursors. Once the decomposed precursors enter the reaction tube, which is connected to the sprayer, and are mixed with catalyst particles, carbon nanotube started growing.
Chapter 2 Electromagnetics and Coils

Electromagnetics is studied as a possible auxiliary approach to affect the nucleation and growth of carbon nanotubes. To produce the longest individual CNT by the floating catalyst method, the main idea is to utilize the multi-field physics approach. It was proposed to stabilize the catalyst particles in the high temperature reaction zone for a longer dwell time. Since the catalyst particles employed in this experiment are Fe nanoparticles, their ferromagnetic property makes it possible for groups of particles to be slowed down or stabilized by an externally applied magnetic field. A static magnetic force can’t be used for this purpose since the particles will be dragged to the maximum gradient point in the field. Instead, an oscillating electromagnetic field might keep the particles relatively stable with the correct magnitude and field flux distribution. This Oscillating magnetic field was attempted to be generated by either permanent magnets vibrated mechanically, as shown in Fig. 2.1, or by electromagnets that can be switched on and off alternatively, as shown in Fig. 2.2. Before this hypothesis can be tested on the furnace, bench tests were conducted to check its feasibility.

2.1 Test with Permanent Magnets

As shown in Fig. 2.3, two rare earth element permanent magnets with a near pole flux density of 0.5 Tesla are employed for this test. They are fixed in a plastic foam frame with a nano particle-containing capsule.
placed between them. The nano particles are ferromagnetic Fe₃O₄ particles with a dimension around 20 nm. The plastic foam frame is fixed to the wall by springs of a certain stiffness. The system is a mass-spring system that vibrates with a tunable frequency.

The nanoparticle capsule was fixed at the middle of the two magnetic poles. An initial displacement was given to the foam frame that held the magnets. Once released, the system started vibrating with a frequency determined by the mass of the system (m) and stiffness (k) of the springs based on the mass-spring-damper system equation:

\[ f = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \]

The setup of the test system is shown in Fig. 2.4.

Since it was difficult to place the particles right at the center of the gap where the particles are at an unstable equilibrium state, most of the particles would tend to attracted to one side of the magnetic field and the rest to the other. Once the magnets started vibrating at a certain frequency, the nanoparticles
would start shaking in the capsule too at the same frequency. However, the particles kept agglomerating together even though they would be broken into parts temporarily. This setup could shake the particles but was not able to stabilize the particles at a fixed spot in the gap. A higher vibration frequency far beyond what this system can realize is probably needed for the stabilization and levitation of the nanoparticles. Mechanical shaking of permanent magnets is not a feasible method since the usual frequency from the RF coils are at the range of MHz.

2.2 Forming Electromagnets
To generate a strong enough alternating magnetic field with the oscillation frequency high enough, several electromagnets were made in the Nanoworld Lab, among which the largest one by volume is shown in Fig. 2.5. The dimensions of the silicon steel core are listed in Table 2.1.

![Image](image.png)

*Fig. 2.5. Right: Electromagnet made in Nanoworld Lab; Left: dimension of the silicon steel core*

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Height</th>
<th>Width</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D = 80$ mm</td>
<td>$2E + G = 280$ mm</td>
<td>$3F = 192$ mm</td>
</tr>
</tbody>
</table>

To make the electromagnet, 5 layers copper coils with an insulating coating were wrapped on the cores. Adhesive tape was attached to the coils to fix the coils together. When the fabrication was finished, four wires were used to connect the power source. Once the two half electromagnets were connected to the power source, a strong magnetic field was generated in the gap between the two C-cores. To stop the cores being attracted to each other by the significant magnetic force, one gap of the electromagnet is held by 4 low carbon steel patches, which have a thickness of 6 mm each. The other gap is left open for the characterization of the electromagnet other relevant tests. A set of charge-discharge tests was conducted on the electromagnet. The current-B curves were recorded in both upward and downward cases. A gauss meter was employed to measure the flux density B.
According to classic electromagnetic theory, the magnetic flux density $B$ that can be generated inside a coil is determined by the following equation:

$$B = \mu \frac{NI}{L}$$

where $\mu$ is the magnetic permeability of the core material, $N$ is the total number of the coils turns, and $L$ is the length covered by the coils. The gap between the two cores was controlled at fixed values. Data collected from the tests are listed in Table 2.2, Table 2.3 and Table 2.4, and a hysteresis curve was plotted based on these data, as shown in Fig. 2.6.

### Table 2.2. Gap $l=6.34\text{mm}$.

<table>
<thead>
<tr>
<th>$I_{coil}(A)$ current ↑</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>5.0</th>
<th>5.5</th>
<th>6.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(mT)</td>
<td>0</td>
<td>82.8</td>
<td>168.3</td>
<td>236.1</td>
<td>332</td>
<td>415</td>
<td>488</td>
<td>593</td>
<td>672</td>
<td>758</td>
<td>848</td>
<td>915</td>
<td>950</td>
</tr>
<tr>
<td>$I_{coil}(A)$ current ↓</td>
<td>6.0</td>
<td>5.5</td>
<td>5.0</td>
<td>4.5</td>
<td>4.0</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>B(mT)</td>
<td>950</td>
<td>925</td>
<td>859</td>
<td>774</td>
<td>699</td>
<td>598</td>
<td>514</td>
<td>432</td>
<td>345</td>
<td>257.1</td>
<td>179</td>
<td>86.4</td>
<td>1.0</td>
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</table>

### Table 2.3. Gap $l=12.64\text{mm}$.

<table>
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<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
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<th>5.0</th>
<th>5.5</th>
<th>6.0</th>
</tr>
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<tbody>
<tr>
<td>B(mT)</td>
<td>0</td>
<td>43.9</td>
<td>80.7</td>
<td>122.2</td>
<td>164.2</td>
<td>206.9</td>
<td>247.7</td>
<td>296</td>
<td>340</td>
<td>367</td>
<td>424</td>
<td>469</td>
<td>508</td>
</tr>
<tr>
<td>$I_{coil}(A)$ current ↓</td>
<td>6.0</td>
<td>5.5</td>
<td>5.0</td>
<td>4.5</td>
<td>4.0</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>B(mT)</td>
<td>508</td>
<td>466</td>
<td>429</td>
<td>384</td>
<td>341</td>
<td>299</td>
<td>255.5</td>
<td>212.9</td>
<td>166.5</td>
<td>126.7</td>
<td>85.7</td>
<td>41.9</td>
<td>.8</td>
</tr>
</tbody>
</table>

### Table 2.4. Gap $l=22.38\text{mm}$.

<table>
<thead>
<tr>
<th>$I_{coil}(A)$ current ↑</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>5.0</th>
<th>5.5</th>
<th>6.0</th>
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<td>49.6</td>
<td>79.0</td>
<td>105.2</td>
<td>129.5</td>
<td>159.8</td>
<td>187.4</td>
<td>218.6</td>
<td>241.5</td>
<td>270.2</td>
<td>297</td>
<td>327</td>
</tr>
<tr>
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<td>6.0</td>
<td>5.5</td>
<td>5.0</td>
<td>4.5</td>
<td>4.0</td>
<td>3.5</td>
<td>3.0</td>
<td>2.5</td>
<td>2.0</td>
<td>1.5</td>
<td>1.0</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>B(mT)</td>
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<td>296</td>
<td>272.5</td>
<td>244.5</td>
<td>219.4</td>
<td>189.3</td>
<td>162.1</td>
<td>135.7</td>
<td>108.5</td>
<td>80.1</td>
<td>53.6</td>
<td>27.35</td>
<td>.4</td>
</tr>
</tbody>
</table>
It could be concluded from Fig. 2.6 that during the charge and discharge cycle, the B-I curve basically overlaps, which means that there wasn’t much magnetic hysteresis during this process. This is because the silicon steel core used in the electromagnet has a relatively soft magnetization, which is beneficial for the generation of a high frequency oscillating magnetic field. It was also noticed that the gap distance \( l \) has a large effect on the magnitude of the flux density. The smaller the gap is, the larger the flux density. Therefore, it is preferable to keep the distance as small as possible in order to generate a large enough magnetic flux density.

In the following experiments, it was discovered that a uniform alternating magnetic field is not sufficient to levitate the magnetic nanoparticles. A field gradient is necessary to have the particles be attracted to the magnetic poles. Therefore, other ‘nail electromagnets’ were formed to generate field gradients with sharp tips.

2.3 Suspension of Catalyst Particles with a Switching Magnetic Field

As discussed in section 2.2, with the electromagnets built in Nanoworld Lab, a switching uniform magnetic field with high flux density can be generated between the two silicon steel cores. To create a non-uniform magnetic field in the gap, an asymmetric layout was tried, as shown in Fig. 2.7. In the symmetrical layout, the magnetic field is almost uniform since the core makes a closed loop. In the asymmetric layout, a non-uniform field was expected to be generated since only one half of the magnets will be charged with current at a given time point. The plastic capsule that contained the catalyst nanoparticles was fixed in the gap.
However, during the experiments, the behavior of nanoparticles in both cases was very similar to that of the nanoparticles between mechanically vibrating magnets. A magnetic field sensor was used to map the field distribution in the gap and it was found that the magnetic field in the gap is still very uniform even with the asymmetric magnetic layouts. The other problem with this setup is that the magnetic hysteresis of the electromagnet made it difficult to raise the oscillating frequency of the magnetic field since the remnant magnetic field will counteract the present field and reduces the efficiency of the system.

Two ‘nail electromagnets’ with pointed tips were made and tested with nanoparticles, as shown in Fig. 2.8. The pointed tips were designed to generate a non-uniform magnetic field so that the gradient of the field can stabilize the nanoparticles. This experiment was conducted with both water and air, where the nanoparticles are immersed. The Fe₃O₄ nanoparticles are contained in small glass jars that are placed between the nails.

As shown in Fig. 2.9, the electric circuit consists of a DC power supply, a signal generator, a 9V battery, a breadboard, a transistor, two relays and two nail electromagnets.
This circuit is made up of three loops. The first and the second are connected via a transistor, and the second and the third are connected via a relay. The square signal generated by a signal generator in the first loop controls the relay in the second loop through the transistor. The on/off state of the relay in the second loop controls the nail electromagnets in the third loop. Every time the electromagnet switches, the magnetic field between the nail tips will change direction. So by adjusting the frequency of the square pulse, the magnetic field switching rate can be tuned. Two different samples were tested under the above alternating magnetic field. The first sample is the magnetic nanoparticles contained in an empty jar. The other sample is the particles contained in jar filled with water, as shown in Fig. 2.10.

The relay used in this experiment was switching at a frequency of 5-20 Hz, which means that the magnetic field between the tips is oscillating at the same frequency. Positive results were obtained from the test and the nanoparticles are nearly levitated in water or against the inner surface of the jar in air.
In the water media, the particles travel between the two magnetic poles more slowly and in a shorter distance. In addition, the particles tend to be suspended in the center of the jar. This is because water, a medium that has more damping force, slows down the motion of the particles and stabilizes the particles within a certain space. Whereas in the empty jar case, particles tend to attach to the wall of the jar and move back and forth between the poles in a more faster frequency and within a bigger distance. Therefore, it is easier to suspend the particles in a liquid medium.

Dr. Lashmore of the University of New Hampshire suggested the particles be dissolved in an anionic surfactant to keep them from clumping as the magnetic characteristics of clumps are different from small particles. In an actual synthesis process, this high frequency vibration of catalyst particles is expected to improve the reaction because this may shake off amorphous carbon that can otherwise coat and deactivate the catalyst particles. Vibration of the particle may also increase diffusion of carbon atoms to the catalyst particle. While floating down the reactor, the catalyst particle may become starved locally of carbon. To implement this test result to the nanotube reactor, one major problem is to find an effective field or condition that can replace the water in the test since the reaction tube cannot be filled with liquid. A slow gas flow rate and a high reaction temperature can be helpful.

2.4 Testing CNT Samples under a RF Field

Another concept for the levitation of the magnetic nanoparticles is to use high frequency (MHz) electromagnetic oscillation. Carbon nanotube loops of different shapes are placed inside of coils made of hollow copper pipes through which high frequency AC was conducted. Since the generation of a high frequency magnetic field creates a lot of heat, the hollow pipe can run cooling water through. The electric
circuit of this test is sketched in Fig. 2.11(a). Fig. 2.11(b) shows the structure of the coil and how it was mounted inside of the test box. Three pieces of metal panel were mounted around the coil for EM shielding.

The signal is applied by a function generator that was connected to the coil through a tuner. The coil is connected to a variable capacitor so that the reflected power can be adjusted to a minimum. The frequency of signal applied is 13.56 MHz. In the first step of the RF test, metal particles were tried. Plastic capsules that contain silver, copper, liquid metal (In+Ga), and magnetic particles were placed inside of the coil respectively. No particles were levitated during the experiments. Metal particles became hot after sitting in the RF field for a few minutes and the plastic capsule that housed the metal was melted, which proved that eddy currents had been generated in the metal. Fig. 2.12 shows how the sample was placed inside of the coil. The experiment was performed under the guidance of Dr. David Mast.
The next step was to use carbon nanotubes as test samples. CNT circles made by Dr. Weifeng Li were tested under the same condition. No levitation was observed either. The plastic capsule containing the CNT sample was melted too, which means that there is a current induced by the RF field going through the CNT loops, as shown in Fig. 2.13. Even though the CNT samples were not levitated, this is still an exciting result, because the generation of eddy current in the CNT sample is a big step toward the goal of levitation.

Based on the above results, the following tests are proposed to be conducted in the future:

(a) Increase the RF Frequency
Since obvious eddy current was generated at 13.56 MHz, levitation is expected to happen at higher frequency and power. Therefore, frequency should be increased within the tolerance of the equipment. The optimal levitation frequency should generate the largest eddy current in the samples.
(b) Samples with variable shapes to be tested
Different shapes of CNT samples should also be tested to mimic the configuration of CNT grown in the reactor. These samples include: single and double CNT loops, CNT ring made from CNT sheet, randomly oriented CNT ball and CNT post, as shown in Fig. 2.14.

![Different Test Samples](image)

Fig. 2.14. Different Test Samples.

(c) Achieve a stable equilibrium state (advised by Dr. Mast)
According to Earnshaw’s theorem, for CNT or catalyst particles to achieve a stable equilibrium state in the electromagnetic field, a solely electromagnetic interaction with the inducted eddy current inside of the particles is not sufficient. Mathematically, forces provided by other fields are necessary to cooperate with the magnetic force to realize the levitation, as shown in Fig. 2.15.

![Magnetic gradient levitation of catalyst nanoparticles](image)

Fig. 2.15. Magnetic gradient levitation of catalyst nanoparticles.

In a floating catalyst reactor, the forces exerted on the catalyst particles as well as the CNT assembly include gravitational force, thermal force caused by the thermal gradient in the radius direction, and the flow drag force. The multi-force field in the reactor may be employed together with an electromagnetic
field to realize stabilization of catalyst particles. The flow drag force applied to the particles is determined by parameters such as temperature and gas pressure. The thermal gradient force is determined by the reaction temperature in the reactor and the tube dimension. Therefore, the overall parameters of the reaction need to be taken into consideration for the optimized effect.

On the other hand, the material of the catalyst particles also has an effect on the levitation. Fe particles will lose their ferromagnetic property above 1100 °C. Cobalt has a good magnetic property even at that high temperature. However, its severe toxicity needs to be dealt with cautiously. Permalloy can be another good option thanks to its good magnetic property at high temperature.

The ultimate goal of the RF and electromagnetic research is to slow down or stabilize the CNT assembly during the growth so that a longer dwell in the sweet spot can be achieved. Moreover, the electromagnetic field may oscillate the catalyst particles and CNT assembly so that the catalyst won’t have an amorphous carbon coating. A longer active synthesis time of catalyst particles can also produce longer individual carbon nanotubes. The function of the electromagnetic field is accompanied by the thermal and flow drag force. This is why the floating catalyst reactor developed in Nanoworld Lab is named a Multi-filed Physics reactor. Fig. 2.16 shows the basic mechanism of the EM levitation.

![Fig. 2.16: RF trap of CNT sock in floating catalyst method. The coil may also be inside the reactor.](image)

A listing of ways to levitate objects is below.

a) Repulsion between like poles of permanent magnets or electromagnets. However, there needs to be a way to constrain the magnets so they don't flip over and become attracted to each other. For example, floating donut magnets have the dowel rod in the center to keep them from flipping over. Catalyst particles would need to be magnetic at high temperature.

b) Repulsion between a magnet and a metallic conductor induced by relative motion. However, the magnet needs to be restrained from moving in the same direction as the conductor, otherwise it will travel with the conductor.
c) Repulsion between a metallic conductor and an AC electromagnet. It is possible to shape the magnetic field to keep the conductor constrained in its motions, otherwise, a mechanical means is needed to keep the conductor in place. This is called electromagnetic induction.

d) Repulsion between a magnetic field and a diamagnetic substance. This is the case of the floating frog, and the floating magnet between two diamagnetic disks. Pyrolitic carbon, water, and bismuth can also be floated above strong magnets or electromagnets by direct repulsion.

e) Repulsion between a magnet and a superconductor. No mechanical constraints are needed for this.

f) Attraction between unlike poles of permanent magnets or electromagnets. This will work as long as there is a mechanical method to constrain the magnets so they don't touch.

g) Attraction between the open core of an electromagnetic solenoid and a piece of iron or a magnet. The iron or magnet will touch the inside surface of the solenoid.

h) Attraction between a permanent magnet or electromagnet and a piece of iron. Again, the iron needs to be constrained.

i) Attraction between an electromagnet and a piece of iron or a magnet, with sensors and active control of the current to the electromagnet used to maintain some distance between them.

j) Repulsion between and electromagnet and a magnet, with sensors and active control of the current to the electromagnet used to maintain some distance between them.

k) A Halbach Array Electromagnet to produce high magnetic flux density to oppose CNT diamagnetism.

2.5 Diamagnetic Levitation Hypothesis

Diamagnetism is a property where an object tends to repel either magnetic pole that is close to it. Diamagnetic susceptibility is the physical quantity that is used to measure the degree of diamagnetism of a material. Some common materials and their diamagnetic susceptibility are listed in Table 2.5. Pyrolytic graphite is a highly laminar structured graphite synthesized by the high temperature CVD method and it has a very good diamagnetic susceptibility in the direction perpendicular to the main surface. Therefore, it is possible to levitate pyrolytic graphite with permanent magnets. In fact, it was reported that biological material, such as a frog, can also be levitated with a strong enough magnetic field [37]. Pyrolytic graphite has a smaller resistivity than carbon nanotubes, therefore theoretically it should be easier to levitate pyrolytic graphite.
Based on the above stated facts, it was considered to grow long carbon nanotubes by the diamagnetic levitation of pyrolytic graphite. A patch of pyrolytic graphite could be used as a ‘flying’ substrate on which the catalyst particles are deposited. The pyrolytic graphite is then placed in the high temperature reaction zone of the multi-field physics CVD reactor. A cooled permanent magnet or electromagnet is mounted inside of the furnace right below the pyrolytic graphite which will then be levitated. Fed with carrier gas and carbon precursor, long carbon nanotubes are anticipated to be grown on the pyrolytic graphite because of the long dwell time in the high temperature reaction zone. The tip growth method could allow the nanotube to be suspended in the flow. The magnet can be tilted with a small angle so that the flow dragging force won’t take the graphite to the outlet of the reactor during the synthesis. Shaking the graphite can also be achieved by vibrating the magnet mechanically. A sketch of this idea is shown in Fig. 2.18.
Fig. 2.18. Using pyrolysis graphite to levitate carbon nanotubes.
Chapter 3 Multi-field Physics Reactor Design

The multi-field physics reactor in Nanoworld Lab was built up from a basic tubing furnace platform that was inherited from previous graduate student Pravahan Salunke who was trying to synthesis graphene with it. Therefore, some modification and major parts was needed for CNT synthesis and the realization of automatic control.

3.1 Floating Catalyst Reactor Design and Development

The development of the reactor went through stages including mechanical adjustment, addition of a glove box, integration with computer controlled mass flow controllers, injection system improvement and changing to higher temperature furnace. The more general term for this type of reaction is gas phase pyrolysis although deposition of nanotubes on a substrate may also be performed in the reactor.

3.1.1 First Generation of Reactor

As shown in Fig. 3.1, the floating catalyst reactor was built in the Nanoworld Lab with a two heating zones furnace (MTI-1200X) and a 1m long quartz tube, and later, ceramic tubes including alumina, silicon carbide and mullite tubes were tried for higher reaction temperatures. This custom reactor was designed and assembled by the Nanoworld Lab team. In the early few tests, the precursors were injected from the right side of the reactor and the product was collected from the left side, as shown in Fig. 3.1. The right and left ends were switched later on, as shown in Fig. 3.2.

![Fig. 3.1. Initial setup of Floating catalyst CVD reactor in Nanoworld Lab.](image)

As can be seen from Fig. 3.1 and Fig. 3.2, the left side of the reactor is the inlet of the precursor solution and carrier gas, argon in this case. A syringe pump was employed to fix the syringe and control the
injection rate of precursor solution. A 32” long needle (ordered from Hamilton Company) was connected to the syringe and installed inside of the reaction tube. A metal cross was used to merge and solution and gas line and a pressure gage was installed on the top of the cross. The main connectors are valves, clamps for intermediate connection and ultra-torr connectors for end connection. The needle was inserted into the reaction tube and fixed at a spot at a critical temperature, which is a key parameter for the synthesis of CNT products.

Fig. 3.2. Precursor and carrier gas were introduced from the left side in the later layout.

Fig. 3.3. Initial furnace setup.

The right side of the reactor consists of an exhaust hose, vacuum pump and reserved outlet. Since the synthesis of carbon nanotubes at high temperature is very dangerous if oxygen leaks into the reactor, the manual vacuum pump is used to create a certain degree of vacuum in the reactor so that the seal can be tested; the system can be purged by this pump before the experiment. The exhaust hose is connected to a
fume hood which generates a constant suction in the system so that the after-reaction gases/particles can be safely exhausted.

3.1.2 Reactor with Glove Box
With the above reactor setup, it was possible to collect samples from the exhaust end of the reactor. However, the reactor had to be turned off to collect the samples which affected the continuity of the process. Besides, there were a large amount of CNT samples that can be collected from the reaction tube, which means the continuous production of the CNT sample was taking placing during the reaction. Therefore, to increase the productivity of the reactor and to run the reactor continuously, a better collecting apparatus needed to be designed and installed. As shown in Fig. 3.4, a glove box was installed at the outlet of the reactor to separate the CNT products from the open air.

![Fig. 3.4. Upgraded reactor with a glove box installed.](image)

The reaction ceramic tube was connected to the glove box through a screw and O-ring fitting and the backside of the glove box was connected to the exhaust hose. An electrical pump was installed on the other end of the glove box to purge the system more effectively before the experiment.

3.2 Labview Interface Design & Arduino Programming
Argon is used in the floating catalyst method as the carrier gas to carry the fuel to high temperature reaction zone and move the product to the collection apparatus (as least as designed, the fuel vaporization was later found to have a greater effect on the flow field in the reactor). Later, other gases such as H₂ and SF₆ will be introduced into the reactor as possible reaction promoters. So there are four available mass flow controllers (MFCs) mounted on the reactor and controlled by a manual MKS 724 box, as shown in
Fig. 3.5. Among the four MFCs, the top three are MKS and the bottom one is AliCat. The Alicat mass flow controller is used for argon flow control.

![Image of four mass flow controllers mounted on the reactor.](image)

Fig. 3.5. Four mass flow controllers mounted on the reactor.

To make the control automatic, a LabVIEW program and hardware system was built together with Guangfeng Hou who is also working on the new reactor development. The connecting configuration is sketched in Fig. 3.6. Using the 26 pin connecting port on the back of the MKS 247 Unit, it can be connected to a computer. Using two NI data acquisition cards, the collected data from the 247 unit can be transmitted to the LabVIEW program and send commands from the program back to the unit. Four channels were programmed to be compatible with the 247 unit and mass flow controllers.
Fig. 3.6. Mass flow control system.

Fig. 3.7. LabVIEW program interface.

Fig. 3.7 shows the LabVIEW program interface that is used to control the mass flow system. On the interface, the flow rate of each gas at different reaction stage can be input manually and each channel can be turned on and off separately. The background block diagram of the LabVIEW program can be found in Appendix 2.2. After the glove box was installed on the furnace, continuous collection of the CNT sock becomes possible. Therefore, an automatic collection mechanism needed to be added. A step motor was installed in the glove box to spin the nanotube in both yarn and sheet format with properly adjusted setup,
as shown in Fig. 30. An Arduino board was used to control the motor. See the step motor and Arduino board in Fig. 3.8. The control program is listed in Appendix A2.3.

![Fig. 3.8. Step motor driven material collection drum and arduino control board.](image)

### 3.3 Spray Apparatus Development

As mentioned in Chapter 1.3, the fuel introduction method is a key technique that affects the CNT synthesis efficiency and results. An apparatus that can generate a fine mist with a relatively low gas flow rate is preferable. During the building of the floating catalyst reactor in Nanoworld Lab, the fuel spraying system has undergone several stages, including direct needle injection, hydraulic pressured injection, electrostatic spraying and gas-fuel mixing sprayer. The hydraulic pressurized injection method and the gas-fuel mixing injection method are discussed in this chapter. Electrostatic spraying is discussed in Chapter 4.

#### 3.3.1 Needle with micro-sized holes

To achieve a smaller droplet size and a faster evaporation rate, which are helpful to form smaller catalyst particles and carbon nanotubes with smaller diameter, pressurized hydraulic injection was tested. Since the metal needle is the easiest tool to build, it was used in the reactor as the first generation spray apparatus.

The metal needles were purchased from the Hamilton Company with a 20 gage and 32” length. Needles were soldered to have the outlet closed to build up hydraulic pressure within the needle, and the first 1-2 inches were bent to be vertically oriented. Then micro-sized holes are drilled on the vertical part using the laser machining station in the Nanoworld Lab, as shown in Fig. 3.9. The laser micro machining center is
manufactured by Oxford Laser Company and belongs to the model A SERIES. The parameters used to drill the holes are listed in Table 3.1.

Fig. 3.9. Laser machine in Nanoworld Lab.

Fig. 3.10 is a sketch of the needle and the position of the micro holes.

Fig. 3.10. Needle with micro-sized holes.

Different numbers of holes and hole sizes have been tested. There was a good spray effect with generally ~100 um size holes. However, this spray mechanism was found not to be very suitable for the high temperature reaction because the holes can be easily clogged by the fuel decomposition products such as Fe, carbon and sulfur. Therefore, there was a regular burst of injection with this setup as the fuel droplets burst into vapor during the experiments, and the properties of the CNT were affected too. One important parameter in the needle injection system is the local temperature of the needle tip which has a large effect on the synthesis result, as discussed in Chapter 6.
### Table 3.1. Sizes of holes drilled on the needle using a laser machine.

<table>
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</tr>
<tr>
<td>30</td>
<td>50</td>
<td>2</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3.3.2 Gas-Fuel Mixing Sprayer

The idea of the gas-fuel mixing sprayer was initiated by Mr. Guangfeng Hou when trying to integrate the air brush spray for fuel injection into the reactor. Fig. 3.11 shows the needle design fuel injector

![Sprayer schematic drawing by Guangfeng Hou](image1)

![Head of the sprayer](image2)

**Fig. 3.11. Needle fuel injector: (a) Sprayer schematic drawing by Guangfeng Hou; (b) the head of the sprayer.**

The sprayer basically consists of a long needle and a hollow metal tube. Fuel is injected through the needle and the needle was put inside of the metal tube. At the outlet of the sprayer, the metal tube connects with an airbrush head and the needle stops at the small hole of the head. The screw-connected tapered head can be adjusted so that the position of the needle tip against the hole can be tuned. During normal injection, argon gas was injected through the hollow tube at a flow rate around 500 sccm. The velocity of the gas increases dramatically when it flows out of the hole on the head. When the droplet coming out of the needle tip meets with the high speed gas, it was vaporized and carried forward with the gas. Therefore, a fine mist of fuel with an initial speed is created. By adjusting the position of the needle in the head hole, the cross section area and initial speed of the spray can be adjusted. With a fuel injection rate of 0.6 ml/min and 500 sccm argon gas flow rate, the spray can generate continuous CNT assembly smoothly. The injection method actually makes the synthesis more fuel efficient and the CNT product cleaner from amorphous carbon.
3.4 Steps for running the reactor

A set of regular steps have to be followed in order to keep the experiment safe and efficient and make sure the material is successfully collected. Fig. 3.12 shows the normal 7 steps for running the current reactor.

Before running the experiment, one needs to make sure that the glove box is clean and every tool needed for the collection of material is included in the glove box. Then the reactor needs to be closed including the furnace, and every mechanical connection and the glove box. When purging the system and checking the vacuum of the system, the maximum vacuum was controlled at 10 inches of water. The exhaust valve must be switched on after the purge is finished and during the heating process. When the temperature rises to the preset reaction temperature, the flow rate of the carrier gas is decreased and the fuel injection spraying is started. One person watches the spray and computer system while another person collects material or takes pictures and videos. When the experiment is finished, the furnace and gas flow are turned off. The reactor is not opened until the temperature is below 200 °C. Otherwise, an explosion may happen when air enters the reactor, due to possible residual gases in the reactor.
1. Close reactor & install sprayer
2. Purge the reactor & check vacuum
3. Reset valves, set temp. profile & turn on the furnace
4. Set gas flow profile in LabVIEW
5. Set injection rate and start the sprayer at right temperature, Take video/photo
6. Start motor and collect products
7. Turned off and gas low when finished; clean the reactor when cooled

Fig. 3.12. Steps for running the reactor.
Chapter 4 Electrostatic Spray for CNT Growth

As mentioned in Section 3.4, the initial experimental setup of the floating catalyst CNT reactor employed a long stainless steel needle as the fuel introduction apparatus. This method successfully generated the continuous CNT cylinder/sock growth. However, this method has an intrinsic limitation that hinders the realization of optimal injection. Since the needle tip reaches the high temperature zone, approximately 400-500 °C, carbon precursor and catalyst would decompose inside of the needle before being injected into the reactor. The products of pyrolysis, carbon species and iron atoms in the solid state, clog the needle regularly resulting in a burst fuel spray pattern. This non-stable fuel introduction method can cause the inconsistency of the CNT cylinder properties. Therefore, as an alternative fuel introduction method, electrostatic spray was employed to generate a more uniform and stable fuel spray.

4.1 Working Mechanism of the Electrostatic Sprayer

The basic idea of electrostatic spray is to create a strong static electric field where charged micro droplets are accelerated towards and later attached to the target objects. To create a strong enough electric field, high static voltage is required. The solution that will be sprayed is connected to the initial pole and charged. The charged solution droplets are then attracted by the electric field into the gap between the two electric poles, where the charged droplets crack into a micro-sized mist due to the repulsion within the droplet induced by the electric charge, called Coulomb Fission [40].

The fine mist created by the spray continues accelerating to coat onto the target electric pole uniformly, as shown in Fig. 35. Electrostatic spray, compared with mechanical spray, has several advantages. It doesn’t require a high hydraulic pressure to spray a fine mist; it generates charged mist that actively goes to a target pole; when the mist is attracted to the target pole, it coats on the entire surface of the target uniformly due to electrostatic attraction instead of only coating onto the front surface, which is a very good property for the CNT yarn/sheet coating, as shown in Fig. 4.1 and Fig. 4.2.

![Electrostatic spray schematic](image)
The upper limit a sphere droplet can carry is given by the Rayleigh limit: [41]

\[ q^2 = 64\pi^2\varepsilon\sigma r^3 \]

Where \( \varepsilon \) is the vacuum permittivity, \( \sigma \) is the surface tension of the liquid and \( r \) is the radius of the droplet.

During the droplet fission, there’s usually an amount of mass and charge loss due to the evaporation of the solution droplet. The charge loss can be as much as 20% for methanol and 40% for water [42]. The sprayed droplet size was found to have a negative correlation with the charge/volume ratio, namely, the smaller the droplet is, the more charge the sprayed solution can carry [40]. For liquids with a relatively high electric conductivity, such as water, the sprayed droplets are generally larger than liquids with a relatively low electric conductivity, such as ethanol. Therefore, during the synthesis of carbon nanotubes, the organic precursor solution can be sprayed as a very fine mist into the reactor. And the relatively large amount of charge carried by the mist can be utilized to synthesize CNT with better qualities. One idea is that the charge carried by the solution will later be transferred to the iron catalyst particles. On one hand, these charged particles will be separated from each other because of the electrically repulsive force among them. Not sticking together and preventing growing into large iron solids can help improve the longevity of catalysts and therefore, longer and stronger nanotubes could be synthesized. On the other hand, by exerting an electromagnetic field into the reaction tube, the particles can be stabilized or oscillated, and thus will have longer dwell time in the high temperature reaction zone, which will be helpful for the longer and purer CNT growth. The electrostatic spray system was developed by a team consisting of Ms. Anli Wang, Mr. Guangfeng Hou, and Mr. Ruitao Su. Mr. Ed Escallion of Terronics Development Company also provided guidance on design of the spray system.
4.2 Sprayer Integrated with the Reactor

The original sprayer before being adapted into a sub-injection system of the reactor is manufactured by the Terronics Corporation, as shown in Fig. 4.3. Modifications were made to the sprayer to be compatible with the CNT synthesis reactor.

Fig. 4.3. Electrostatic spraying system. (a) 20KV power supply; (b) nozzle holder and syringe pump.

To integrate the sprayer with the high temperature reactor, the plastic holder was removed and the nozzle holder was directly placed inside of the reactor. The following sketches were made by Mr. Guangfeng Hou. In the first series of experiments, setup in Fig. 4.4 was employed. The sprayer was put inside a plastic tube that is kept at room temperature during the experiment. The plastic tube was connected with the ceramic tube to be airtight. At room temperature, the system worked well and a fine spray can be observed through the transparent plastic tube. However, it was noticed that the temperature has a significant effect on the arcing combined with the 20 KV voltage. Arcing did not happen in an air environment, or when N₂ was passed through without heating. However, when the furnace was heated to 1200 °C, hot gas could reach back to nozzle region due to convection, and the arcing started. The arcing locations are show in Fig. 4.4(a) and the cable connection, plug and nozzle tip are positions where arcing happened most often.
After tested several sealing/insulation methods which didn’t effectively stop the arcing, it was decided to move the main part of the sprayer out of the plastic tube, as shown in Fig. 4.5. Now the only part of the nozzle placed inside the plastic tube is the nozzle tip. With this configuration, the arcing at high temperature was prevented. However, the main problem with the current set-up is that the nozzle tip is too far from the reaction zone. Thus the sprayed ethanol mist is in the low temperature zone, which could not provide enough material for reaction. A sprayer with extended nozzle is preferred, with which the spraying location could be adjusted easily. This involves ceramic machining and is suggested as future work.
Based on the previous above tests, a longer ceramic nozzle was proposed. As shown in Fig. 4.6, the new nozzle machined from macor ceramic should be placed into the ceramic reaction tube through the plastic hose. The major electric part of the sprayer is left outside of the hose. This design will make sure that the electric part is separated from argon and high temperature while the fuel can still be effectively delivered to the reaction zone.

![Diagram](image)

**Fig. 4.6.** Future electrostatic spray system with machined long nozzle.
Chapter 5 Synthesis of Carbon Nanotubes using the Floating Catalyst Method

Important parameters of the floating catalyst method include: injection location (tip temperature), carrier gas (argon) flow rate, fuel composition (carbon source, catalyst, promoter), and reaction temperature. All these parameters have been tested on the multi-field physics reactor and it has been tried to find the optimized combination for a limited number of parameters. Because of the increased number of parameters, this thesis could not go into depth studying the multi-field effect. The main principles were demonstrated including high temperature synthesis, electrostatic fuel injection, RF electromagnetic coupling, and generation of an electrically conductive fluid in the reactor that can be manipulated.

5.1 Temperature Distribution Mapping inside of the Reaction Tube

The floating catalyst method for CNT synthesis is very sensitive to the fuel injection location (injector tip temperature). The effect of injection temperature on the CNT synthesis was investigated by other groups [27]. The quality of carbon nanotubes, length of individual tubes and Raman spectrum are also influenced significantly by the synthesis temperature [43], [44]. Therefore, it is important to map the temperature distribution within the tube.

(a) Test setup
A 120 cm long high temperature Omega thermocouple was inserted inside of the quartz tube from the right first. Later it was inserted from the left end since it was not long enough to cover the whole length of the tube. A Swagelok KF50×1/4 adapter was used to close the end to minimize the amount of air leakage into the reactor. This setup allows mapping the temperature field inside of the quartz tube under an 1100 °C furnace setting temperature. During the measurement, the tip of the probe was aligned with the center of the tube as close as possible. An infrared thermal meter was also used to measure the temperature of the metal fitting that houses O-ring seals.

(b) Test illustration
The test temperature was controlled at 1100 °C, as shown in Fig. 5.1. Temperature mapping was conducted within the 88cm tube section between the two metal fittings, as shown in Fig. 5.2. Nine points were chosen to represent the local temperatures.
(c) Test result

As shown in Table 5.1 and Fig. 5.3, the temperature inside the tube in the middle zone was relatively constant around 1094 °C and the temperature was around 1005 °C at the two ends of the heating zone. The temperature drops dramatically to 300 °C outside of the heating zone. The temperature of the two metal fittings are 45.2 °C (left) and 50.7 °C (right) respectively as measured by the infrared thermal meter. In addition, as measured by the thermal couple inserted into the reactor, the gas temperature inside of the tube at the location of the O-rings was around 90 °C. Therefore, the O-rings
wouldn’t be too hot since their ambient temperatures on both sides isn’t too high. After staying at 1100 °C for 40 min, the O-rings are still flexible and in good conditions, which means that the reactor had been sealed.

As discovered by other groups, the optimal injection temperature is around 300 °C, which occurs only a few centimeters inside of the furnace. The following experiments on the CNT synthesis are all based on the above measurement in order to estimate the temperatures at which different reactions would take place.

![Temperature distribution along the reaction tube](image)

*Fig. 5.3. Plot of temperature distribution along the reaction tube.*

5.2 Using Ferrocene as the Catalyst Source to Grow Long Carbon Nanotubes

The typical reaction catalysts for carbon nanotube growth are transition metals include Fe, Co, Ni and Cu. Fe is the most commonly used catalyst among them. In the substrate CNT growth method, Fe is usually deposited onto a silicon wafer in the clean room and a buffer Al/Al₂O₃ layer is deposited under the Fe layer. During the synthesis process, the catalyst coated wafer is placed in the high temperature reaction zone. The catalyst layer starts melting and shrinking into nano size droplets at such a high temperature, which will act as the ‘seeds’ of carbon nanotube growth. The carbon precursors, typically organic gases, are introduced into the reactor by carrier gas and decompose into smaller molecules and further single carbon atoms. These carbon atoms tend to dissolve into the molten catalyst droplets and started ‘growing
out’ to be carbon nanotubes once the catalyst is saturated with carbon atoms. The CNT growth mechanism can be identified as tip-based growth and root-based growth.

The substrate growth method needs a relatively low temperature, usually between 600 °C and 800 °C, since the catalyst has a long dwell time during the reaction, and therefore the active carbon atoms have enough time to deposit onto the growing CNT’s. The silicon-catalyst package takes a longer time to prepare and the amount of CNT forest grown on a wafer is limited since some of the catalyst particles will become deactivated during the growth for various reasons. Therefore, the conversion rate of the carbon atoms is low [14].

Another method is to use Fe containing metallic organic materials, such as ferrocene, to generate instant catalyst particles when decomposed at high reacting temperature [45]–[65]. The molecular structure of ferrocene is shown in Fig. 5.4.

![Molecular structure of ferrocene.](image)

Other groups have reported a long carbon nanotube ‘sock’ assembly that can be continuously drawn directly from the reaction tube [28], [66]. In this method, the silicon substrate that was used to support the catalyst coating was removed. Instead, the high temperature reaction zone is left empty for the fuel mixture to decompose and react. A higher furnace temperature of 1200 °C was used because of the shorter growth time of the floating catalyst method. During the reaction, after the hydrocarbon-ferrocene fuel mixture is injected into the furnace, ferrocene decomposes into different products that contain Fe atoms and hydrocarbon decomposes into smaller organic molecules and carbon atoms. The decomposition of ferrocene occurs at 175 °C, thiophene around 270 °C, methanol and hexane around 490 °C. Fe atoms then assemble into larger catalyst particles. The size distribution of the particles determines the diameter distribution of carbon nanotubes that grow on the iron particles. A reaction promoter thiophene decomposes into products that contain sulfur. The deposition of sulfur on the surface of iron particles stops the continuing growth of the particle. Larger particles tend to increase in size through Ostwald
Ripening. The following scenario is similar to what happens in the substrate growth case. Carbon atoms dissolve into the already formed Fe particles [67]. The sulfur coating on the Fe particles also plays a role here to keep the carbon atoms at the surface of the Fe particles. Therefore, it takes shorter time to make the particles ‘saturated’ with carbon atoms. Once the Fe particles surface is filled with carbon atoms, carbon atoms start precipitating out of the ‘iron seeds’ in the form of carbon nanotube [66]. The important parameters in this process include nanotube diameters, number of walls, chirality of carbon nanotubes and tip or root growth mechanism.

The collection of the CNT products becomes very easy since the format of the carbon nanotubes is a sock like continuous tube. There are several hypotheses regarding the CNT sock formation process, which are based on experimental observations. However, what is certain about the CNT sock is that it consists of individual carbon nanotubes that assemble together by the Van der Walls forces. The sock can be collected at the outlet end in a yarn or sheet format.

A large quantity of carbon films was synthesized in the Nanoworld Lab using the reactor described. The basic recipe is: 90% methanol, 10% hexane, 0.5% thiophene, 0.5-2% ferrocene. The 9:1 ratio by volume of methanol and hexane should produce mostly double-wall carbon nanotubes (DWCNT), according to Jiannong Wang et al [68].

5.3 Recipe Development

The fuel composition of the floating catalyst method for CNT growth can be divided into three categories. The first one is carbon precursors that provide carbon atoms in the reaction. The second one is catalyst provider, ferrocene in most cases, and the third one is reaction promoter, sulfur-containing compounds in most cases. Recipes used by different groups may vary in use of these elements.

5.3.1 Using Ethanol as the Carbon Precursor

The common carbon sources for CNT growth include methane, hexane, methanol, ethanol, butanol, and toluene. In some cases, the carbon atoms in the catalyst provider, such as ferrocene, can also be used for CNT growth.

Here, ethanol was first tried as the possible precursor since many other groups have used it to grow carbon nanotubes successfully. The quartz tube used in the experiment can only stand a maximum of 1150 °C temperature. The flow rate of argon was kept at around 500 sccm.
Table 5.2. Recipe with ethanol as carbon source.

<table>
<thead>
<tr>
<th>Carbon source</th>
<th>Catalyst</th>
<th>Promoter</th>
<th>Reaction tube</th>
<th>Temperature</th>
<th>Carrier gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>Ferrocene (0.5-2g/100ml)</td>
<td>Thiophene (0.3g/100ml)</td>
<td>Quartz (1.8&quot;, 2&quot;, 1m)</td>
<td>1150 ºC</td>
<td>Argon ~500 sccm</td>
</tr>
</tbody>
</table>

No large size CNT products were synthesized from this recipe, except for some CNT fibers. During the experiments, the inner wall of the quartz tube was gradually coated with black carbon, mostly amorphous carbon with some CNT fiber. A mesh that was used to collect the CNT was placed at the outlet of the tube, as shown in Fig. 5.5.

![Fig. 5.5. Mesh and CNT growth in quartz tube.](image)

The injection needle was placed at the inlet of the quartz tube, and it was also covered with long CNT fibers. This revealed a very interesting gas flow field distribution inside the tube and an assumption was made based on what was observed, as shown in Fig. 5.6. The hot argon that circulated back to the inlet of the quartz tube brings the CNT with it and the CNTs assemble into fibers on the needle.

When the ceramic tube (Alumina and silicon carbide) was used to grow carbon nanotubes, the reaction temperature was increased to 1200 ºC per the ceramic tube’s higher thermal tolerance. The
characterization of the CNT products at 1200°C didn’t show much improvement as other groups have reported. See details in Chapter 6 where properties characterization is introduced. It is not very clear why ethanol didn’t produce the right CNT assembly on the reactor. Probably other conditions such as injection temperature and degree of vacuum in the reactor are not matched to the ethanol recipe yet.

5.3.2 Using Methanol and Hexane as Carbon Precursors
Fortunately, ethanol is not the only hydrocarbon that has been used for the CNT synthesis. There are other chemicals such as hexane and methanol reported to be able to enable the synthesis of carbon nanotubes. A series of relevant experiments were conducted to investigate different fuels.

(a) The role of ferrocene—catalyst provider
As an organometallic compound, ferrocene can decompose into both carbon atoms that are available for CNT growth and iron atoms that are used as catalyst in the growth. In fact, it has been reported than CNT can be synthesized exclusively from ferrocene [46]. Ferrocene is a solid state yellow powder under room temperature. Some of the important properties of ferrocene are listed in Table 5.3.

<table>
<thead>
<tr>
<th>Properties of ferrocene [69].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
</tr>
<tr>
<td>Density under Room Temperature</td>
</tr>
<tr>
<td>Melting Point</td>
</tr>
<tr>
<td>Boiling Point</td>
</tr>
<tr>
<td>Starting Decomposing Temp.</td>
</tr>
<tr>
<td>Critical Decomposition Temp.</td>
</tr>
<tr>
<td>Fe Generation Temp.</td>
</tr>
</tbody>
</table>

As shown in Table 5.3, ferrocene started melting when heated up to 172.5°C and boiling at 249°C. However, the decomposition starts at 72°C and reaches the largest reaction rate at 175°C. The main products at this temperature range are mainly smaller hydrocarbon and iron-atom containing molecules, no individual iron atoms are available. It is only when the temperature is above 497°C that ferrocene started decompose into iron atoms that is available for CNT growth. The reaction follows the following formula.

\[(C_5H_5)_2Fe \rightarrow Fe + H_2 + CH_4 + C_5H_6 + \cdots\]

However, the carbon atoms generated from ferrocene decomposition are not enough to grow scalable amount of CNT products. Extra carbon precursors, methanol and hexane in this case, need to be added to provide necessary carbon atoms.
Based on the above information, it is predictable that once ferrocene that evaporates with carbon precursors enters the part of ceramic tube where temperature is above 497°C, it breaks down to iron atoms that later assemble into nano size particles. These particles absorb the carbon atoms around and start growing carbon nanotubes. Therefore, the size distribution of iron particles determines the size distribution of carbon nanotubes.

(b) The role of thiophene -- promotor
Thiophene is a sulfur containing aromatic compound that can decompose into sulfur atoms above a certain temperature. It is a colorless liquid with a mildly unpleasant odor under room temperature. T. E. Caldwell et al [70] reported that thiophene can decompose into S and C₄ species with the Pd (111) as catalyst. Sulfur will deposit onto Pd; C₄ species mainly exist in the format of C₄H₄ and C₄H₅. Thiophene is stable below 7°C and 1-3-butadiene is observed above 27°C. F. Zaera reported that thiophene is C-S bond started breaking above 90K (-183°C). With Nickel as catalyst, metallacycles form on the surface of nickel and the metallacycles remain stable until 227°C. During research about thiophene pyrolysis in coal, Li-Xia Ling et al proposed that the decomposition of thiophene started with the migration of H atoms within the molecule and cleavage of C-S bond. And then smaller molecules, H₂S and hydrocarbons, are formed [71], [70], [72].

![Molecular structure of thiophene](image)

**Table 5.4. Properties of thiophene.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C₄H₄S</td>
</tr>
<tr>
<td>Density</td>
<td>1.05 g/cm³</td>
</tr>
<tr>
<td>Melting Point</td>
<td>-39.4°C</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>84°C</td>
</tr>
<tr>
<td>Stable temperature</td>
<td>≤ -183°C</td>
</tr>
<tr>
<td>S formation temperature</td>
<td>&gt; 227°C</td>
</tr>
</tbody>
</table>

Overall, thiophene is not a stable molecule at room temperature and smaller molecules can be produced from a certain degree of decomposition. The generation of sulfur atoms are possible above 227 °C with the presence of catalyst. It can be assumed that, during the pyrolysis of thiophene during the growth of
carbon nanotubes, the Fe particles from the pyrolysis of ferrocene activate the sulfur formation process and the sulfur deposit onto the particle surfaces. As described above, the growth of CNT on Fe particles resulted from the saturation of carbon atoms into Fe and this process would take much long time, which in turn reduces the efficiency of CNT growth. Instead, the coating of sulfure onto the Fe particle surface caused by thiophene pyrolysis prevents the carbon diffusion into the particles volume, which mean that the CNT will start growing once the particles surfaces are filled with carbon atoms. This effectively improves the growth rate of CNT [73]. However, too much sulfur in the reaction will cause the failure of catalysts resulting in low production as well as quality of CNT. This has been verified by the experiments. (see the Appendix A2.1 for experiment log). The optimal concentration of thiophene was found to be 0.3ml/100ml. The accurate understanding of sulfur’s role in CNT formation hasn’t been achieved. Koziol et al reported that ultra-pure SWCNT with large G/D ratio (30) was synthesized without any sulfur-containing promotor [27].

(c) The role of Methanol and Hexane – carbon precursor

After testing different combinations of methanol and normal hexane (n-Hexane), a volume ratio of 9:1 was found to have a good production of carbon nanotube films. Some basic properties of methanol and n-Hexane are shown in Table 5.5.

<table>
<thead>
<tr>
<th>properties</th>
<th>Methanol</th>
<th>n-Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>CH₃OH</td>
<td>C₆H₁₄</td>
</tr>
<tr>
<td>Melting point</td>
<td>-97.6°C</td>
<td>-96°C</td>
</tr>
<tr>
<td>Boiling point</td>
<td>64.7°C</td>
<td>68.5°C</td>
</tr>
<tr>
<td>Pyrolysis temperature</td>
<td>&gt;700°C [74]</td>
<td>&gt;450°C[75]</td>
</tr>
<tr>
<td>Main products</td>
<td>CO, CH₄, C₂H₆, C₂H₄, HCHO</td>
<td>Radicals, e.g., CH₃, C₂H₅, H[75] Molecules, e.g., H₂, C1-C4 paraffins, C2-C5 olefins, iso-hexanes, and coke [76]</td>
</tr>
</tbody>
</table>

As can be seen in Table 5.5, methanol and n-hexane have very similar physical properties regarding melting and boiling points. This is very good for the reaction since these two components will evaporates almost simultaneously ensuring a uniform behavior of the fuel. However, in respect to pyrolysis mechanism, methanol and hexane both have a chain process; the parameters and productions of these two processes are slightly different.

Methanol, also called methyl alcohol, is a transparent liquid under room temperature. According to D. Aronowiltz et al, the pyrolysis of methanol in the temperature range of 800-955 °C consists of as many as
The main products of methanol pyrolysis are smaller carbon containing molecules, organic or nonorganic. These products will provide carbon atoms during later CNT growth. N-hexane is a transparent liquid under room temperature. N-hexane has a lower pyrolysis temperature than methanol. The portion of H₂ and dehydrogenized coke increases with temperature. The chain reaction length is around 6 as and this number decreases with time [76].

From the above statement, we can propose a chemical evaporation and pyrolysis roadmap along the reaction tube. Once the mixed fuel is injected into the reaction tube from a needle, they evaporate immediately. Actually, ferrocene and thiophene already start pyrolysis inside of the needle on their way to be injected. The spots for them to start pyrolysis depend on their initial pyrolysis temperature which can be found in Table 5.5. Since n-hexane has a much lower pyrolysis temperature than methanol, its pyrolysis spot is ahead of that of n-hexane. These evaporated and pyrolysis chemicals cause a high pressure inside of the needle and clog the needle periodically. This can explain why a regular squirt of mist was sprayed out of the needle tip when observing from the outlet of the reactor. When the mist was sprayed out of the needle tip, it evaporated immediately because of the high ambient temperature. This evaporation and pyrolysis mixture is carried into the hotter reaction zone by argon/nitrogen.

When the mixture reaches the corresponding pyrolysis temperature spots, the relevant chemical will be pyrolysed completely into the products mentioned in Table 5.5. For example, n-hexane decomposes into radicals, H₂, C2-C5 olefins et al at 450 °C spot; methanol decomposes into CO, CH₄, C₂H₆, et al at 700 °C spot. Since the S coated iron Nano particles are already available when these small carbon containing molecules formed, they can easily deposit the carbon atoms onto the S-Fe particle system through a collision chemical reaction mechanism. A cylindrical carbon nanotube sock is assembled under the rich concentration of CNTs, proper thermal and gas flow fields, as has been observed here and by other groups.

A position sequential distribution along the reaction tube was mapped in Fig. 5.8. This model basically describes the chemical injection, evaporation and pyrolysis distribution along the reactor based on the above analysis.
Ferrocene pyrolyzes into smaller molecules, 175°C.

Individual Fe atoms generated, 490°C.

Thiophene pyrolyzes into small molecules.

CNT grown Fe particles.

Assembled CNT sock.

Carbon containing molecules mixture.
5.3.3 CNT Cylinder Collection

The theory for the CNT ‘sock’ formation in floating catalyst method has not been well developed yet. Dr. Koziol has an explanation that assumes there is an optimized zone for the carbon atoms to gather a certain distance away from the reaction tube’s inner surface [66]. However, based on the experimental observation in Nanoworld, it is highly possible that the well-believed ‘sock’ format of CNT assembly is actually a solid cylinder. See Fig. 5.9 for the image of a normal sock coming out of the reactor.

![CNT cylinder assembly](image)

*Fig. 5.9. CNT cylinder coming out of the reactor.*

Depending on the ratio between precursor solution and carrier gas introduction rate, the transparency of the sock can be tuned. The usual fuel injection rate is 0.8 ml/min and the argon flow rate can change between 500 to 2500 sccm. The higher the argon flow rate is, the lighter the CNT cylinder color will be. This can be caused by the diluting effect to the CNT concentration from argon gas. It can be seen that within the almost transparent CNT cylinder, there are spider web like fibers filling the inner space of the assembly. Therefore the normally called CNT ‘sock’ can be a solid CNT assembly under a certain circumstance. A theory for the formation of this solid CNT cylindrical assembly needs to be developed.

One of the interesting properties of the CNT cylinder is that it shrinks immediately after it meets liquids, such as water and alcohol. The whole CNT assembly collapses to an extremely small solid when sprayed by or immersed in liquids. Because the highly porous structure of CNT cylinder has very little resistance to external pressure, the surface tension and inter-molecular force crash the originally formed structure during CNT growth. In fact, not only the CNT assembly collapses when large amount of liquid is present, it also shrinks significantly when placed in air because of the absorption of humidity. Therefore, the
common collection method of CNT assembly for afterward characterization and application purposes is going through a water container with a glass rod placed inside of water to generate a CNT fiber, as shown in Fig. 5.10.

![Diagram of CNT fiber production](image)

*Fig. 5.10. Production of CNT fiber directly from cylindrical assembly.*

To spin the CNT fiber continuously, there should be a good match between the motor rotation speed and CNT cylinder yielding rate, which are determined by fuel injection rate and carrier gas flow rate. When the carrier gas flow rate is around 1000 sccm, a 50 r/min rotation speed is proper. A good combination occurs when the CNT cylinder is stretched enough but not broken. The stretch can help to align the individually CNTs inside of the sock and therefore improve the mechanical and electrical properties of the collected fiber.

Compared with water, alcohol has a much better shrinking effect on CNT assembly. When making CNT films out of CNT cylinder, alcohol is sprayed onto the spool where CNT is wrapped onto to make a dense CNT film, as shown in Fig. 5.11. Usually, a Teflon film is wrapped onto the spool first so that the CNT film can be placed on the Teflon film, which makes it much easier to peel off the CNT film for afterwards characterization. Shown in Fig. 5.12 is the CNT fiber and film produced from the floating catalyst method.
The properties of the CNT fiber and film is discussed in Chapter 6.

5.3.4 Addition of Water and Gadolinium Salt

The addition of water and other chemicals in the synthesis of substrate-based CNT growth has been explored and positive effects have been discovered. 4-centimeter long vertically-aligned multiwall carbon nanotubes (MWCNT) were synthesized in Nanoworld Lab in 2006 [20]. The role of water in ultra-long single wall carbon nanotube (SWCNT) growth was found to be effective in inhibiting Ostwald Ripening thanks to the oxygen and hydroxyl which can prevent the Fe catalysts from diffusing into substrates. However, for the floating catalyst growth method, the growing recipe has been rarely change and the effects of other chemicals are rarely tested. After successfully synthesis of spinnable CNT cylinder, H\textsubscript{2}O and GdCl\textsubscript{3} were tested as addition into the original Ferrocene-Thiophene-Methanol-Hexane recipe.

Test of H\textsubscript{2}O

Different amount of High purity water (TEDIA WS2211-001) was added into the original solution for the CNT cylinder growth. The concentration of water ranges from 1 ml/100 ml solution to 5 ml/100 ml solution. The test was conducted with the needle injection method and all the other parameters remained the same as described in 6.2. The H\textsubscript{2} gas produced by H\textsubscript{2}O at high temperature can help clean the Fe
particles from cokes and sustain a longer active period. The experiment log of water test on the furnace is shown in Table 5.6.

Based on the test, a water concentration ranging from 1%-4%, by volume, can generate CNT cylinder. The CNT cylinder generated with water are more transparent compared that without water, which partially verifies the function of water in the CNT growth. A more detailed characterization of water-added grown CNT characterization can be found in chapter 6.

### Table 5.6. Water test on floating catalyst reactor.

<table>
<thead>
<tr>
<th>Date</th>
<th>Catalyst</th>
<th>Diameter</th>
<th>Flow Rate</th>
<th>Ferrocene Concentration</th>
<th>Hexane + Methanol Concentration</th>
<th>Water Concentration</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/13/14</td>
<td>alumina</td>
<td>1200</td>
<td>2&quot;</td>
<td>1% ferrocene</td>
<td>Hexane + Methanol 0.0% water</td>
<td>0.0% water</td>
<td>Adding water generate thinner CNT cylinder</td>
</tr>
<tr>
<td>11/14/14</td>
<td>alumina</td>
<td>1200</td>
<td>2&quot;</td>
<td>1% ferrocene</td>
<td>Hexane + Methanol 0.0% water</td>
<td>2.0% water</td>
<td>all water concentrations generate CNT cylinder except for 5.0%</td>
</tr>
</tbody>
</table>

**Test of GdCl₃·6H₂O**

Dr. Shanov proposed that gadolinium salt as a new addition can potentially extend the longevity of Fe catalyst particles. To explore if gadolinium salt would have any positive effect on the floating catalyst CNT growth, a series of experiments were conducted utilizing GdCl₃·6H₂O. GdCl₃·6H₂O is a solid white crystal under room temperature. Some of its related properties are included in Table 5.7. The interaction between gadolinium atoms and Fe atoms are of very much importance for the CNT growing efficiency. The collision theory is a very plausible explanation for the functional mechanism, according to which the collision helps remove the amorphous carbon coating on the surface of Fe particles.

### Table 5.7. Properties of GdCl₃·6H₂O.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiling point</td>
<td>1580 ºC</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>609 ºC</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>100 mM (3.717g/100ml)</td>
</tr>
<tr>
<td>Solubility in alcohol</td>
<td>1.91 M (71g/100ml)[77]</td>
</tr>
</tbody>
</table>
By improving the longevity and activity of Fe particles, longer and strong CNT is expected to grow. By spinning the CNT cylinder onto a spool, the CNT cylinder with the addition of gadolinium salt feels more resilient than the one without gadolinium salt.

Table 5.8. CNT growth catalog with addition of GdCl₃•6H₂O.

<table>
<thead>
<tr>
<th>Precursor solution introduction rate</th>
<th>Argon rate (sccm)</th>
<th>Concentr. Of GdCl₃</th>
<th>Thiophene Concentr.</th>
<th>Results summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05–0.08*16 Ml/min</td>
<td>100-500</td>
<td>0.25 ferrocene</td>
<td>0.15</td>
<td>Only short fibers and black particles observed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No GdCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td>0.3</td>
<td>No continuous sock</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2:1 Fe:Ga(ac)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td>0.3</td>
<td>No continuous sock</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4:1Fe:Ga(ac)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05–0.12*16 Ml/min</td>
<td>50 - 500</td>
<td>0.35 ferrocene</td>
<td>0.21</td>
<td>Small amount of sock, not continuous</td>
</tr>
<tr>
<td></td>
<td></td>
<td>No GdCl₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td>0.3</td>
<td>No continuous sock</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2:1 Fe:Ga(ac)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.05-0.07*16 Ml/min</td>
<td>200 (motor 55RPM)</td>
<td>0.4 ferrocene</td>
<td>0.3</td>
<td>Thin continuous sock</td>
</tr>
<tr>
<td></td>
<td></td>
<td>¼ Ga</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td>0.3</td>
<td>Continuous sock spun</td>
</tr>
</tbody>
</table>

60
5.4 The Role of Vacuum in the CNT Synthesis

The effect of pressure in CNT growth has been widely explored in other CNT growth methods. [67] For the floating catalyst reactor in Nanoworld Lab, the low pressure tests were tried by adjusting the suction of fume hood which is connected to the exhaust end of the reactor. At the left side of the reactor, the exhaust is connected to a fume hood by a metal-plastic hose. The magnitude of the vacuum caused by the suction is adjustable by varying the opening area of the fume hood and is read out by a barometer. The vacuum range of 0-0.9 inch of water was tried on the reactor and the materials are collected for characterization.

The experiment log of vacuum test can be found in Appendix 2, from 08/28/2014 to 10/01/2014. Based on the experiment results, no obvious change in the CNT assembly’s format or properties were detected. It is possible that the vacuum degree was too low to have any significant effect on the synthesis.

5.5 Effect of Electromagnetic Field on the CNT product

Since CNT is electrically conductive, it is possible to manipulate it with electromagnetic field. Based on the hypothesis introduced in chapter 2 and chapter 3, some initial test were done on the multi-field physics approach CVD reactor. With the help of Dr. Mast, a series of electromagnetic test on the reactor were conducted. Fig. 5.13 shows the setup of the coils and supporting capacitors for the tuning of the magnetic field oscillating frequency. Amplifiers and frequency tuners were placed on top of the reactor. A Faraday cage was built around the furnace to eliminate any magnetic radiation from the experiments that may injure humans.

![Fig. 5.13. RF coils installed on the silicon carbide tube.](image)

The test of the RF frequency was conducted at both room temperature and 1200 °C. However, no carbon precursors were injected into the reactor for the synthesis yet. A small pick-up coil that was coated with ceramic insulations was inserted into the reactor to monitor the magnetic field distribution inside of the reaction tube during the experiments. The pick-up coil was connected with an oscilloscope.
As shown in Fig. 5.14, when a sine wave was generated by the generator inside of the reaction tube, the signal was successfully picked up the pick-up coil and displayed on the oscilloscope. Combined with the experimental results introduced in chapter 2 and 3, these tests showed great potential for the application of electromagnetic filed on the synthesis of carbon nanotubes.

In the meanwhile, it was possible that cold plasma was generated in the reaction tube by thermal heating as well as oscillating electromagnetic field induced by the furnace circuitry. A sine wave signal of 60 Hz was detected on the ceramic tube when the furnace was turned on. Moreover, when the CNT assembly was coming out of the tube during synthesis, a similar voltage signal with higher magnitude was also detected. One possible scenario is that the Argon atoms are ionized at the 1200 °C reaction temperature. The Argon plasma acted as a conductor that fills the tube, or at least the high temperature reaction zone. Usually, it takes at least 11,000 eV to generate cold plasma, it is more likely that the ionization of argon atoms are accompanied by the electrons collision activated by the oscillating electromagnetic field [78]. At 60Hz, the electrons tend to follow the electromagnetic oscillating frequency but the Argon ions will have a movement hysteresis for its much larger density. Therefore, electrons generated by the plasma are the main conducting element in the reaction tube. To prove the conductivity of argon at higher temperature, the resistance of the gas was measured with a two probe apparatus and it was found that argon is relatively conductive at over 1000 °C.
Chapter 6 Properties Characterization of Carbon Nanotubes

Characterization of carbon nanotube products’ properties is another important link in the research. The main properties that are usually characterized in Nanoworld Lab include: Scanning Electron Microscope (SEM) imaging, Raman Spectrum, Thermal Gravimetric Analysis (TGA), mechanical strength characterization and electrical/magnetic properties characterization. These characterization methods are described in this chapter. All the CNT yarns and sheets produced in Nanoworld Lab are characterized by the above stated devices or methods. It is necessary to describe the working mechanism of equipment used and the procedure of certain characterization method before presenting the characterization results.

6.1 SEM Imaging

6.1.1 Introduction

The information that can be revealed by SEM images is very helpful for the understanding of carbon nanotube fiber/sheet structure at micro and nano scale. It helps to identify how well the nanotubes are aligned, how long an individual tube is, and where the impurities concentrate. Scanning Electron Microscope that is used in UC Material Characterization Center is a XL-30 ESEM, as shown in Fig. 6.1. With a maximum resolution of 3.5 nm at 30 KV, it doesn’t require a vacuum environment to acquire the image. Images with higher resolution were obtained North Carolina Agricultural and Technical State University (NCAT).

As a basic imaging tool for nanomaterials and nanostructures, SEM has been widely used to observe the micro and nano structure. The working mechanism of SEM is illustrated as follows.
As shown in Fig. 6.2, the electron beam emitted by the electron gun is narrowed down to a parallel beam by a hollow anode plate which carries opposite charge to the electrons. A magnetic lens then focuses this beam to the desired observation depth. Scanning coils are utilized to scan the surface of the specimen at a certain frequency so that an area can be imaged instead of just a dot. The electrons that are shot onto the specimen surface generate four different types of output, namely, the backscattered electrons, the secondary electrons that are emitted by specimen atoms that are activated by the incident electron beam, X-rays from the specimen atoms and electrons that transmit through the specimen body. For SEM, it is the backscattered and secondary electrons that are detected for the imaging. The signals transformed from the backscattered and secondary electron detectors are sent from the two detectors to the TV scanner (display). The beam position information and the detected electron information are combined to generate image on the display. The X-ray signal can also be collected to analyze the composition of the specimen, which is called E-DEX. (en.wikipedia.org/wiki/scanning_electron_microscope)

Compared to optical microscope, SEM has a much better resolution since the electron beam directly interacts with atoms. SEM also has larger field depth since the magnetic lens can be tuned as needed. Some of the images taken in this research are from the ESEM in Nanoworld Lab and some others are from the vacuum SEM in engineering characterization center.
6.1.2 Characterization

Fig. 6.3 shows the SEM image of CNT samples synthesized on 09/11/2014. The experimental parameters can be found in Appendix 2. These images characterize the micro structure of CNT synthesized at the early stage of this series of experiments. 10 KV or 20 KV voltage was used in the imaging. Nanotube has from this sample has a diameter around 10 nm. A large amount of residual catalysts can also be seen from the image. Edex result shows a 26% of Fe in the CNT sample by weight. This means that there is a big portion of the collected CNT sample is catalyst, which is one of the reasons for the low strength of the sample. The carbon nanotubes generally have a diameter range of 12-50 nm.

![SEM images of samples synthesized on 09/11/2014 (NCAT)](image)

The samples characterized by the HRSEM in NCAT can be divided into two groups that are processed by FeCl₃ solutions of different concentrations. The moderate of concentration of H⁺ can corrode Fe catalysts while preserve the structure of carbon nanotubes [79]. The SEM images of samples processed with 0.5% and 1% by volume FeCl₃ are shown in Fig. 6.4.
There is no obvious morphology difference in the two groups of samples. The catalyst particles with a diameter range of 20-50 nm can be observed around the tip of the carbon nanotubes, which indicates a possible tip growth mechanism. The large sized particles concentrates at the inside body part of the tubes while smaller sized particles get attached to the outside wall of the tubes, which can be a cause for the branching growth of carbon nanotubes. From sub graph (d), a bamboo like MWNT was captured and its inner diameter can be estimated to be 5-20 nm. The catalysts concentrations has various shapes: spherical, conical and cylindrical.

With the yarn spun from the floating catalyst, its mechanical tensile strength can be determined by stretching and cross section area measurement. In Fig. 6.5 (a) and (c), the CNT yarn produced with gadolinium salt addition are cut by laser machine in Nanoworld Lab. By aligning the yarn vertically to the viewer, its cross section area can be precisely determined. In sub graph (a), multifold layers of CNT sheet are seen in the cross section area of the yarn, which means that the cylindrical CNT assembly collected from the reactor is not completely hollow. In sub graph (c), a laser burned smooth surfaces on the cross section of the CNT yarn can be seen. With respect to sub graph (b) and (d), better alignment of the CNT fibers are observed than in the CNT film shown in Fig. 6.5.
Besides SEM, transmission electroscope (TEM) was also utilized to get images of carbon nanotubes of higher resolution. Images of carbon nanotubes synthesized at different temperatures were taken at the Material Characterization Center in UC, as shown in Fig. 6.6. Under TEM, the samples showed mostly double wall carbon nanotubes (DWCNT) and the nanotubes were more aligned compared to the images described in 6.1, which were taken in the early stage of the synthesis. In the TEM images, the nanotubes show more clear crystalline structure and less amorphous carbon coating. A phenomenon that is shared by all these samples is that the catalyst particles tend to coalesce into islands and only a small portion of the catalyst particles have CNT grown. Some catalyst particles tend to be encapsulated by sphere carbon structures too and therefore lose the ability to grow CNT. Nevertheless, the tests at higher temperatures are still very encouraging because it indicates a much stronger CNT assembly at higher temperature. Some more experiments at higher temperature needed to be conducted confirm the property improvement and more applications are to be proposed based on the enhanced property.
6.2 Raman spectrum

6.2.1 Introduction

The Raman spectroscope used in Nanoworld Lab is Renishaw inVia, as shown in Fig. 6.7.

![Raman Spectroscope in Nanoworld Lab](image)

Raman Spectroscope is an electromagnetic absorption spectrum that helps identify chemical species. Based on the quantum theory, the possible vibrational/rotational energy of a molecule has limited number of values, different electronic excited states. A molecule can switch between these states by absorbing or emitting photons that have certain energy values. The energy level of a molecule is levitated if photons are absorbed, and the energy level is lowered if photons are emitted/scattered. An elastic scattering...
happens if the final energy level is the same as the initial energy level and an inelastic scattering happens if there is a difference between the two.

Raman scattering is an inelastic scattering and it can be categorized into Stokes and Anti-Stoke scattering. In Stokes scattering, the absorbed photon energy is greater than scattered photon energy and the molecule ends up in a higher electronic excited state than the initial state; In Anti-Stokes scattering, the absorbed photon energy is less than scattered photon energy and the molecule ends up in a lower electronic excited state than the initial state. What are measured by the Raman electroscope is the difference of the energy state of molecules, $\Delta \sigma$, as shown in Fig. 6.8. In a Raman test, a laser with a certain wavelength, usually 514 nm or 785 nm, is shot onto the specimen. Scattered photons are generated and detected by detectors in the testing chamber. Since a certain kind of molecules only have a certain few $\Delta \sigma$ values, the spectrum of $\Delta \sigma$ versus its intensity can be used to identify the molecule and its quantity. The $\Delta \sigma$ is measured by wave number per centimeter ($cm^{-1}$).

For carbon nanotubes, the main $\Delta \sigma$ is caused by graphitic vibration, which results in a $\Delta \sigma$ of $\sim 1590 cm^{-1}$. This is usually shown in the Raman spectrum by a G peak, as shown in Fig. 6.9. Another important peak in Raman spectrum is the D peak, usually occurs at $\sim 1350 cm^{-1}$, which indicates the vibrations caused by disordered structures in the CNT material. D peak can be caused by impurities and structural defects in carbon nanotubes. The G/D ratio is one of the most important parameters to determine the quality of the crystalline structure of CNT. The carbon nanotubes produced by floating catalyst method in Nanoworld Lab has a G/D ratio of 3-8 when the synthesis temperature was controlled 1200 ℃. However, a G/D ratio of more than 30 was observed, which is very close to what was report by Dr. Koziol el al [27]. another important peak on the CNT Raman spectrum is radial breathing mode (RBM), which is caused by the
vibration of SWCNT in the radial direction. Therefore, RBM is a characteristic peak for SWCNT and receives a particular attention because of SWCNT’s superior properties among others.

During a normal Raman test, the user could choose which laser line to use, 514nm or 785 nm. The 785 nm laser line has less fluorescence effect, but generates less Raman scattering too [80] [81]. The sample for Raman characterization is very easy to prepare and the test process is relatively simple.

![Raman spectrum](image)

*Fig. 6.9. The characteristics of CNT Raman spectrum*

### 6.2.2 Characterization of Raman Spectrum

![Raman spectra](image)

*Fig. 6.10. Original (left) and normalized (right) Raman spectra of CNT film synthesized on 09/02/2014*

As shown in Fig. 6.10, the CNT film synthesized on 09/02/2014 was tested with the Raman spectroscope in Nanoworld Lab. It is a sample that was synthesized with an early stage recipe, which can be found in Appendix 2. The temperature was lower compared to the conditioned later employed. The graphitic peak (G peak) has an intensity of 6808 and the disordered peak (D peak) has an intensity of 1088, therefore the G/D ratio of this sample is 6.3, which is a relatively high value compared with CNT products by substrate
growth method. A higher G/D ratio indicates better graphitic structure and less defects in the carbon nanotube molecular structure.

It can also be noticed that there is a RBM on the spectrum, which occurs around the wave number of 230 cm\(^{-1}\). The presence of RBM on the Raman spectrum means that a fraction of the CNT in the sample is SWCNT, which is the desired type of carbon nanotubes in most synthesis processes. Furthermore, the diameter of the SWCNT can be estimated based on the following rule of thumb:

\[
D(\text{nm}) = \frac{248}{\omega} = \frac{248}{230} = 1.08
\]

Where \(D\) is the diameter of the SWCNT and \(\omega\) is the wave number of the RBM.

When a high temperature furnace that can go up to 1700 °C was installed and tested to grow carbon nanotubes, an interesting correlation between reaction temperature and G/D ratio as well as SWNT diameter was observed, as shown in Fig. 6.11.

All the samples were collected during one single experiment to make sure they are synthesized under the same conditions except for the temperature that was employed. The material was collected as a CNT film onto TEFLON film with the apparatus introduced in Chapter 6. The samples were then processed by ethanol and prepared by for the Raman test.

![Fig. 6.11. G/D ratio and diameter influenced by synthesis temperature](image)

The averaged G/D ratio was taken from three measurements for each sample and denoted by height ratio. What was noticed was that for the same sample, the test did at different spot may have very different G/D ratio. For example, the averaged G/D ratio for 1350 °C sample is 12.3, whereas the largest ratio is 25.9 and lowest ratio is 10.5. The large deviation of Raman data indicates an inhomogeneous distribution of crystalline defects. Overall, the G/D ratio shows a monotonous increase relation with reaction temperature, expanded by nearly 6 times when the temperature increases from 1200 °C to 1400 °C. This
verifies the point that, for floating catalyst method, higher temperature and therefore more energy for molecule growth is vital for high quality CNT synthesis [82].

As the synthesis temperature went up, companied with the increase of G/D ratio is the increase of the diameter of SWCNT deduced from RBM. It shows in table one that the diameter of SWCNT doubles when the synthesis temperature goes up from 1200 °C to 1400 °C. According to particles dynamics, catalyst particles tend to grow to larger size at higher reaction temperature, which will yield carbon nanotubes with larger diameters [66].

![Raman spectrum of CNT sheet synthesized at 1300 °C (upper) and 1400 °C (lower) respectively](image)

**Fig. 6.12.** Raman spectrum of CNT sheet synthesized at 1300 °C (upper) and 1400 °C (lower) respectively

### 6.3 Thermal Gravimetric Analysis

#### 6.3.1 Introduction

Thermal Gravimetric Analysis is a technique that can monitor the samples' mass change as a function of temperature. A pre-defined heating program heats up samples during the measurement and a balance of high accuracy is used to track the mass change. TGA used in Nanoworld Lab is manufactured by the NETZSCH Company, as shown in Fig. 6.13.
A TGA mainly consists of a balance and a furnace which is used to heat or cool the samples. An inert or reactive gas is used to purge the system. For the characterization of carbon nanotube products, air is the most commonly used purge gas. Amorphous carbon and carbon nanotubes are oxidized at different temperatures based on following reaction. Usually amorphous’ oxidation temperature is lower than that of carbon nanotubes [83], [84].

\[ C + O_2 = CO_2 \]

Therefore, the percentage of amorphous carbon in a CNT sample can be read out from a TGA result. What can also be quantified is the graphitic particles in the sample since they have different oxidation temperatures too. Moreover, since the catalyst metal, usually Fe or Ni, are oxidized during the heating and left as remains after the test, the amount of catalyst can also be identified. [85] TGA as an important characterization method of carbon nanotubes not only denotes the percentage of different compositions in a sample, it also reveals the oxidization stability of carbon nanotubes. [86] Rate of loss of weight is used as an oxidization temperature indicator. Usually, the higher the oxidation temperature is, the more stable the chemical bonding is.

However, TGA is not a very repeatable characterization method so far. A same group of sample may yield different results on different equipment. Different results can be obtained even on the same equipment ran at different time. There are many factors that can affect the result, such as the purge gas, sample preparation process and apparatus, environmental temperature and noise. Researchers have been trying to standardize most of the possible conditions that can influence the result to make the measurement more comparable.
6.3.2 Characterization

The main credit is given to Mr. Rachit Malik for these tests and data. As shown in Fig. 6.14, the TGA curve shows the characterization of CNT sample synthesized on 11/3/2014. The black curve represents the mass loss (TG) and the red curve represents the derivation of loss of weight with respect to temperature (DTG). [87] DTG reaches the largest absolute value at 550.6 °C, which is the CNT oxidation temperature of this sample. When the temperature goes up to 1000 °C, the mass of the sample tends to become steady with a remnant mass of more than 20%. The composition of the remnant mass is mostly iron oxides. This agrees well with the E-Dex test result of the iron concentration.

![TGA curve](image.png)

*Fig. 6.14. TGA of CNT sample synthesized on 11/03/2014*

In November 2014, CNT samples were collected for TGA test. The recipes and experimental conditions can be found in Appendix 2. The purpose of the serial experiments were to investigate the influence of the gas phase pressure/vacuum inside the reactor on the material’s property. The vacuum of inside of the reactor ranged from 0-10 inch of water and the other conditions remain the same. Multiple experiments and tests were conducted with the help of Rachit. All of the tests showed similar carbon oxidation temperature and percentage of iron oxide impurities.
6.4 Mechanical and Electric Properties

6.4.1 Introduction

Mechanical strength is one of the most important macro properties of CNT yarns and sheets. Since CNT has a high theoretical tensile strength, a high strength is also expected from its macro assembly. Therefore, doing the mechanical strength characterization and monitoring the property change in each experiment is very important for the experiment result evaluation. The Instron mechanical property test station used in Nanoworld Lab is shown in Fig. 6.15.

During the mechanical test of carbon nanotubes, CNT yarns and sheet strips are cut into segments that are then fixed on the Instron testing station. The length of the yarns or sheet strips are controlled at 2 cm for the estimation of the ductility of the material, which is characterized by the ultimate strain of the sample. By keying in the cross section area of the sample, which is usually measured by high resolution optical microscope or SEM, the computer can convert the measured force into tensile stress. An ultimate stress was recorded when the sample breaks. The material’s elastic modulus, i.e. Young’s Modulus, can be deduced from the strain and stress based on the following equation.

\[ E = \frac{\sigma}{\varepsilon} \]

Fig. 6.16 shows the measurement of the diameter of a CNT yarn. The measurement was conducted with an optical microscope in Nanoworld Lab. Fig. 6.17 shows a typical tensile strength test graph for four
different samples. CNT yarn has a similar stretching process as the traditional structural material such as steel. The largest stress before was recorded as the tensile strength of the yarn.

Fig. 6.16. Diameter measurement of CNT yarn

Fig. 6.17. A typical tensile strength test graph

The possible application of carbon nanotubes to conductive wires makes the measurement of its electric conductivity another important aspect of the characterization [88]. It was reported that the CNT yarn made from floating catalyst method reached a conductivity of 1.82-2.24 s/cm. This shows a very promising future of carbon nanotube’s practical applications [28].

The method used to measure the electric conductivity is based on the following equation.

\[ k = \frac{L}{RA} \]
Where \( L \) is the length of the sample, \( R \) is the resistance of the sample and \( A \) is the cross section area of the sample.

Therefore, the simplest way of measuring the electric conductivity of a CNT yarn sample is to measure the above mentioned quantities respectively. Usually, a multi-meter, a ruler and a SEM can accomplish the measurement.

An alternatively more easy-to-operate method is the four-probe method, as shown in Fig. 6.18. A constant current is conducted through the CNT sample between the outer two probes. A voltage is measured between the two middle probes. Obviously, the length between the two probes is fixed, which is the length of the sample in test. With the cross section area of the sample known, the electric conductivity can be calculated. If connected with a LabVIEW program, the current going through the sample can be changed continuously and a linear relationship between the voltage and current can be plotted. Therefore, a more accurate resistance can be obtained.

6.4.2 Characterization
CNT samples including yarns and sheets were collected and tested for the research of different experimental parameters and conditions. The main credit should be given to Anli Wang for the tests and data. Precursor fuel with different concentration of water addition was introduced into the reactor to synthesize CNT yarn. These yarns were then tested for their tensile strength and electric conductivity respectively.

As shown in Table 6.1, with the change of water concentration in the fuel, the CNT yarns’ tensile strength increases first and then decreases, with the maximum strength occurs at 1%. The maximum tensile strength is 63.86 MPa, which is the value measured from pristine material without any post processing such as densification and acid washing. A similar dependence of electric conductivity on the water concentration can be observed from the Table 6.1 too. The maximum electric conductivity occurs at 2% of water concentration. This table shows that addition of water has an effect on the material properties, but the data are not enough for making any sound conclusion of the precise relationship between water concentration and CNT yarns’ property. More detailed data need to be collected for further verification.

Table 6.1. Effect of water addition on the CNT mechanical strength

<table>
<thead>
<tr>
<th>Water concentration</th>
<th>Diameter (µm)</th>
<th>Force (N)</th>
<th>Tensile strength (MPa)</th>
<th>Conductivity (s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water 0%</td>
<td>89.02</td>
<td>0.1984</td>
<td>32.58</td>
<td>2.11E+02</td>
</tr>
<tr>
<td>water 1%</td>
<td>73.81</td>
<td>0.3129</td>
<td>63.86</td>
<td>4.15E+02</td>
</tr>
<tr>
<td>water 2%</td>
<td>98.43</td>
<td>0.1749</td>
<td>24.79</td>
<td>6.42E+02</td>
</tr>
<tr>
<td>water 3%</td>
<td>76.23</td>
<td>0.1391</td>
<td>30.78</td>
<td>3.54E+02</td>
</tr>
</tbody>
</table>

Table 6.2 shows the data collected for the research of carrier gas flow rate’s influence on the material’s properties. Argon was used as the carrier gas during the experiments and its flow rates range from 500-2500 sccm.

Table 6.2. Effect of carrier gas flow rate on CNT properties

<table>
<thead>
<tr>
<th>Flow rate (sccm)</th>
<th>Diameter (µm)</th>
<th>Tensile strength (MPa)</th>
<th>Strain (%)</th>
<th>Conductivity (s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>103.02</td>
<td>43.9262</td>
<td>16.35</td>
<td>1.87E+02</td>
</tr>
<tr>
<td>1500</td>
<td>82.42</td>
<td>58.6249</td>
<td>14.20</td>
<td>3.41E+02</td>
</tr>
<tr>
<td>2500</td>
<td>70.56</td>
<td>75.0206</td>
<td>15.34</td>
<td>3.49E+02</td>
</tr>
</tbody>
</table>

Fig. 6.19 are Fig.s plotted based on the experimental result listed in Table 6.2. It shows that the CNT yarns’ tensile strength increases with the carrier gas flow rate and resistivity decreases. Therefore, a higher flow rate should benefit the synthesized material’s properties the most. However, from experiences of the yarn-sheet collection, a complete CNT cylinder can be collected at 1000 sccm and the CNT...
assembly tends to collapse once the flow rate goes above 1000 sccm. That is the reason why a flow rate of 1000 sccm is most often used in the experiments.

Fig. 6.19. Influence of carrier gas flow rate on the sample’s tensile strength (left) and resistivity (right)

![Graph showing the relationship between flow rate and tensile strength and resistivity.]

With the installation of the higher temperature furnace in Nanoworld Lab, CNT yarns synthesized at a series of temperature were collected and characterized. As shown in Fig. 6.20, the increase of the synthesis temperature has a positive effect on the CNT yarn’s strength. The overall strength of the sample yarns are not very high because the samples are pristine and a post processing should increase the property further.

CNT sheets collected by the method described in chapter 6 are usually not densified enough. The loose structure of the pristine sheets reduces the tensile strength and electric conductivity of the material.

Fig. 6.20. Influence of synthesis temperature on the CNT yarn's strength
Therefore, a roller with adjustable loading pressure was employed to roll the CNT sheets. The properties were characterized afterwards, as listed in Table 6.3.

<table>
<thead>
<tr>
<th>Roller distance (negative)</th>
<th>Rolling force (N)</th>
<th>Thickness (mm)</th>
<th>Tensile Strength (MPa)</th>
<th>Conductivity (s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-produced</td>
<td>0</td>
<td>0.0194</td>
<td>28.1134</td>
<td>2.67E+02</td>
</tr>
<tr>
<td>30µm</td>
<td>100</td>
<td>0.0170</td>
<td>17.8551</td>
<td>2.17E+02</td>
</tr>
<tr>
<td>50µm</td>
<td>200</td>
<td>0.0138</td>
<td>25.0182</td>
<td>2.83E+02</td>
</tr>
<tr>
<td>55µm, teflon</td>
<td>250</td>
<td>0.0112</td>
<td>43.0050</td>
<td>3.43E+02</td>
</tr>
<tr>
<td>60µm</td>
<td>300</td>
<td>0.0123</td>
<td>22.4176</td>
<td>3.93E+02</td>
</tr>
</tbody>
</table>

Thickness of the sheets decreases with the roller force increasing except when Teflon film was used together with the CNT sheets to make it easier to peel off the sheets from the roller. The thickness of the roller can be further squeezed because of the presence of the Teflon sheets. In regards of the tensile strength, the maximum strength occurs when the sheet thickness is the smallest. This can be explained by the stronger inter-molecular interactions because of the smaller distance between them as well as the reduced cross section area. For the electric conductivity, the increasing rolling force obviously has a positive effect on the sheets’ conductivity since the mechanical rolling can reduce the bandgap.
Chapter 7 Possible Applications of Carbon Nanotube Materials

Carbon nanotubes have huge application potential in thermally, electrically, mechanically and optically areas [89], [90]. Most of these applications have the possibility to revolutionize human being’s energy consumption pattern, material and device manufacture and micro and nano scale manipulating ability. However, there are some factors that have been preventing the more widespread application of carbon nanotubes. For example, the relatively high cost of synthesis of carbon nanotubes make it not as attractive as traditional low cost material to the industry; the difficulty to fill the gap between the carbon nanotubes’ theoretical properties and experimental results makes the application of carbon nanotubes in some advanced areas immature yet [91], [92].

Table 7.1 lists some of the applications that are being explored in Nanoworld Lab as well as in other labs. With the synthesis of long carbon nanotube using multi-field physics method getting improved gradually, the vast application of carbon nanotubes in but not limited to these direction is expected. Different application emphasizes different property excellence.

Table 7.1. Potential Applications of CNT yarn and sheet

<table>
<thead>
<tr>
<th>Applications</th>
<th>Property Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composite Reinforcement (yarn)</td>
<td>High strength, good electrical and thermal conductivity</td>
</tr>
<tr>
<td>Firefighter Apparel</td>
<td>Good Porosity, good thermal tolerance and conductivity, thermal stability, high heat dissipation</td>
</tr>
<tr>
<td>Conductive Wires for Nano Submarine Control(yarn)</td>
<td>Flexibility, high tensile strength, good electrical conductivity, biocompatibility</td>
</tr>
<tr>
<td>Soft Electronics</td>
<td>Good semi-conductivity, elasticity and flexibility</td>
</tr>
<tr>
<td>Capacitive Energy Storage</td>
<td>Good conductivity</td>
</tr>
</tbody>
</table>

7.1 Cost of Producing Carbon Nanotube Materials

Carbon fibers have been used in industry as the reinforcement fibers of composite material or structural materials. The cost of nanotube fiber is compared to the cost of carbon fiber. According to a sampling of people at a trade show, carbon fiber for automotive use costs $10 to $12 a pound [93]. But to see more widespread adoption in automotive applications, it needs to get down to about $5 or $6 a pound. The cost of manufacturing nanotube material is estimated roughly in Table 7.2. The cost of nanotube material is estimated to be $392/lb. The cost of nanotube sheet and tape is above the cost of high grade...
carbon fiber (about $250/lb), but no other material offers the combination of mechanical and electrical properties of nanotube materials. The cost might be reduced by using lower cost materials (lower purity gases).

Table 7.2. Cost estimation of CNT industrial manufacturing.

<table>
<thead>
<tr>
<th>A. Cost of an ideal reactor:</th>
<th>Housing frame: $5,000; 1700C furnace: $30,000; Industrial computer: $1,000; Ceramic tubes: $1,000; Collecting apparatus, airtight glove box, motor, roller, sensors: $10,000; Electrostatic injection $30K; RF generator $43k; labor $20k. Total price: $140,000. The Cost of Equipment Amortized over a 10 year life is estimated. The cost of equipment is; $140,000/(10yr*1960hr/yr)= $7.14/hr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. Material cost (Retail price of chemicals from Sigma-Aldrich):</td>
<td>Hexane: $137/2L=$0.0685/ml; Methanol: $80/2L=$0.04/ml; Ferrocene: $32.8/100g=$0.328/g; Thiophene: $24.70/100ml=$0.247/ml; Argon gas: $295/cubic feet=$0.083/L. The solution used to produce continuous CNT cylindrical assembly has the following compositions (every100ml): Hexane: 10ml $0.685; Methanol: 90ml $6.165; Ferrocene: 1g $0.328; Thiophene: 0.3ml $0.00741. Therefore, the cost for 100ml solution is $7.19, or $7.19 * 0.8 /100 = $0.0575/min. Argon: 300ml/min $0.025/min. For a normal run, the injection rate of the mixture solution made from the above chemicals is 0.8 ml/min, so the material cost is $0.0825/min or $4.95/hr. The price may vary a little bit with the amount of ferrocene in the fuel. Cost will be lower if Argon 99.999% purity can be replaced by 99.9% purity, or N2. No H2 is needed.</td>
</tr>
<tr>
<td>C. Electricity cost:</td>
<td>Power of furnace: 4 KW; Gas control system: 500W; Solution injection system: 100W; Computer system: 100 W, EFI 100 W, ELS 1000W. So the power of the reactor is 5.8 KW. The industrial electricity price in Ohio state is c6.67/kw h. Therefore, the electricity cost of the reactor is: 5.8 KW * $0.067 / KW*hr = $0.39/h.</td>
</tr>
<tr>
<td>D. Labor cost:</td>
<td>It takes one technician to operate 10 reactors. Thus the labor cost per reactor is 1/10 the salary with benefits, of $80k/yr. The cost of labor per reactor is $8000/1960 hrs= $4.08/hr.</td>
</tr>
<tr>
<td>E. Throughput:</td>
<td>An estimation is made. The mass conversion rate is about 0.4, the mass production of CNT cylindrical assembly will be 19.2g/hr.</td>
</tr>
<tr>
<td>F. Total Cost:</td>
<td>The cost of materials, labor and equipment is: $7.14/hr+ $4.95/hr+ $0.39/hr+ $4.08/hr = $16.56/hr. The cost is: $16.56/hr/19.2 g/hr = $0.86/gram. The cost is $0.86/g * 454 g/lb = $392/lb.</td>
</tr>
</tbody>
</table>

Based on the above estimation, the cost for carbon nanotubes yarns/fibers with floating catalyst method is still relatively high compared with that of carbon fibers. However, with good tuning of the synthesis parameters, the properties of nanotube yarns/fibers can be much preferable than that of carbon fibers, which make nanotube fibers more suitable for the advanced applications mentioned above.
7.2 Composites using CNT super fibers

The expected long carbon nanotubes synthesized by the floating catalyst method, with an individual tube length of 1-2 cm, can be spun into super fibers [94]–[98] or other uses [99]–[101]. Nanotube yarn reinforcement by a method of stitching for composites and composite is expected to prevent the interlaminar shear in composites. Carbon nanotubes have been used to add in composite materials in various forms. One group tried to deposit/coat carbon nanotubes onto the surface of fibers which are reinforcement in composite materials. The addition of carbon nanotubes in this manner changes the interfacial stress behavior and add functionalities to the composite. [102] The other group tried to simulate the effect of employing SWCNT in the epoxy based composite material – carbon nanotube reinforced polymer composites. [15] Research has shown positive effects carbon nanotube has on the strength, flexibility and thermal/electric conductivity of composites. However, the improvement is limited by the length of the individual carbon nanotubes and the common defects.

![Image](a) ![Image](b) ![Image](c)

*Fig. 7.1. CNT yarn (a) and sheet b) synthesized by the multi-field physics CVD method; (c) shows the CNT reinforced fiber’s effect on the micro alignment of composites (Polymer/carbon nanotube nano composite fibers-A review).*

CNT yarn synthesized by floating catalyst methods has achieved the tensile strength of more than 4 GPa and conductivity of $2 - 3 \times 10^4 \text{ S} \cdot \text{cm}^{-1}$ [28]. With the implementation of multi-field physics method, the CNT assemblies’ overall properties could be further improved because of less defects as well longer
individual tubes. Internamilar shear failure of composites, also called delamination crack, is induced initially by interlaminar normal stress. And during the growth of delamination crack, direction parallel to the reinforcement fibers becomes the weakest direction [103]. Delamination can reduce the stiffness and reliability of the composite material. However, with the improved strength of CNT super fibers, delamination resistance can be significantly improved. Besides the mechanical strength improvement, the addition of CNT super fiber can also improve the material’s thermal stability, thermal conductivity, electrical conductivity and chemical resistance [104].

7.3 Firefighter Apparel

The composite material team in Nanoworld Lab has discovered that carbon nanotube fabric has high heat dissipation and fire resistance. This means that carbon nanotubes can be employed for new multi-purpose fabric for firefighter applications. Two forms of bulk fabric are considered, non-woven sheet and woven/stitched sheet using nanotube yarn. Nanotube fabric can be coated or laminated between existing fabrics to protect the nanotube layer. The nanotube fabric has high thermal conductivity and can wick perspiration, increase evaporation, and cool the skin. Nanotube fabric has anisotropic heat conduction and can direct heat to an optional cold pack to increase cooling.

![Graph and Images]

*Fig. 7.2. Water evaporation test with four fabrics, (a) pristine nanotube sheet, (b) functionalized nanotube sheet, (c) cotton fabric, (d) wicking commercial performance sportswear*

Some initial tests were done by Albert Song, a post doctor in Nanoworld Lab. As shown in Fig. 7.2, four different or differently processed fabrics were soaked with water and placed in the same condition for evaporation. The trend is nitric acid functionalized CNT sheet has a high water evaporation rate for these specific test conditions. Some properties of carbon nanotube sheet important for firefighter apparel application are listed in table 6. The properties that are expected to be achieved in the near term are listed in Table 7.3. The properties are based on properties in the literature and are expected to be the minimum properties achievable. Material properties optimization and post-processing methods are in progress. The
EFI and EMS methods are expected to improve the properties in Table 3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Planned Application Areas</th>
<th>Sheet</th>
<th>Tape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (GPa)</td>
<td>Composites, Biomedical</td>
<td>0.5</td>
<td>2 – 4</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>Composites</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Strain to failure (%)</td>
<td>Composites</td>
<td>8 depending on pre-stretching</td>
<td>4</td>
</tr>
<tr>
<td>Electrical Resistivity (ohm cm)</td>
<td>Low resistivity needed for Power, Biomedical wires</td>
<td>1x10^4</td>
<td>5x10^5</td>
</tr>
<tr>
<td>Thermal Conductivity W/(mK)</td>
<td>Firefighter, Composites</td>
<td>30 as-produced isotropic or 100 stretched in one direction in-plane; 1-2 normal to the plane (0.04 if sheet is loosely packed w/air)</td>
<td>160 in axial direction</td>
</tr>
<tr>
<td>Sheet Resistance (ohm/square)</td>
<td>Composites for EMI shielding or static discharge</td>
<td>0.2 (depends on acid treatment, stretching, direction)</td>
<td>NA</td>
</tr>
<tr>
<td>Seebeck Coefficient (microV/K)</td>
<td>Sensing or Energy Harvesting on surfaces with large ΔT</td>
<td>-60 n type, 70 p type (potentially up to 300)</td>
<td>Not measured</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>Composites, EMI shielding</td>
<td>0.4, depends on densification</td>
<td>1.2</td>
</tr>
<tr>
<td>Burning Temperature in Air (deg C)</td>
<td>Firefighter garment</td>
<td>High resistance to flame</td>
<td>640</td>
</tr>
<tr>
<td>Specific Surface Area (m^2/g)</td>
<td>Water and air filter</td>
<td>~250</td>
<td>~50</td>
</tr>
</tbody>
</table>

Nanotube fabric is also multi-purpose. It spreads heat to provide uniform isotropic cooling through conduction, convection and radiation, it discharges static electricity, has low specific heat (low thermal mass), is flame resistant, thin, lightweight, and has a large effective surface area. It can also have high capillarity to wick perspiration away from the body, and permeability to breathe and evaporate perspiration. The fabric can be strong, tough, or moderately elastic by adjusting fabrication parameters. The new fabric will be evaluated to reduce core body temperature, prevent local high heat flux and hot spots, provide burn protection, and reduce heat stress for firefighters.

7.4 Medical Nano Submarine

UC Nanoworld Lab is also developing a medical nano submarine. Electric suture thread based on carbon nanotubes is one of the key components of the system. Suture thread is fine carbon wire for use inside the body and percutaneous (across the skin) for sensing, power delivery, replacing pacemaker wire, antennas, flexible, pliable, soft, strong, electrically and thermally conductive, biocompatible, non-thrombogenic replacement for metal wire. The research in the electric suture thread can actually bring about more
meaningful applications. Once succeeded, the body can be powered for temporary and semi-permanent applications which will open up new diagnostics and therapies for many indications and for sensing, electrodes, scaffolds, and actuation. Eventually artificial organs and computers will be integrated in the body using electrical suture thread.

The submarine has mm to sub-mm size magnetic body with a tether. The submarine is moved in the direction of blood flow to investigate areas of the circulatory system that may be too small or not accessible by catheters. The tether is formed using electrical suture thread manufactured in UC Nanoworld by applying a dielectric coating to carbon nanotube yarn. In the future, the thread may be braided or hollow to deliver drugs or sample fluids. The tether is also used to communicate with the submarine. The submarine is envisioned to house a small sensor to measure different parameters in vivo in locations where conventional sensors cannot reach. The submarine is delivered and removed by a catheter where the tether replaces the inner wire of the catheter. Blood flow carries the submarine which is turned using an external strong magnet. Navigating the submarine is envisioned using fluoroscopy, or sending an RF signal from the submarine, or tracking using external ultrasound. The submarine has been tested on the bench in a flow system. The tether is made of Carbon Nanotube thread and will be coated with biocompatible polymers approved by FDA. This will eliminate any concerns about toxicity of nanotubes. Using carbon nanotube yarn as the navigation and signal transmission wire for medical nano submarine can bring about breakthrough in the healthcare research. Sensing and delivery of drugs in locations in the vascular highway that have been inaccessible previously. Potentially actuating devices could be designed into the submarine to perform cleaning, micro-surgery, or removal of stents.

Nanoworld Lab has several possible cooperation partners in this research, including Children’s Cancer for proton radiation monitoring (with John Perentesis); Intravascular cancer diagnostics and therapy (with Denise Adams); Cancer Sensing in the lung using impedance sensing or liquid biopsy (with Sandra Starnes); Pathobiology and infectious disease in vitro sensing using a micro sensor (with Melanie Cushion, Sarah Pixley); and Cancer diagnostics (with Dr. Zhongyun Dong).

Besides the applications mentioned above, ultra-long carbon nanotubes can be used for other applications too. For example, the fluffy cylindrical CNT assembly could be used to make air and water filter thanks to its nanoscale porous structure; CNT super fiber could be a good feeding thread for 3-D printing and its good thermal and electric conductivity add unique properties to the printed objects; the conductive CNT yarn can be used as electrodes directly and made into flexible capacitors, which has demonstrated promising energy and power density by other groups.
Chapter 8 Conclusions and Future Work

The engineering and scientific research describe in this thesis all aims to synthesize long and strong carbon nanotubes by the proposed multi-field physics approach. The main work was on a floating catalyst reactor that gradually built up from scratch. These research mainly includes the following aspects:

- Build up a strong electromagnet that can generate a 1.5T magnetic field at room temperature, which creates a good condition for the bench test of the nanoparticle levitation hypothesis.
- Bench test of the nanoparticles levitation; using RF coils to levitate CNT bundles and nanoparticles; integration of the reactor and the RF coils.
- Design and building the floating catalyst reactor which provides a platform for the multi-field physics approach; gradual perfection of the system including LabVIEW control of the gas flow system, installation of the glovebox, experiments of a stable and effective injection system; design and building an effecting yarn and sheet colleting apparatus.
- Chemical recipe development for the synthesis of cylindrical CNT assembly; test of chemical additions in the precursor fuel.
- Various characterization of the carbon nanotubes from floating catalyst method.

Table 8.1 was suggested as a summary of the parameters influencing the synthesis process and their working mechanisms.

<table>
<thead>
<tr>
<th>Experimental Parameters</th>
<th>Working Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis temperature</td>
<td>Amount of carbon atoms available; mobility of carbon atoms and thus reaction rate</td>
</tr>
<tr>
<td>Fuel injection method</td>
<td>Affects how dispersed the catalyst and promoter particles are and their agglomeration</td>
</tr>
<tr>
<td>Fuel injection location</td>
<td>Affects the Mean Free Path (MFP) of catalyst and promoter particles and thus their agglomeration</td>
</tr>
<tr>
<td>Fuel injection rate</td>
<td>Carbon/Iron/Sulfur atoms concentration</td>
</tr>
<tr>
<td>Carrier gas flow rate</td>
<td>Flow pattern in the reaction tube and concentration of chemicals</td>
</tr>
<tr>
<td>Chemical addition</td>
<td>Enhance/weaken a certain reaction step (removing amorphous carbon, prevent volume diffusion of carbon atoms in catalyst particles)</td>
</tr>
<tr>
<td>Reactor pressure/vacuum</td>
<td>Affects carbon atoms concentration</td>
</tr>
</tbody>
</table>

This research is only a beginning of the multi-field physics approach for the ultra-long carbon nanotube synthesis. There are still some fundamental and creative hypothesis need to be further tested on the reactor to improve the properties of the CNT assembly. Following are some but not all of the possible areas for further exploration:
Fig. 8.1 shows the setup of the new furnace. The operation procedure of the new reactor is basically the same as the 1200 °C reactor. The higher synthesis temperature definitely has a positive influence on the properties of the CNT assembly, as discussed in chapter 6. Some more engineering work needs to be done on the new furnace.

Implementation of multi-field approach to the reactor. In a traditional floating catalyst CVD reactor, the forces that carry the particles include a pushing force caused by the thermal gradient in the radius direction and a flow dragging force that can be decomposed into a vertical and a horizontal component. These forces can be employed to control the particles and therefore the CNT assembly’s movement in the reaction tube.
As described before, a RF coils will be installed on the reactor to an additional dimension of controlling the particles’ movement. A high frequency coil is introduced to generate eddy current in both catalyst particles and the CNT cylinder. The force on catalyst particles and the nanotube mat depend on the frequency, number of turns, coil length, and current used to create the magnetic field. The multi-field method could have better effects if the electrostatic sprayer is implemented together. The electric charge carried by the particles will make it easier to gain a magnetic force form the magnetic field.

- More chemical recipes and experimental parameters are to be experimented with. Thiophene has been used as the reaction promoter provider. A gas phase promoter, SF₆, is to be tested. Even better, no sulfur addition recipe could be tested and the absence of sulfur should generate cleaner carbon nanotubes. As for the catalyst, catalyst source such as Fe(OH)₃ will possibly generate long CNT without introducing excessive Fe impurities. Experimental parameters such as degree of vacuum in the reactor, carrier gas flow rate at high synthesis temperature needs to be tuned too.

The following tasks are recommended in order to enable commercialization of nanotube materials.

- **Properties Improvement.**
- **T1. Evaluate growth with catalyst on a high temperature substrate.** Use a ceramic substrate to grow CNT in the high temperature reactor to understand if nanotube quality increases with high temperature of if the substrate is the main factor for low quality (waviness, defects) or time in the reactor is the major factor.
- **T2. Investigate Temperature Effect on Nanotube Properties.** Synthesize nanotubes from 1200 C to 1700 C (or as high as possible up to 1700 C) and evaluate nanotube tape and sheet quality. Tune the process parameters to understand how temperature affects the optimal fuel ratio,
thiophene and water concentrations, and the quality of the nanotubes. Study how temperature can control the number of walls, diameters, and chirality of nanotubes.

- **T3. Evaluate post-processing methods.** Post processing including acid cleaning, rolling, and stretching will be used to increase the properties of nanotubes.

- **T4. Modeling.** Molecular dynamics will be used to model the strength of nanotube sheet and yarn without twisting and only nanotube length, diameter, and impurities affect properties. Flow modeling using COMSOL will be used to predict the optimal injection rates for different temperatures.

- **T5. Fuel Injection.** Investigate electrostatic fuel injection (EFI) in combination with the high pressure injector.

- **T6. Levitation.** Investigate the electromagnetic levitation system (ELS) in combination with EFI.

- **T7. Fuel Composition.** Study nucleation efficiency using different fuels with promoters and additives.

- **Application Orientated Synthesis.**

- **T8. Sheet Manufacturing.** A translating carriage will be built and a belt system fabricated so that large sheet can be manufactured for the textile and composites applications.

- **T9. Fuel Doping.** This is to add activator particles to the fuel to decorate the nanotubes for water and air filtering applications.

- **T10. Strong Tape.** Fabricate laminated composites with nanotube tape reinforcement. Tape should be strong and tough.
Appendix 1. Images of Multi-field Physics Reactor
Fig. A.1. Images of the multi-field physics reactor. (a) overview of the reactor with Faraday cage, door closed; (b) overview of the reactor with door open, 1200 °C furnace installed; (c) left end of the reactor for fuel and gas introduction; (d) left end of the reactor, glove box installed for the material collection; (e) cylinder gas and exhaust system; (f) mass flow controllers.
Appendix 2. Experiment Documentation

A2.1 Experiment Log

Following tables show part of the experiment log record during the early stages of experimental parameters and chemical recipe tests.

<table>
<thead>
<tr>
<th>Date</th>
<th>Temp. (°C)</th>
<th>Injection Rate (ml/min)</th>
<th>Argon Flow Rate (sccm)</th>
<th>Ferrocene Wt%</th>
<th>Thiopene Wt%</th>
<th>Ethanol Wt%</th>
<th>Result</th>
<th>Suction (inch water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>08/02/2014</td>
<td>1000</td>
<td>manually</td>
<td>800</td>
<td>1</td>
<td>0.3</td>
<td>98.7</td>
<td>CNT detected</td>
<td></td>
</tr>
<tr>
<td>08/08/2014</td>
<td>1100</td>
<td>4</td>
<td>500</td>
<td>1</td>
<td>0.3</td>
<td>98.7</td>
<td>CNT detected</td>
<td></td>
</tr>
<tr>
<td>08/15/2014</td>
<td>1100</td>
<td>0.25 (evaporated before droplet formation)</td>
<td>800</td>
<td>1</td>
<td>0.3</td>
<td>98.7</td>
<td>CNT detected, good</td>
<td></td>
</tr>
<tr>
<td>08/18/2014</td>
<td>1100</td>
<td>0.25 (one needle ferrocene, syringe ethanol)</td>
<td>300</td>
<td>1</td>
<td>0.3</td>
<td>98.7</td>
<td>No CNT, carbon particles</td>
<td></td>
</tr>
<tr>
<td>08/20/2014</td>
<td>1150</td>
<td>0.8</td>
<td>400</td>
<td>0.3</td>
<td>0.3</td>
<td>99.4</td>
<td>No CNT</td>
<td>0.92</td>
</tr>
<tr>
<td>08/22/2014</td>
<td>1150</td>
<td>0.25</td>
<td>500</td>
<td>2 (precipitation)</td>
<td>0.3</td>
<td>97.7</td>
<td></td>
<td>0.92</td>
</tr>
<tr>
<td>08/24/2014</td>
<td>1150</td>
<td>0.6</td>
<td>1000</td>
<td>2</td>
<td>0.3</td>
<td>Hexane+methanol 97.7</td>
<td>Centimeter long fiber</td>
<td>0.9</td>
</tr>
<tr>
<td>08/25/2014</td>
<td>1150</td>
<td>0.6</td>
<td>3000</td>
<td>2</td>
<td>0.3</td>
<td>Hexane+methanol</td>
<td>No CNT; Small</td>
<td>0.9</td>
</tr>
<tr>
<td>Date</td>
<td>Temp. (°C)</td>
<td>Growth Time (min)</td>
<td>Injection Rate (ml/min)</td>
<td>Argon Flow Rate (sccm)</td>
<td>Ferrocene Wt%</td>
<td>Thiopehe Wt%</td>
<td>Ethanol Wt%</td>
<td>Result</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>-------------------</td>
<td>-------------------------</td>
<td>------------------------</td>
<td>----------------</td>
<td>--------------</td>
<td>-------------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>08/26/2014</td>
<td>1150</td>
<td>3</td>
<td>3000</td>
<td>2</td>
<td>0.3</td>
<td>Hexane+methanol 97.7</td>
<td>Little fiber</td>
<td>0.9</td>
</tr>
<tr>
<td>08/28/2014</td>
<td>1150</td>
<td>0.64</td>
<td>1.6</td>
<td>1.6</td>
<td>1</td>
<td>1.6</td>
<td>1.6</td>
<td>98.7</td>
</tr>
<tr>
<td>08/29/2014</td>
<td>1200</td>
<td>0.64</td>
<td>3000</td>
<td>2</td>
<td>0.3</td>
<td>Hexane+methanol 97.7</td>
<td>No CNT or Amorphous carbon</td>
<td>0.2</td>
</tr>
<tr>
<td>08/31/2014</td>
<td>1200</td>
<td>10</td>
<td>0.8</td>
<td>800</td>
<td>2</td>
<td>0.3</td>
<td>Hexane+methanol 97.7)</td>
<td>Large area of CNT films and fiber at both ends</td>
</tr>
<tr>
<td>09/02/2014</td>
<td>1200</td>
<td>10</td>
<td>0.8</td>
<td>500</td>
<td>2</td>
<td>0.3</td>
<td>Hexane+methanol 97.7)</td>
<td>CNT smoke/large films found full of the tube</td>
</tr>
<tr>
<td>Date</td>
<td>Temperature</td>
<td>Time</td>
<td>Flow Rate</td>
<td>Pressure</td>
<td>Gas Composition</td>
<td>Result</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>-------------</td>
<td>-------</td>
<td>-----------</td>
<td>----------</td>
<td>---------------------</td>
<td>----------------------------------------------------------------------</td>
<td>------------------------------</td>
<td></td>
</tr>
<tr>
<td>09/09/2014</td>
<td>1200</td>
<td>15</td>
<td>0.8</td>
<td>500</td>
<td>2</td>
<td>Hexane+methanol (97.7)</td>
<td>CNT smoke</td>
<td>0.1</td>
</tr>
<tr>
<td>09/09/2014</td>
<td>1200</td>
<td>15</td>
<td>0.64</td>
<td>500</td>
<td>2</td>
<td>Hexane+methanol (97.7)</td>
<td>Huge CNT smoke</td>
<td>0.1</td>
</tr>
<tr>
<td>09/10/2014</td>
<td>1200</td>
<td>15</td>
<td>0.48</td>
<td>400</td>
<td>1</td>
<td>Hexane+methanol (97.7)</td>
<td>Huge CNT smoke; no observable magnetic effect</td>
<td>0.06</td>
</tr>
<tr>
<td>09/12/2014</td>
<td>1200</td>
<td>10</td>
<td>1.92</td>
<td>400</td>
<td>2</td>
<td>Ethanol (97.7)</td>
<td>Mainly amorphous carbon was grown.</td>
<td>0.07</td>
</tr>
<tr>
<td>09/13/2014</td>
<td>1150</td>
<td>10</td>
<td>0.8</td>
<td>500</td>
<td>2</td>
<td>Hexane+methanol (97.7)</td>
<td>Similar result to temperature at 1200, large CNT sock</td>
<td>0.07</td>
</tr>
<tr>
<td>09/18/2014</td>
<td>1150</td>
<td>20</td>
<td>0.8</td>
<td>600</td>
<td>2</td>
<td>Hexane+Methanol (97.7)</td>
<td>A little CNT film was collected</td>
<td>0.07</td>
</tr>
<tr>
<td>09/22/2014</td>
<td>1150</td>
<td>20</td>
<td>0.8</td>
<td>500</td>
<td>2</td>
<td>Hexane+Methanol (97.7)</td>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td>10/09/2014</td>
<td>1200</td>
<td>10 min</td>
<td>0.96 ml/min</td>
<td>500 sccm</td>
<td>0</td>
<td>Tolune+ferrocene C:Fe (1000:3)</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>10/14/2014</td>
<td>1200</td>
<td>10 min</td>
<td>0.05*16 ml/min floating</td>
<td>0-1000 sccm</td>
<td>0</td>
<td>Tolune+ferrocene C:Fe (1000:3)</td>
<td>CNT cylindrical assembly produced as Shanghai group</td>
<td>0.1~0.9</td>
</tr>
<tr>
<td>Date</td>
<td>Time</td>
<td>Duration</td>
<td>Flow Rate</td>
<td>Rotation</td>
<td>Concentration</td>
<td>Result</td>
<td>Notes</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>----------</td>
<td>-----------</td>
<td>----------</td>
<td>---------------</td>
<td>-------------</td>
<td>-----------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>10/16/2014</td>
<td>1200</td>
<td>10 min</td>
<td>0.05*16 ml/min floating</td>
<td>0-1000 sccm</td>
<td>0</td>
<td>Tolune+ferrocene C:Fe (1000:3)</td>
<td>Result like Shanghai</td>
<td></td>
</tr>
<tr>
<td>10/17/2014</td>
<td>1200</td>
<td>30</td>
<td>0.05*16 ml/min</td>
<td>500 sccm</td>
<td>2</td>
<td>0.3 (Hexane+Methanol)</td>
<td>Successful spinning</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>30</td>
<td>0.05*16 ml/min</td>
<td>500 sccm</td>
<td>1</td>
<td>0.3 (Hexane+Methanol)</td>
<td>Successful spinning</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>30</td>
<td>0.05*16 ml/min</td>
<td>500 sccm</td>
<td>0.5</td>
<td>0.3 (Hexane+Methanol)</td>
<td>Successful spinning</td>
<td></td>
</tr>
<tr>
<td>10/19/2014</td>
<td>1200</td>
<td>30</td>
<td>0.05*16 ml/min</td>
<td>500 sccm</td>
<td>1</td>
<td>0.3 (Hexane+Methanol)</td>
<td>Successful spinning</td>
<td></td>
</tr>
<tr>
<td>10/23/2014</td>
<td>1200</td>
<td></td>
<td>0.05~0.08*16 ml/min</td>
<td>50-500</td>
<td>0.5 ferrocene+0.5 GaCl3</td>
<td>0.3 (Hexane+Methanol)</td>
<td>Sock rises to attach to the outlet of the tube; needle easy to be clogged; fiber spinned seemed thinner and stronger.</td>
<td></td>
</tr>
<tr>
<td>10/24/2014</td>
<td>1200</td>
<td></td>
<td>0.05~0.08*16 ml/min</td>
<td>100-500</td>
<td>0.15</td>
<td>0.3 (Hexane+Methanol)</td>
<td>Only short fibers and particles; No continuous</td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Volume Range</td>
<td>Flow Rate</td>
<td>Reactant Molar Ratio</td>
<td>Solvent</td>
<td>Observation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>--------------</td>
<td>-----------</td>
<td>----------------------</td>
<td>------------------------</td>
<td>--------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/25/14</td>
<td>0.05–0.12*16 ML/min</td>
<td>50-500</td>
<td>2:1 Fe:Ga(ac)</td>
<td>Hexane+Methanol</td>
<td>Small amount of sock, not continuous sock</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 ferrocene</td>
<td></td>
<td>No continuous sock</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2:1 Fe:Ga(ac)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
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<td></td>
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</tr>
<tr>
<td>10/25/14</td>
<td>0.05–0.12*16 ML/min</td>
<td>50-500</td>
<td>2:1 Fe:Ga(ac)</td>
<td>Hexane+Methanol</td>
<td>Small amount of sock, not continuous sock</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 ferrocene</td>
<td></td>
<td>No continuous sock</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 ferrocene</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>2:1 Fe:Ga(ac)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10/28/14</td>
<td>0.05-0.07*16 ML/min</td>
<td>200 (motor 55RPM)</td>
<td>2:1 Fe:Ga(ac)</td>
<td>Hexane+Methanol</td>
<td>Thin continuous sock; Continuous sock spinned</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.5 ferrocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/05/14</td>
<td>1200</td>
<td>8</td>
<td>2:1 Fe:Ga(ac)</td>
<td>Hexane+Methanol</td>
<td>Sock formed, didn’t see the sock on spike wires, which means that Metal spikes are used to</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Time</td>
<td>Flowrate</td>
<td>Temperature</td>
<td>Ferrocene</td>
<td>Solution</td>
<td>Result</td>
<td>Comments</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>----------</td>
<td>-------------</td>
<td>-----------</td>
<td>----------</td>
<td>--------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>11/09/14</td>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene</td>
<td>0.2</td>
<td>Hexane+Methanol</td>
<td>No sock formation; black carbon smoke was observed</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene</td>
<td>0.1</td>
<td>Hexane+Methanol</td>
<td>Didn’t try</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene</td>
<td>0.05</td>
<td>Hexane+Methanol</td>
<td>Didn’t try</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene Fe:Gd 4:1</td>
<td>0</td>
<td>Hexane+Methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene Fe:Gd 8:1</td>
<td>0</td>
<td>Hexane+Methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/10/14</td>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene</td>
<td>0.4/0.6/0.8</td>
<td>Hexane+Methanol</td>
<td>No sock formation; black carbon smoke was observed</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>0.05*16 ML/min</td>
<td>-</td>
<td>1% ferrocene Fe:Gd 4:1</td>
<td>0.3</td>
<td>Hexane+Methanol</td>
<td>Even the solution color changed, it could generate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Time</td>
<td>Flow Rate</td>
<td>Injection</td>
<td>Ferrocene (%)</td>
<td>Solvent</td>
<td>Description</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------</td>
<td>-----------</td>
<td>-----------</td>
<td>---------------</td>
<td>----------------</td>
<td>----------------------------------------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/13/14</td>
<td>1200</td>
<td>0.05*16</td>
<td>-</td>
<td>1%</td>
<td>Hexane+Methanol</td>
<td>Adding water generate thinner sock</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ML/min</td>
<td></td>
<td>0.3</td>
<td>0.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11/14/14</td>
<td>1200</td>
<td>0.05*16</td>
<td>-</td>
<td>1%</td>
<td>Hexane+Methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ML/min</td>
<td></td>
<td>0.3</td>
<td>0.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.0% water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Date</td>
<td>Temp. (°C)</td>
<td>Growth Time (min)</td>
<td>ESS injection distance from furnace (ring-ring-nozzle) inch</td>
<td>Voltage</td>
<td>Injection Rate (ml/min)</td>
<td>Argon Flow (sccm)</td>
<td>Ferrocene Thiophene (%)</td>
<td>Methanol Hexane Wt%</td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
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<td>-------------------------------------------------------------</td>
<td>---------</td>
<td>-------------------------</td>
<td>------------------</td>
<td>--------------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>03/25/2015</td>
<td>1200</td>
<td>xx</td>
<td>2-8.1-9.5</td>
<td>20kV</td>
<td>(0.03-0.05)*16</td>
<td>1000</td>
<td>1/0.3</td>
<td>90/10</td>
</tr>
<tr>
<td>03/27/2015</td>
<td>1200</td>
<td>xx</td>
<td>2-9.5/8-11</td>
<td>20kV</td>
<td>(0.03-0.05)*16</td>
<td>1000</td>
<td>1/0.3</td>
<td>90/10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2-9.5/8-10.1/4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>03/30/2015</td>
<td>1200</td>
<td>15min</td>
<td>2-9-10</td>
<td>17-20K (~25mA with peaks when discharge)</td>
<td>(0.05-0.08)*16</td>
<td>500-1500</td>
<td>1/0.3</td>
<td>90/10</td>
</tr>
</tbody>
</table>
A2.2 Reactor Operation Procedure and Safety Manual

Running Procedure:

1. KMS 247 unit should be turned on 1 hour before running the furnace to warm up the mass flow controllers (MFCs). So it should be the first operation to conduct if the furnace is going to be used on the specific day.
2. Install syringe or atomizer if any liquid is going to be injected.
3. Close all the valves except the one connecting air pump and pressure meter on the right end. Pump air manually to reach a 10 in of water vacuum. Then turn on the valve for argon introduction and set argon to the highest flow rate to bring down the vacuum to atmosphere pressure.
4. Close the valves connecting pressure meter and air pump and open the rest valves. Key in the gases flow recipe and temperature curve in computer and furnace respectively. And turn on the gases and heating simultaneously.
5. Start injecting fuel and adjust the argon flow rate to proper value. Turn on the motor and start collecting materials.
6. When the experiment is finished, turn off the motor, furnace and gas flow.
7. In the cooling stage, the furnace lid cannot be open unless the temperature reading is below 200 °C.
8. Clean the reactor and remove the samples when the reactor is cool.

Carbon cleaning procedure:
Since the reaction tubes, ceramic tube and quartz tube that is used in Floating Catalyst CVD Reactor (FCR) is relatively long, it has to be cleaned in two steps with the same heating process.

1. Open the right end of the tube by detaching it from the soft connector; Remove the o-ring, washer and screw cylinder form the quartz tube.
2. Move the right-end cross to the very right end, push the furnace to right until most of the black part of the quartz tube is within the furnace heating zone.
3. Keep the left end connected so the suction will stay on.
4. Run the heating process to clean the tube: 0 ℃ → 30 mins → 900 ℃ → 20 mins → 900 ℃ → −121 (natural cooling and stop code).
5. After the right-end tube is cleaned, open the left end connect and turn around the quartz tube. Connect the left end so that the black part of the tube is still in the heating zone.
6. Run the heating process again as in step four.
Iron/sulfur cleaning procedure for quartz tube:
After the carbon is burned in air, there is usually some red iron oxides and sulfur left on the inner wall of the tube. For quartz tube, it is better to remove these impurities. For ceramic tube, these remnant material doesn’t affect the experiment since there is no need to view the reaction through the tube. HCl is more effective than HNO₃ in cleaning the remnant Iron Oxide on the quartz tube. A 2.5 L HCL can be used for around 10 times.

1. Fix the tube with a stand clamp vertically and close the bottom opening with a plug. Pour in 35% HCL solution until half of the tube is immerse in it.
2. Wait for 2 hours before taking off the tube and set it upside down. Put it back and wait for another two hours.
3. After taking the tube off the stand clamp, pour the HCL solution back into the chemical container for recycling use. Wash the tube with water and use brush to get rid of any left stains on the inner surface.
4. Wait for the tube to be dry before put it back to the furnace for experiments.

Safety Manual (by Michael Schulz, Dr. Vesselin Shanov, Dr. Mark Schulz)

Section One – Introduction
Safety is the most important consideration when working in the labs. The Nanoworld Laboratories has a safety manual for general use of the labs. The present manual (Carbon Nanotube Synthesis using Reactor 4) covers special safety procedures that must be followed when performing carbon nanotube synthesis using Reactor 4 in 611 Rhodes Hall. The present manual is a supplement to the general manual.

Section Two – Basic Safety Rules
1. Carbon nanotubes are a potentially hazardous material.
2. Students must wear gloves, masks, and lab coats when working with nanotubes.
3. Students should avoid skin contact with nanotubes and always wash hands after experiments.
4. Carbon nanotubes are never to become airborne or free on bench tops.
5. Any equipment or surfaces that come in contact with nanotubes must be wiped thoroughly. A vacuum cleaner with special filter is available in Nanoworld and should be used for cleaning areas where nanotubes or nanotube residue may collect.

6. No food or drinks in lab
7. Wear goggles and coat in lab at all times and mask/gloves if needed
8. A nano-camera records activity in all the Nanoworld labs
9. Know safety procedures, eyewash, fire extinguishers use, read the general safety manual
10. Keep manuals with tools or in black cabinet
11. Properly use tools and return to toolbox daily
12. Use storage boxes to keep personal experimental items
13. Know where tools and supplies are
14. Fume hood use with clean gloves in glove box, do not contaminate gloves in glove box
15. Get manuals on line or in black cabinet for instrumentation

Section Three – Special Procedures for working with Reactor 4

Reactor 4 is for gas phase synthesis of carbon nanotubes. This reactor has high temperature, high voltage applied to the ceramic tube, flammable liquids, and high frequency signals depending on the configuration of the reactor. Nanotubes are also released into a glove box. Therefore the following procedures and precautions must be followed when operating the reactor.

1. No combustible materials should be stored near the reactor.
2. Ar gas should be turned on to purge oxygen from the reactor and glove box before any fuel being injected. The oxygen level should be below TBD (4% suggested by Dr. Lashmore). The glove box should have a slight vacuum (1 inch water) or it may have a slight pressure (1 inch water). The furnace vacuum should be checked before every run using the vacuum gage on the reactor inlet with the system closed. Then vacuum should be checked using the manometer in the glove box.
3. If electrostatic fuel injection (EFI) is used, the system should be set up and the reactor run without touching the reactor or using the gloves in the glove box. All parts of the reactor should be well grounded.
4. If RF coils are used, the doors of the reactor should be closed always and a metal mesh (removable) must be put over the ends and back of the reactor. A sensor (TBD) should be used to check if there is any EM leaks from the reactor.
5. Nanotubes accumulate in the glove box. The glove box should be cleaned by using the gloves and paper towels and spray. Spray the inside of the glove box with a cleaner to prevent the nanotube from becoming airborne. Then wipe with the towels. Dispose of the paper towels in a plastic bottle for nanotube waste.

6. When removing the nanotube yarn or sheet always put the nanotube material in a closed container and label the container (plastic box).

7. When making electrical measurements from inside the glove box, set up all connections and then run the experiment without touching the metal rod or conductors to avoid possible electrical shock.

8. All the holes drilled on the glovebox for electric connection must be tightly sealed.

9. The filter in the outlet of the reactor may collect nanotubes. The filter should be changed when needed (if the manometer suction decreases indicating the outlet is getting restricted). The outlet tubing can be disconnected and any open tube covered. The filter can be removed and put in plastic and disposed of following the procedure for disposing nanotube materials.

10. At times the exhaust tubing from the glove box may need to be cleaned. The procedure is to remove the tube, cover the ends, take the tube to the fume hood in 507 Rhodes Hall, spray the tube with a cleaner and then wipe with paper towels. Dispose of the paper towels by putting the towels in a plastic bottle and have removed as nanotube waste.

11. UC Health and Safety and NIOSH will check lab for safety (air and desk samples)

12. Lab coats should be cleaned as arranged by the lab directors.

13. If acid is used in the glove box it should labeled and covered after each use.

14. All experiments in 611 RH should be listed in a note book or in the online experiment log.

A2.3 Arduino Programming

```c
#include <Stepper.h>

const int pwmA = 3;
const int pwmB = 11;
const int brakeA = 9;
const int brakeB = 8;
const int dirA = 12;
const int dirB = 13;
```
// The amount of steps for a full revolution of your motor.
// 360 / stepAngle
const int STEPS = 800;
// Initialize the Stepper class
Stepper myStepper(STEPS, dirA, dirB);

void setup() {
  // Set the RPM of the motor
  myStepper.setSpeed(6);

  // Turn on pulse width modulation
  pinMode(pwmA, OUTPUT);
  digitalWrite(pwmA, HIGH);
  pinMode(pwmB, OUTPUT);
  digitalWrite(pwmB, HIGH);

  // Turn off the brakes
  pinMode(brakeA, OUTPUT);
  digitalWrite(brakeA, LOW);
  pinMode(brakeB, OUTPUT);
  digitalWrite(brakeB, LOW);

  // Log some shit
  Serial.begin(9600);
}

void loop() {
  // Move the motor X amount of steps
  myStepper.step(1*STEPS);
  Serial.println(-1*STEPS);
  while (0);
}
A2.4 LabVIEW Graphic Programming Structure

First half of the background structure of the LabVIEW program
References


W. Cho and M. Schulz, “Growth termination mechanism of vertically aligned centimeter long carbon nanotube arrays.”


[78] “http://www.uccs.edu/~tchriste/courses/PHYS549/549lectures/plasma.html.”.


