PROCESSING OF MULTI-WALLED CARBON NANOTUBES AS MAGNETIC ADDITIVES FOR POLYMER NANOCOMPOSITES

A Thesis in
Aerospace Engineering
by
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Abstract

Magnetic nano-additives for polymer nanocomposites are achieved using multi-walled carbon nanotubes (MWCNTs) by functionalizing with oxygen plasma and by coating with ferromagnetic nickel (Ni) layers. CNT-polymer nanocomposites are highly sought multi-functional materials for their tailorable properties. If integrated properly, CNT-polymer nanocomposites can deliver improved interlayer mechanical strength and fracture toughness, high electrical conductivity and current carrying capacity, anisotropic thermal management, and smart functions like actuation and sensing. Currently, the most commonly used commercial aerospace structural material, carbon fiber reinforced plastic (CFRP), has high mass-specific mechanical strength, but is prone to delamination due to weak interlaminar strength and require additional heavy, metal mesh layers due to low electrical and thermal conductivities. Thus many studies have been conducted to integrate light-weight CNT-polymer nanocomposites with high performance in order to improve properties of CFPRPs. However, bulk application of CNT-polymer nanocomposites is currently limited due to lack of scalable manufacturing while maintaining organization of CNTs. Dispersion and organization of CNTs are difficult as CNTs tend to agglomerate due van der Waals forces and often entangle due to their high aspect ratios (>~100). These CNT agglomerates in polymer matrices cause voids and behave as defects rather than reinforcement, resulting in property degradation. Interfaces and interphases formed between CNTs and polymer matrices also need to be tuned to avoid functioning as defects or boundary layers. Thus, it is critical to develop a method to effectively disperse and organize CNTs within polymer matrices to improve and tailor the nanocomposite’s multi-functional properties. Here, application of magnetic fields is a promising, scalable method to deliver bulk amount of nanocomposites while maintaining organized nanoparticle assembly throughout the polymer matrix before the curing step. Previous studies showed effective alignment of nanoparticles with the small magnetic field (~10 G, an order of magnitude above the earth’s natural magnetic field) for reasonable time (~1 hour). In addition, nanoparticle alignment spacing was successfully controlled by varying field oscillation frequency, enabling particle patterning and interface tuning. In this work, MWCNTs (~35 nm diameter and ~200 um length) were processed to be magnetic, so that they can function as additives that can be effectively organized with magnetic fields. MWCNTs, being diamagnetic as fabricated, are coated with a thin layer of Ni with high aspect ratio to exhibit anisotropic ferromagnetism. The process consisted of three steps. First, MWCNTs were synthesized with chemical vapor deposition (CVD). Second, these MWCNTs were treated with low temperature air plasma; the amorphous carbon present on the side walls and entangled CNT layers on the top surface were eliminated. The CNT surfaces were also functionalized, in order to increase adhesion with Ni coating and to improve dispersion and suspension within matrix solutions. The air plasma conditions (power and treatment time) were varied to ensure adequate cleaning, and to maximize functionalization of CNTs without overly damaging the CNT crystal structure.
Treated CNTs and their dispersion degree were inspected visually with scanning electron microscopy (SEM), and functional group attachment was quantitatively evaluated using X-ray photoelectron spectroscopy (XPS). From these preliminary results, better CNT dispersion and suspension in isopropyl alcohol (IPA) was observed with the plasma treatment with low (~6.8 W) power setting for moderate duration (~4 min), which can be attributed to most attachment of ether (C-O) functional groups. Third, thin Ni layers, with varying thickness from 20 nm to 100 nm, were e-beam evaporated on the functionalized CNTs. Anisotropic ferromagnetic properties, such as hysteresis, coercivity, and remanence were measured using a vibrating sample magnetometer (VSM). With increasing thickness, magnetization increased but magnetic anisotropy decreased. Finally, preliminary study confirmed effective magnetic alignment of MWCNTs with ~100 nm thick Ni coating dispersed in IPA when applied with weak magnetic fields of ~100 G for 15 min.
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List of Acronyms

ALD  Atomic Layer Deposition
CNT  Carbon Nanotube
CVD  Chemical Vapor Deposition
DI water  De-Ionized water
EDS  Energy Dispersive Spectroscopy
EDX  Energy Dispersive X-ray Spectroscopy
IPA  Isopropyl Alcohol
MWCNT Multi-walled Carbon Nanotube
SEM  Scanning Electron Microscope
TEM  Transmission Electron Microscope
VSM  Vibrating Sample Magnetometer
XPS  X-ray Photoelectron Spectroscopy
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Chapter 1
Introduction and Motivation

Since the discovery of carbon nanotubes (CNTs) by Iijima [1] in 1991, researchers have been studying this novel allotrope of carbon because of its superior mechanical, thermal, and electrical properties [2]. Since the aviation industry has always been on the cutting edge of scientific advancement in its quest for light yet strong structures, it was merely a matter of time before researchers started thinking about the applications of CNTs to the fields of aerospace engineering.

Carbon nanotubes are often described as rolled up graphene sheets, forming cylindrical microtubules having very high length-to-diameter (l/d) ratio. The Young’s modulus of MWCNT structures is predicted to be in excess of 1 TPa [3,4] and that is attributed to the strong C-C bonding. Electrically, CNTs display a capacity of conducting very high currents (upto 1 A/cm) at low voltages (5 V/mm) [5]. Depending on the roll-up angle (chirality) and diameter, CNTs exhibit a range of electronic behaviors (semiconducting, metallic or semimetallic) [6].

1.1 Multifunctional Nanocomposites for Aerospace Applications

Owing to the exceptional mechanical and multifunctional properties, CNTs find various potential applications in the aerospace industry, which are listed as follows:

**Improved Mechanical Properties of CNT-Polymer Composites:**

Very small quantities of CNT fillers are needed to achieve significant improvement in the mechanical and electrical properties of CNT-polymer nanocomposites. Tensile testing on CNT-reinforced composites shows that the addition of 1 wt% of CNTs to a host matrix material results in a 36-42% increase in the elastic modulus, and ~25% increase in its ultimate tensile strength. This phenomenon was found to be a result of CNTs bridging the crack faces generated under tensile strain [7]. To achieve the same extent of increase in the matrix modulus achieved by 1 wt% of CNTs, it is necessary to add almost 10 wt% of carbon fibers [8]. In addition, due to the small filler amounts needed, other performance aspects of the polymer,
such as optical clarity and high melt flow viscosity can be maintained, to develop stronger windows and windshields for aircrafts. [9].

**Improved Shock Absorption and Impact Resistance:**
Addition of CNTs to the epoxy matrix of carbon fiber reinforced polymer (CFRP) laminates improves the low-energy impact absorption and after impact compression, which extends the fatigue life of the CNT-modified CFRPs [10]. Similar improvement in the impact resistance to glass fiber reinforced polymers as a result of CNT addition was also observed [11]. CNT discs have been found effective in increasing the energy damping properties of a CNT-polycarbonate multilayer system [12] and find interesting applications in energy dissipation, shock absorption and vibration mitigation.

**Interlaminar and Intralaminar Fracture Resistance:**
MWCNTs can be dispersed on CFRP prepregs to improve the interlaminar fracture toughness of the finished structure [13]. The presence of nanotube fillers increases fiber bridging between the ply interfaces and mitigates crack propagation. Similar increase in the fracture energy was also observed when the CNTs were added as fillers directly in the epoxy matrix [14,15] and in resin transfer molding [16]. CNTs were also grown directly on the fiber surface to form fuzzy-fibers, with CNTs growing radially on the surface of the fiber [17–19]. Fuzzy fiber hybrid woven composites can provide better interlaminar reinforcement by using the CNTs to stitch the plies together. Fuzzy fibers also have better interlaminar shear strength, as the radially oriented CNTs make it difficult for the reinforcing fiber to fracture from the polymer matrix.

**Electrical Conductivity and Thermal Tailoring:**
Owing to their excellent electrical conductivity, CNTs can potentially be used in the aerospace industry for lightning protection and in anti-radar coatings. Electrical conduction and discharge is critical for composite aircraft structures to protect the structure in case of lightning strikes and to shield sensitive systems from electromagnetic interference. Electromagnetic shields made by embedding CNTs in a CFRP are used for stealth applications and as radar absorbents [20]. CNTs embedded in the polymer form conductive pathways between the plies and between the tows for electrical discharge. The high aspect ratio of CNTs helps to form a physical network in the polymer, enhancing the thermal and electrical conductivity [21]. It has been observed that a 1 vol% CNT composite more than doubles the thermal conductivity of the base polymer, and denser CNT arrays improve the conductivity by as much as a factor of 18 [22].

**Sensing, Actuation, and Structural Health Monitoring:**
With increasing use of CFRP for airplane structures (Boeing 787, Airbus A350 XWB, Learjet 85 and HondaJet being among the most notable examples), efficient and constant health monitoring becomes increasingly essential, as cracks within CFRPs are difficult to detect, but can cause sudden fatal failure of the structure if they exceed a critical threshold. The electric resistance
change (ERC) of CNT-doped layers in polymer composites can be used to identify internal
damage in the composite. Due to their excellent thermal, electrical, and piezoelectric properties,
CNT fillers can be used as modifiers for the polymer matrix of composites leading to a significant
increase in the electrical conductivity of the polymer without increasing the structural weight
or deteriorating the mechanical performance, while providing reasonable sensitivity for in-situ
damage detection [23]. The sensing mechanism of conductive polymer composites (CPCs) is based
on the polymer’s reaction to environmental changes, which affect the conductive CNT network.
CNT-based CPCs can thus be used as electromechanical and electrochemical sensors [24].

Reversing the principle of CNTs as sensors, CNTs can be used as actuators for in-plane and
bimorph actuation [25, 26] The use of CNT-polymer nanocomposites in aircraft structures can
be potentially extended to develop dynamically actuated adaptive control surfaces [27].

1.2 Existing Challenges and Limitations

To realize the full potential of the CNT-polymer nanocomposites, it is necessary to overcome a
number of technical challenges, to make CNT-polymer nanocomposites commercially viable.

Challenges in Dispersion: [28, 29]
The primary limitation to the large scale adaptability of CNT reinforced polymer nanocomposites
is poor CNT dispersion within the polymer matrix. Due to their extreme hydrophilic nature,
CNTs are prone to clustering and agglomeration in organic solvents and polymer matrices. The
clustering behavior can be reduced by ultrasonication, while the dispersion can be improved by
chemical functionalization of the CNT surface. Electron and ion beam irradiation has also been
used to introduce defects in the CNT bundles for functionalization.

Challenges in Scalability: [30]
Another important factor limiting the widespread implementation of CNT composites is the high
cost of nanotube synthesis. Research is being conducted to improve the mass-production yield
and quality of CNTs, and the cost of is expected to decrease with the success and implementation
of new, large-scale CNT synthesis methods like chemical vapor deposition (CVD) which makes
continuous CNT synthesis possible. Low cost CNT synthesis is also made possible due to the
development of new, easily available materials as catalyst and feedstock.

Challenges in Control and Alignment: [31]
Due to the nano-sized scale CNTs, challenges exist in controlling dispersion orientation of the
CNTs in bulk-sized polymer matrix. It is relatively easier to manufacture isotropic
nanocomposites by bulk dispersion of CNT powders in the polymer. However, techniques to
manufacture composites with directional CNTs are still being developed, with respect to
scalability and controlling of the morphology of the dispersed CNTs. Several methods to
control CNT orientation using electric fields and magnetic fields have been developed, but their scalability still needs improvement.

1.3 Objective of this Thesis

The objective of this thesis work is to develop novel magnetic CNT nano-additives that can be dispersed within polymer matrices and can be organized using magnetic fields, allowing scalable manufacturing of CNT-polymer nanocomposites with organized CNT morphology. CNTs are highly sought nano-fillers for polymer nanocomposites due to their unique properties, but currently their application is limited due to non-optimal property improvement due to poor dispersion of CNTs. In addition, bulk fabrication of such composites without degrading nano-scale organization of CNTs is currently not possible. Here, CNT organization within uncured polymer matrices using external magnetic field can potentially be a solution to this problem, enabling bulk organization of CNTs and thus bulk application of CNT-polymer nanocomposites. Approach to this objective will be given in chapter 3.
Chapter 2
Background and Prior Work

As explained in chapter 1, the primary focus of this thesis is to synthesize magnetically-responsive CNTs in order to fabricate CNT-polymer nanocomposites for multi-functional aerospace applications. In addition to the assembly of highly organized CNT nanofillers, the process to manufacture and organize these magnetically responsive CNTs should be scalable to enable bulk application. In this chapter, I first summarize the existing work done to achieve such scalable manufacturing of CNT-polymer nanocomposites with organization of nano-fillers and specifically the magnetic organization of CNTs as fillers in nanocomposites. Then, I will explain the difference between these previous work and my work to be presented in this thesis.

2.1 Overview of Existing Methods to Align CNTs

Various methods are currently in use for alignment of CNTs dispersed in solutions. Each method comes with its own set of advantages and drawbacks [32]. The following sections give a brief summary of some of these methods.

Alignment using gas flow: [33,34]
This method uses gas flow over a drop of CNT solution to align the CNTs and simultaneously dry the solution. However, in case of a polymer matrix like epoxy, the viscosity of the solvent is too high to allow alignment due to gas flow. Also this method relies on the films being very thin. In case of higher film thickness, only the CNTs near the films surface will get aligned. Hence this technique cannot be extended to three dimensional assembly of CNTs.

Langmuir-Blodgett method: [35,36]
In this method, a substrate is pulled through a CNT solution. The pulling mechanism causes layer-wise deposition of aligned CNTs on the substrate, which is in alignment with the pulling direction. This technique can be automated and can be applied to larger scale. This technique is suitable for CNT alignment on a solid substrate, but cannot be extended to assembly within a liquid matrix such as epoxy.
**Application of uniaxial pressure** [37]

Previous literature shows that application of moderate uniaxial pressure of about 10 kbars can cause isotropic orientation of bundles in a raw powder bulk sample of CNTs. The bundles are oriented in a plane perpendicular to the direction of application of pressure. This method cannot be applied to a continuous assembly process, and also limits the size of the pellets that can be processed in each batch.

**Calendering and shear alignment** [38,39]

In this technique, a MWCNT-filled polymer composite film is heated and softened it, and is subjected to unidirectional rubbing with a blade with parallel grooves. The rubbing induces elastic force in the softened polymer matrix, which aligns the embedded CNTs along the blading direction. Another technique uses calender roll milling to achieve intense shear mixing of the CNTs dispersed in a epoxy matrix. As the CNT-polymer mix passes through the calendering rolls, the shear stresses induced untangle and uniformly disperse the CNTs in the polymer matrix, without damaging the nanotubes or reducing their lengths. These processes can be performed automatically, and on a larger scale, but their degree of alignment is not ideal.

**Integration as micro-components** [40–42]

Another approach for CNT nanocomposite assembly is to fabricate the CNTs into larger micro-components such as CNT yarns, buckypapers, CNT felt or woven CNT fabrics. It is relatively simpler to handle these micro-components and to control their alignment and morphology when integrating in a polymer matrix to obtain CNT-polymer nanocomposites.

**Electrophoresis** [43,44]

Owing to their inherent electrical conductivity, CNTs get aligned along the flux direction between the electrodes when subjected to a strong electric field. A DC field can possibly cause possible movement of the CNTs towards the electrode, while an AC field aligns individual CNTs in the field direction by re-orientation. For successful alignment, a field strength of the order of $10^3$ V/cm and frequency in the kHz-MHz range is necessary. Due to the very high voltage and frequency needed, scalability can be an issue with this method.

**Alignment using magnetic field** [45,46]

Magnetic alignment of CNTs is similar to electrophoresis, except that it uses a magnetic field to align CNTs in the desired direction. Unlike electric field, the magnetic field merely reorients the CNTs without causing possible movement. This ensures better uniformity of CNT dispersion in the polymer matrix. However, as-grown, the CNTs possess very weak diamagnetic property. Hence the nanotubes have to be processed to improve their response to an external magnetic field. This technique can be used to align CNTs in any direction in which the magnetic field can be applied, either within the substrate or normal to it.
Magnetic assembly was selected as a method of CNT organization because it shows a potential for excellent scalability, and faster assembly, combined with the benefit of using smaller magnetic fields, which needs a simpler, energy-efficient experimental setup.

2.2 Previous Work on Magnetically Responsive CNTs

Since as-grown CNTs have a very weak response to external magnetic fields, the CNTs have to be processed to make them magnetically responsive. Three main approaches have been taken in the past:

**Filling the inner cavity of CNTs with magnetic ferrofluids or nanoparticles:** [47–50]
Also known as endohedral functionalization, this approach takes advantage of the hollow nature of CNTs to fill them with magnetic metals or nanoparticles. These filled CNTs will then respond to external magnetic fields by reorienting themselves in the direction of the field. As manufactured, generally the CNTs have spherical, closed end caps; but for the magnetic material to be filled, the ends of the CNTs must be opened. Synthesis of CNTs with open ends can be done using the template method [51].

**Dispersion of CNTs in a liquid crystal medium:** [52–54]
Liquid crystals (LCs) have fluid properties like a liquid, but have a regular molecular orientation like crystals. When liquid crystals are subjected to a magnetic field, the crystal-like molecules form a dipole and get oriented along the direction of the field. When CNTs are dispersed in a liquid crystal solution, the LC molecules act as a director to change the orientation of the CNTs. This property can be used to achieve assembly of CNTs using magnetic field.

**Coating of outer surface of CNTs with magnetic thin-films or nanoparticles:** [47,55]
In this technique, the external surface of the CNTs is coated with magnetic nanoparticles or metals in the form of thin films. The magnetic anisotropy of the coatings helps to align the nanotubes along the direction of the field. This technique can be used for any type of CNT synthesis, as the external coating does not require any special CNT properties. A wide variety of metals and nanoparticles can be coated externally on the CNT sidewalls, assisted by chemical functionalization.

Continuous coating of magnetic materials on the CNT surface gives more uniformity in terms of magnetic properties as compared to deposition of magnetic nanoparticles, as nanoparticles have a tendency to agglomerate. However, a higher coating thickness is necessary to form a continuous film, as compared to nanoparticle deposition. [56,57]


2.3 Approach in this Thesis

Ferromagnetic metal coating on CNT surface was selected as a method to deliver magnetically responsive CNTs. Metal coating requires much less sample preparation than nano-particle deposition or filling of inner CNT cavity, and magnetic assembly can be achieved within common polymer matrices without depending on the unique property of liquid crystals. Deposition of continuous Ni film was selected over Ni nanoparticle attachment due to enhanced magnetic anisotropy; rectangular thin Ni layer with high aspect ratio can potentially result in anisotropic properties due to their geometry, allowing more effective alignment against the externally applied magnetic fields. In addition to ferromagnetic layer coating, CNTs will be processed with plasma treatment for better dispersion and suspension within polymer matrices. More details about the experimental approach will be discussed in Chapter 3.
Chapter 3
Experimental Approach

3.1 Overview

The approach to fabricate magnetically responsive CNTs in this study consists of three steps, as summarized in figure 3.1. The three steps are (a) Chemical Vapor Deposition (CVD) synthesis of MWCNTs (b) oxygen plasma treatment and (c) ferromagnetic nickel (Ni) coating by electron beam (e-beam) evaporation. As grown, the MWCNTs have amorphous carbon on the sidewalls and top surfaces. The oxygen plasma treatment helps to eliminate these amorphous carbon and also functionalizes the CNT surface. Cleaner, functionalized CNT surfaces promote more conformal nickel coating, and also exhibit better dispersion and suspension in matrix solutions [58–60]. After this three-step process, these magnetically-responsive MWCNTs are dispersed within DI water and applied with the magnetic fields.

3.2 CVD Synthesis of MWCNTs

I developed a CVD apparatus to synthesize MWCNTs, and obtained the standard recipe for the growth of directional MWCNTs by conducting parametric growth study. The CNT morphology and wall structure were characterized using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The details of these processes will be explained in chapter 4.

The CVD method was chosen over other CNT synthesis methods such as laser vaporization and arc discharge because the CVD method produces the largest amount of moderate-quality MWCNTs. Endo first synthesized MWCNTs using CVD in 1993 [61]. In this method a carbon source, either in the gaseous or liquid phase, is introduced in a growth chamber with a suitable energy source, such as high temperature (~750°C) or plasma. The hydrocarbons within the carbon source are transformed into pure carbon molecules, are diffused onto the substrate and are deposited on the catalyst nanoparticles on the substrate. These carbon molecules are regularly arranged, forming carbon nanotubes.
3.3 Plasma Treatment of CNTs

Plasma treatment cleans the CNT forest surface by eliminating the rough top surface, comprising of entangled CNTs, and also functionalizes the CNT surface. Clean surfaces and exposed spacing between CNTs are essential for conformal nickel coating by directional e-beam deposition. Functionalization improves the suspension of the CNTs in organic solvents and polymers [58], and also potentially enhances the adhesion of nickel coating to the CNT walls [59]. In this work, oxygen (or air) was selected as the plasma source gas in order to eliminate amorphous carbon and to attach oxygen-containing groups (ether, carbonyl, and carboxyl) [62]. Oxygen plasma treatment also increases the wettability of the CNT film surface [63], which can potentially help in improving the dispersion characteristics of CNTs in DI water. Treatment time and power settings were varied using the plasma asher in Dr. Terrones’ lab to adjust the degree of functionalization and to improve CNT dispersion in solvents such as DI water and isopropyl alcohol (IPA). The degree of functionalization and dispersion were evaluated both qualitatively and quantitatively using optical and SEM imaging and X-ray Photoelectron Spectroscopy (XPS) analysis. The details of plasma treatment will be discussed in chapter 5. Previous literature has established that oxygen plasma functionalization is useful in eliminating amorphous carbon [64] and to attach oxygen-containing groups (hydroxyl, carbonyl, and carboxyl) to the CNT sidewalls [65]. CNTs containing these functional groups exhibit better dispersion in an epoxy matrix, reduced agglomeration, and resulting in improved mechanical properties of CNT-epoxy nanocomposites [66].

Various methods exist to functionalize the surface of CNTs; ozone oxidation, acid oxidation, flourination, electrochemical and chemical functionalization. Unlike these other functionalization methods, plasma treatment is non-polluting and scalable and only requires a short reaction time. The treatment can be moderated to avoid excessive tip-opening or damage to the CNT sidewalls. Also, a wide range of functional groups can be provided by modulating the plasma parameters such as power, gas, treatment time, and pressure [58,65].

3.4 Ferromagnetic Layer Deposition on CNTs

After functionalization, the CNTs were coated with a thin ferromagnetic layer of nickel (Ni, ~20-100 nm) using e-beam evaporation in Dr. Suzanne Mohney’s lab (Department of Materials Science and Engineering, Penn State). The nickel layers deposited on the CNTs were inspected using SEM imaging and Energy Dispersive Spectroscopy (EDS). The magnetic properties of the Ni-coated CNTs were measured using a Vibrating Sample Magnetometer in Dr. Paris von Lockette’s lab (Department of Mechanical and Nuclear Engineering, Penn State). The details of the ferromagnetic coating and characterization will be explained in chapter 6.

E-beam evaporation was selected as a coating method because reasonable conformal coating was anticipated by placing vertically aligned CNTs directly above the Ni crucible. Other methods,
such as Atomic Layer Deposition (ALD) and electroplating are available for more conformal coating, but these require extensive recipe development or involve a wet process. Among the ferromagnetic material sources available for deposition, nickel was selected over iron or cobalt because nickel does not react with the CNT sidewalls to form carbides, and leaves the sidewalls undamaged.

The aim was to deposit a thin, continuous layer of nickel on the CNT tips. In the past, iron oxide nanoparticles have been deposited on the CNTs. Those CNTs showed magnetization, but without anisotropy [46]. Meanwhile, when a thin, continuous ferromagnetic layer is deposited on a CNT in the form of a rectangular shape with high aspect ratio, a collection of single magnetic domains, whose directions are aligned along the CNT direction are expected to be formed due to the small thickness (< ~50 nm) [55]. The presence of such anisotropy in magnetic properties helps magnetic assembly even with the application of relatively smaller magnetic fields (~100 G).

3.5 Assembly using Magnetic Fields

The Ni-coated CNTs were dispersed in DI water and were subjected to the external magnetic field for alignment. The magnetic assembly setup was designed and built by Mychal Spencer in Dr. Yamamoto’s lab (Department of Aerospace Engineering, Penn State). The CNT’s assembly behavior was observed and recorded in-situ using an optical microscope. The degree of assembly and the response time were studied in relation to the nickel layer thickness and the anisotropic magnetic properties. The goal of this study was to demonstrate the assembly of Ni-coated CNTs with a small magnetic field (order of ~100 G) in a short time (~15 minutes). The details of the magnetic assembly setup and procedure will be explained in chapter 7.
Figure 3.1: Overview of the fabrication steps of magnetically responsive CNTs
Chapter 4
Chemical Vapor Deposition of Multiwalled Carbon Nanotubes

The multi-walled carbon nanotubes (MWCNTs) used in this study were fabricated with the Chemical Vapor Deposition (CVD) \[67,68\] process, using an apparatus that I designed and built specially for this study. The CVD apparatus is located in Dr. Yamamoto's lab (Room 113M, Research West Building) at the Pennsylvania State University (PSU). In this chapter, I will first discuss about the CVD apparatus design and build, second about CVD synthesis process and CNT growth behavior and third about the characterization of the synthesized CNTs.

4.1 Design and Development of CVD Apparatus

The CVD synthesis apparatus, as shown in figure 4.1 and figure 4.2, consists of controlled gas supply (gas cylinders and mass flow controllers(MFCs)), CNT growth chamber with controlled temperature (a quartz tube sitting inside a tube furnace with digital temperature control), and exhaust connections (vacuum trap connected to a fume hood). The function of each component in relation to the CVD growth process will be discussed further in Section 4.2.

As for the controlled gas supply, three types of gas cylinders (argon, ethylene and hydrogen) were each connected to a MKS GM50A mass flow controller. The gas flow rate was controlled from 10 sccm to 650 sccm for argon and ethylene and at 10 sccm for hydrogen. The MKS GM50A MFC can handle full scale flow ranges of 5-50000 sccm N\textsubscript{2} equivalent. The N\textsubscript{2} equivalent flow rate was converted to the flow rates of the desired gases by multiplying with the conversion factor based on the calibration gas of N\textsubscript{2}. Communication with the MFCs is done using the inbuilt Ethernet ports, connected to a computer.

The CNT growth chamber has a Lindberg Blue M HTF55347C Single-zone Tube Furnace coupled with a CC58434PC Furnace Controller from Thermo Scientific. This setup can handle temperatures up to 1200\degree C, which is well above the CNT growth temperature range. The temperature and ramp-rate are set manually on the control panel of the furnace controller. A quartz tube (107 cm length, 3.5 cm diameter) is installed inside the tube furnace and is used as the growth chamber that can withstand the high growth temperature (~750\degree C). Both ends of
the quartz tube are sealed using flange clamps with fluorocarbon O-rings (operational up to 220°C) as shown in figure 4.3. Since the O-rings are well away from the furnace heating zone, this temperature range is suitable. Hinged flange clamps are used to seal the chamber as they are easy to remove and re-fit. To load substrates into the quartz tube, the upstream flange seal is removed to open the chamber. The substrate is then placed on a quartz boat and pushed to the furnace center using a quartz rod as shown in figure 4.3(a). Considering both the furnace controller and the MFCs are equipped with RS-485 communication ports, the process can be automated in future by writing a LabVIEW code to control both the temperature and the gas flow rates.

The exhaust gases from the quartz tube are passed through a vacuum trap (Sigma Aldrich Z549444-1EA) filled with silicon oil (see figure 4.1). The by-products of CNT synthesis can include methane, volatile organic compounds, and hydrocarbons [69], and these substances can be trapped within the silicon oil before venting to the fume hood exhaust. The connection tubes carrying the gases between various components are 1/4 inch stainless steel tubes, joined together using Swagelok end connectors. The gas lines are equipped with quarter turn plug valves at multiple locations to prevent inadvertent flow or leaks. These connections ensure a robust system to prevent diffusion of flammable gases in the lab environment, and also helps to maintain constant moisture levels within the apparatus for consistent CNT growth [70].

### 4.2 CVD Process and Recipe for CNT Growth

The chemical vapor deposition process mechanism is illustrated in figure 4.4 and the recipe is summarized in table 4.1. The CVD process was carried out at atmospheric pressure. First, the substrates were prepared by depositing an aluminum oxide (Al₂O₃) diffusion barrier (10-30 nm) and an iron (Fe) catalyst layer (1-30 nm) on silicon wafers (Si, <100> p-type, with boron dopant, 0.5 mm thick). The layers are deposited on the wafer using electron-beam evaporation (Kurt J Lesker Lab-18 E-gun and Thermal Evaporator). The substrates were then cut into 1 inch² pieces with a diamond cutter and cleaned with compressed air to eliminate the silicon debris. A cleaned Si substrate was loaded into the growth chamber as described previously in section 4.1. The chamber was first purged with inert argon gas (Ar, 650 sccm, 99.999% pure) and the chamber was heated to the CNT growth temperature (750°C) under the mixture of argon and hydrogen gas (H₂, 10 sccm). The hydrogen gas acts as a reducing agent, and pre-conditions the Fe catalyst into metallic nanoparticles. After temperature stabilization, ethylene (C₂H₄, 400 sccm) was introduced as a carbon source for CNT growth. After 15 minutes, the ethylene flow was stopped and the chamber was cooled, maintaining an inert atmosphere by flushing argon.

Both, tip-growth and base-growth models for CNT synthesis are observed in the past [71]. Figure 4.4 presents the base-growth mechanism, where the catalyst particles stay at the bottom of the CNTs. Previous studies have observed a transition from base-growth to tip-growth as the catalyst layer thickness increased (> 5 nm) [72].
The initial CNT growth recipe, which is different from the one given in table 4.1, was obtained based on a recipe developed previously for a similar system [73]. The gas flow rates were converted for this setup based on the volume and the cross section of the quartz tube, the gas tubes and the gas travel length within the heated section of the growth chamber.

This original recipe was used as a preliminary test to evaluate the apparatus base conditions. The first run with the original recipe (505 sccm of C\textsubscript{2}H\textsubscript{4}) yielded excessive deposition of sooty carbon on the inner walls of the growth chamber, and also on the substrates. After reducing the ethylene flow rate to 400 sccm, the carbon deposition was confirmed to be multiwalled structures using TEM (FEI Tecnai G2 20 XTWIN), as shown in figure 4.10(c). On the other hand, low ethylene flow rate yielded non-uniform coverage of CNTs on the Si substrate due to insufficient carbon supply. The growth remained largely unaffected by variation of argon flow rate. The recipe was further improved through parametric studies to grow consistent, directional MWCNTS. The final version of the recipe is described in table 4.1. The following sections present the correlations between the growth parameters and the resulting CNTs that was studied during the recipe improvement process.

### 4.2.1 Effect of Catalyst Layer Thickness

The catalyst layer thickness plays a critical role to grow directional CNTs on the substrate, rather than to deposit general carbon compounds. As shown in table 4.2, four substrate configurations with different combination of catalyst and diffusion barrier layer thicknesses were studied. The CNTs grown on these substrates were studied using SEM (Zeiss Merlin FE-SEM) for their morphology as shown in figure 4.5.

Substrate 1 (1 nm Fe on 10 nm Al\textsubscript{2}O\textsubscript{3}) was prepared based on previous successful growth studies [73]. SEM analysis of the growth on this substrate showed that the Fe catalyst layer delaminated from the substrate, causing primary and secondary CNT growth on both sides of the catalyst layer, as seen in figure 4.5(a) and as illustrated in figure 4.6(a). This delamination can be attributed to the poor attachment of the e-beam deposited layers to the substrate. In order to improve the structural robustness of the e-beam deposited layers, both the thickness of the catalyst and the diffusion barrier layer was increased to 30 nm each. These thicker layers successfully prevented delamination on substrate 2 after the CVD process. But the resulting carbon deposition was not CNTs, but non-organized carbon compounds, as seen in figure 4.5(b). With the larger thickness, the Fe catalyst layer did not get reduced to nanoparticles small enough to initiate CNT growth [74]. To overcome this poor nucleation, substrate 3 was prepared with a thinner (15 nm) catalyst layer, while maintaining the same diffusion barrier layer thickness as substrate 2. The growth obtained on substrate 3 were CNTs, but their morphology was not vertically oriented (see figure 4.5(c)). Again, this behavior can be explained by the catalyst particle size; the the reduced Fe nanoparticles are still relatively large, resulting in grouped growth of CNTs as illustrated in figure 4.6(b). Similar results about the correlation between catalyst nanoparticles and carbon deposition have been observed in...
previous studies [75, 76]. In order to grow vertically aligned MWCNTs, substrate 4 was prepared with an even thinner Fe layer (1 nm) and the same Al$_2$O$_3$ thickness (30 nm). This substrate 4 successfully yielded a forest of vertically oriented CNTs, as seen in figure 4.5(d). From this section on, all the CNTs in this study were grown on substrate 4 (1 nm Fe on 30 nm Al$_2$O$_3$), using the recipe given in table 4.1.

4.2.2 Effect of Hydrogen Pretreatment

As shown in figure 4.7, hydrogen pretreatment reduces the amount of amorphous carbon present on the CNT surface and yields cleaner nanotubes. This purification of CNTs with increasing H$_2$ pretreatment time is consistent with previous work in the literature [73].

4.2.3 Effect of Substrate Size, Position and Configuration in the Chamber

Factors such as substrate size, substrate position, and the number of substrates within the growth chamber also affect the quality and uniformity of the CNT growth. More consistent and homogeneous growth was observed at the substrate location of the longitudinal midpoint of the quartz tube, slightly upstream as shown in figure 4.8. When more than two samples were loaded in the quartz tube, poor CNT coverage was observed on the one sample placed downstream of the gas flow. This growth behavior can be attributed to the conditioning and depletion of gas supplies as the gases travel through the growth chamber. The ethylene gas mixed with the hydrogen reduction gas is properly conditioned by traveling through the heated chamber, before their carbon components are deposited on the substrate. Thus the substrate needs to be placed a certain distance away from the upstream heated end of the quartz tube. In addition, the carbon source ethylene gas in the gas mixture will be expended during the growth. Hence an upper limit exists about the maximum area of the substrate that can be deposited with CNTs. With our current setup and recipe, one substrate up to 0.5 inches x 0.5 inches can be easily deposited with CNTs of uniform substrate coverage and satisfactory quality. With a larger quartz tube and higher gas input, this substrate size can be scaled up to match production needs.

4.2.4 Effect of Ambient Humidity

Existing literature confirms that excessive ambient humidity adversely affects the CNT growth process [70, 77]. A similar trend was observed with our CVD system. The presence of excessive humidity in the growth chamber, or on the substrate due to presence of moisture in the environment due to rain adversely affected the CNT growth. Figure 4.9(a) shows a CNT sample grown on a regular day without any atmospheric precipitation, while figure 4.9(b) shows
a sample grown on a day with precipitation. In future, we will eliminate and control moisture levels by pre-growth baking of the growth chamber and substrates.

4.3 Characterization of Grown MWCNT Forests

The MWCNT samples grown using the standard CVD recipe (table 4.1) on substrate 4 (1 nm Fe, 30 nm Al₂O₃) were visually inspected using SEM (Zeiss Merlin FE-SEM) and TEM (FEI Tecnai G2 20 XTWIN TEM). TEM images confirmed the presence of multiwalled structure, as shown in figure 4.10(c). The diameter of the CNTs was measured to be 35±10 nm, with an average of 20 to 30 walls. SEM imaging helped to gather information about the CNT forests; specially about the aligned CNT morphology, length (~200 µm) and diameter of individual CNTs, clustering of CNTs characteristics of CNT tips and surface, and the presence of impurities and amorphous carbon. As shown in figure 4.10(a) and (b), the presence of entangled CNT growth was observed on the top surface of CNT forests. These entangled CNTs could possibly originate from dispersed catalyst particles in the growth chamber, or from the delamination of catalyst layer as observed previously with substrate 1 (see figure 4.5(a)). These entangled CNTs need to be eliminated for more conformal metal coating during the later stages of this experiment (see figure 3.1)

In the next chapter, I will discuss the process of plasma treatment, in order to eliminate these entangled CNT layers and also to functionalize the CNT surfaces.
Figure 4.1: Digital image of the CVD setup used for CNT synthesis

Figure 4.2: Schematic of the CVD setup used for CNT synthesis
Figure 4.3: Digital images of (a) a sample being loaded into the quartz tube using the quartz boat and rod and (b) flange clamp to seal the quartz tube

Figure 4.4: Schematic explaining mechanism of CNT growth
Figure 4.5: SEM images showing the effect of catalyst thickness on CNT growth (a) 1 nm Fe, 10 nm Al₂O₃ (b) 30 nm Fe, 30 nm Al₂O₃ (c) 15 nm Fe, 30 nm Al₂O₃ (d) 1 nm Fe, 30 nm Al₂O₃
Figure 4.6: Schematics of CNT growth affected by the catalyst layer thickness (a) 1 nm Fe, 10 nm Al₂O₃ (b) 15 nm Fe, 30 nm Al₂O₃

Figure 4.7: SEM images showing the effect of hydrogen pretreatment time on CNT surface (a) without pretreatment (b) with 10 minutes pretreatment
Figure 4.8: Digital images showing the effect of position of the substrate in the quartz tube on the CNT coverage

Figure 4.9: Digital images showing the effect of atmospheric moisture on CNT growth and coverage (a) sample grown on a regular day (b) sample grown on a rainy day
Figure 4.10: Electron microscopy images of CVD-grown MWCNTs: (a) SEM image of cross-section of vertically oriented CNT bundles, (b) SEM image of the top entangled CNTs, and (c) TEM image of an individual CNT confirming presence of multi-walled structure.
Table 4.1: Standard CNT growth recipe

<table>
<thead>
<tr>
<th>Process Steps</th>
<th>Ar (sccm)</th>
<th>C$_2$H$_4$ (sccm)</th>
<th>H$_2$ (sccm)</th>
<th>Temperature (°C)</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purge gas lines</td>
<td>650</td>
<td>400</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Purge quartz tube</td>
<td>650</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Temperature ramp</td>
<td>650</td>
<td>0</td>
<td>10</td>
<td>750</td>
<td>15</td>
</tr>
<tr>
<td>Temperature stabilization</td>
<td>650</td>
<td>0</td>
<td>10</td>
<td>750</td>
<td>10</td>
</tr>
<tr>
<td>CNT growth</td>
<td>650</td>
<td>400</td>
<td>10</td>
<td>750</td>
<td>15</td>
</tr>
<tr>
<td>Furnace cooling and purge</td>
<td>650</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stop gas flow and extract substrate</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2: Catalyst and diffusion barrier layer thicknesses of substrates for CVD growth of CNTs

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst (Fe) thickness (nm)</th>
<th>Diffusion barrier layer (Al$_2$O$_3$) thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>30</td>
</tr>
</tbody>
</table>
Chapter 5
Plasma Treatment of CNTs

The grown CNT forests were treated with air plasma for two purposes: elimination of amorphous carbon and functionalization of the CNT surface.

As discussed in Chapter 4, the CNT forests have a rough top layer of entangled CNTs as seen in figure 5.1(a). In addition, though hydrogen pretreatment largely can prevent the formation of amorphous carbon by reduction reaction, some amorphous carbon is still observed on the CNT sidewalls, after the sample comes out of the growth chamber. For effective dispersion and conformal nickel coating on individual nanotubes, it is essential that the tips of the CNTs are exposed, as shown in figure 5.1(b). Oxygen plasma treatment is effective to eliminate amorphous carbon [62, 64] and the entangled top layer of CNTs. Plasma treatment also functionalizes the nanotube surface and creates chemically active sites to attach functional groups. These functional groups enhance the suspension and dispersion characteristics of the CNTs in solutions [58]. Additionally, the same functional groups can also make the nanotubes more receptive towards metal deposition [59] and improve adhesion of surface coatings [60].

In this chapter, I conduct a parametric experimental study to evaluate the effects of oxygen containing air plasma treatment on the MWCNTs. Treatment time and power setting of the plasma was varied and the treated MWCNTs were inspected for changes in their morphology under a SEM. The chemical status of the CNTs was measured using X-ray photoelectron spectroscopy (XPS) to correlate with the properties of their suspension in solvents.

5.1 Advantages of Oxygen Plasma Treatment

As briefly noted in section 3.3, compared to other methods like acid oxidation or ozone oxidation, plasma treatment is a non polluting, scalable functionalization method with a shorter reaction time. Also, plasma treatment does not cause excessive tip-opening or damage to the CNT sidewalls. In addition, a wide range of functional groups can be provided by modulating the plasma parameters such as power, gases, treatment time, and pressure [58,65]. Previous literature confirms that oxygen plasma etching is effective in removing more than 95% of the amorphous carbon present on CNT surface [64]. Functionalization is the introduction of chemically active sites on a surface, such as nanotube sidewalls or caps. The process is often conducted to alter
the adhesion properties of surfaces prior to coating or painting. Surface activation using plasma treatment is a result of three main steps: (a) aggressive oxidation of atoms to break bonds on the CNT sidewalls, (b) addition and bridging to introduce more reactive groups, and (c) substitution reaction to introduce groups with the desired functionality on the CNT sidewalls [78, 79]. These surface modifications help to reduce CNT agglomeration in organic solvents such as isopropyl alcohol (IPA) and potentially enhance bonding with applied coating materials [60]. In this work, oxygen was selected as the treatment gas in order to eliminate amorphous carbon and to attach oxygen-containing groups (hydroxyl, carbonyl, and carboxyl) to the CNT sidewalls. Previous literature shows that these oxygen-containing functional groups exhibit better dispersion in an epoxy matrix, reduced agglomeration, and potentially improved mechanical properties of CNT/epoxy nanocomposites [66].

5.2 Oxygen Plasma Treatment using Asher

MWCNTs were plasma-treated using Harrick PDC-32G Basic Plasma Cleaner, (see figure 5.2) in Dr. Mauricio Terrones’ lab (Department of Physics, PSU). This plasma cleaner operates with an RF frequency range of 8-12 MHz, and has a cylindrical process chamber (3 inch diameter, 7 inch depth). Air is used as the process gas. After placing the as-grown CNTs on a substrate in the process chamber, the chamber is pumped down to create a vacuum. The RF coil is then energized to the desired power setting and a small amount of atmospheric air is introduced into the process chamber by controlling the opening on a 3-way valve attached to the chamber door, while the vacuum pump is still on. The amount of air allowed is adjusted to be just enough for ionization at that particular power setting to effectively spark a plasma discharge. The plasma acts on the sample from all the sides, immersing the sample in air plasma. Two parameters, the treatment time (4, 6, 8, and 10 mins) and the RF power (6.8 W low, 10.5 W medium, and 18 W high), were varied as summarized in table 5.1.

5.3 Characterization of Plasma-Treated MWCNTs

The degree of functionalization were evaluated both qualitatively and quantitatively using digital imaging, SEM imaging and XPS characterization.

5.3.1 CNT Suspension Study

The effect of plasma treatment on CNT suspension was evaluated by observing the settlement of CNTs dispersed in IPA. Suspension is the ability of the dispersed CNTs to stay floating in the solution. For the magnetic assembly process, CNT solutions with longer suspension time and uniform particle dispersion are desired. The CNT-IPA solution was prepared by immersing a CNT sample (~0.25 cm² size) while still attached to the substrate, in 1500 µL of IPA in a glass
vial. The vial was placed in a VWR Symphony 97043-976 Ultrasonic Cleaner for 1 minute to
detach the CNTs from the substrate and disperse them in the solution. Digital images of CNT
settlement were recorded over time, from immediately after the ultrasonic dispersion to three
days after the dispersion preparation.

The CNT suspension was observed to be maintained the most when plasma-treated with
moderate treatment time (4 minutes) at a low power setting (6.8 W). When inspected with
bare eyes, the CNT suspension improved with increasing treatment time, but the effect
plateaued and diminished for treatment time beyond 6 minutes. The difference between
suspension characteristics of different vials is not obvious in figure 5.3 as a result of undesirable
vignetting of the digital photograph due to the larger viewing angle. As shown in figure 5.4, the
better suspension was obtained with low power setting (6.8 W). More settlement was observed
when the CNTs were treated with higher power setting (10.5 W and 18 W). With the
parameters available within the existing experimental setup, the condition that showed longer
suspension time and finer dispersion was the combination of low power setting (6.8 W) for 4
minutes. This plasma treatment condition is used to prepare the Ni coated CNTs in chapter 6.

5.3.2 SEM Imaging for Carbon Elimination and CNT Dispersion

The plasma-treated CNT samples were inspected using a Zeiss Merlin FE-SEM. First, the cross-
section of the aligned CNT forest was inspected (see figure 5.1). As noted earlier, the rough top
surface of the entangled CNTs was eliminated. Second, the CNT dispersion in IPA, as prepared
in 5.3.1, was evaluated by inspecting a sample prepared by evaporating a drop of the CNT-IPA
solution on a clean silicon substrate. As the IPA was evaporated naturally, the CNT morphology
was expected to be condensed. The SEM images of the CNTs obtained with different plasma-
treatment times are shown in figure 5.5. As the treatment time increases beyond 4 minutes,
the cluster size and CNT length decreases, indicating damage. CNTs treated for 4 minutes
showed the most loosely packed clusters, showing compatibility with the observations made in
the suspension study (see figure 5.3).

5.3.3 X-ray Photoelectron Spectroscopy (XPS) for Functionalization

The type and percentage of the elements of plasma-treated MWCNTs and their attached
functional groups were evaluated using XPS (PHI VersaProbe II Scanning XPS Microprobe).

5.3.3.1 Measurement

XPS is a surface characterization technique for analyzing the chemical and electronic state of the
elements within a sample. The principles of XPS are based on the phenomenon of photoemission
was discovered by Einstein [80], and XPS was further developed as a characterization technique
by Seigbahn [81,82]. Since XPS is a surface characterization technique, it is effective for analysis
up to a depth of few atomic layers (~10 nm) below the surface. When the samples are irradiated with X-rays, loosely-bound electrons from the near-surface layers of the sample are emitted. By measuring the amount and kinetic energy of these emitted electrons, it is possible to calculate the binding energy, and hence deduce the shell and spin-orbit peaks of the electrons which are unique to the chemical and electronic configuration of the materials. As a result, XPS is an effective and commonly used method to identify the functional groups attached to CNT surface [83–85].

XPS experiments were performed using monochromatic Al $\text{K}\alpha$ X-ray source ($h\nu = 1486.7$ eV) and a concentric hemispherical analyzer. Charge neutralization was performed using both low energy electrons (< 5 eV) and argon ions. Peaks were charge referenced to C-C band in the carbon 1s spectra at 284.4 eV. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3-6 nm (95% of the signal originated from this depth or shallower). Quantification was done using instrumental relative sensitivity factors (RSFs) that account for the x-ray cross section and inelastic mean free path of the electrons.

For analysis of the plasma-treated MWCNTs used in this study, two types of XPS measurements were taken; (a) survey measurement to identify the material elements present in the sample, and (b) higher resolution measurements of the carbon 1s peak (C 1s) to identify the relative quantity of the various functional groups present in the sample (see figure 5.6). The samples used for XPS analysis were plasma-treated MWCNTs, backed with the Si substrate. The samples were stored in airtight containers to prevent surface contamination from the atmospheric oxygen and moisture. Special care was taken to ensure that minimum amount of time passed between preparing the sample and loading them into the XPS chamber to reduce the chances of atmospheric contamination. A base Si substrate with the catalyst (substrate 4), and a pristine CNT sample without plasma-treatment were also measured as references.

Survey

The low resolution survey scan was taken for the binding energy range of 1350 eV - 0 eV with 0.8 eV step size, and a pass energy of 187.85 eV. The purpose was to identify the material elements within the sample and select the measurement spot locations free from silicon debris to obtain clean data for the C 1s peaks. Pristine CNT samples without plasma treatment confirmed the absence of an oxygen peak (see figure 5.6(a)). Also, spot locations that show minimal Si peaks were selected on the plasma-treated CNT samples, in order to more accurately evaluate the amount of oxygen introduced by plasma treatment, and to eliminate the error due to silicon oxidization.

C 1s peak

The high resolution scan was taken with a 0.1 eV step size, and a pass energy of 23.5 eV. The measurement was repeated three times at different locations on each sample, to reduce the effects
of localized impurities on the surface. The purpose of this measurement was to quantitatively evaluate the different functional group types, and their percentages, attached to the CNT surface as a result of the plasma-treatment, by peak fitting.

The asymmetric peak shape for the pristine nanotubes was derived by a high resolution scan of the reference sample, as shown in figure 5.6(b). The CNT peak is located at 284.4 eV, which corresponds to the sp2 hybridized orbitals within graphene structure [86]. This graphitic carbon structure can also be confirmed by a small increase in the shake-up peak at ~291 eV, which corresponds with the π-π transition.

5.3.3.2 Peak Fitting

The type and percentage of functional groups attached to the plasma-treated CNTs were evaluated by peak fitting as illustrated in figure 5.7(b). The peak fitting was performed using CASA XPS (ver. 2.3.17). Before data processing, the background counts from scattered electrons were subtracted. The experimentally obtained C 1s peak of pristine CNT sample was used to identify the changes made to the peak due to plasma-treatment. Then the peak fitting was done using symmetric peaks for four functional groups; hydrocarbon (CHx), ether (C-O), carbonyl (C=O) and carboxyl (O-C=O). The positions and position constraints for each of the functional groups are obtained from the Scienta ESCA300 database [86], as given in table 5.2.

The XPS peak fitting process needs to be carefully conducted as the peaks positions of various functional groups overlap closely. In order to confirm the feasibility of the peak-fitting process, the oxygen percentage contributed from the attached functional groups of the C 1s peak was compared with the oxygen percentage from the survey plots [85]. The background counts from the scattered electrons were subtracted before data processing. The percentages of carbon, oxygen and silicon were calculated from the survey plots by integrating the area under the respective peaks. In order to calculate only the contribution of oxygen due to the functional groups, the oxygen contribution from the oxidized silicon was eliminated; this was done by subtracting twice the percentage of silicon from the oxygen percentage using equation (5.1), since oxygen is present in the 2:1 ratio in the stable oxide of silicon (SiO$_2$). Based on the peak fitting of the C 1s peak, the oxygen contribution of only the functional groups formed by plasma treatment was calculated using equation (5.2). As shown in figure 5.8, amount of oxygen obtained from the two methods was comparable for most samples.

\[
(O\% \text{ calculated from survey}) = (O\% \text{ from survey plot}) - 2 \times (Si\% \text{ from survey plot}) \quad (5.1)
\]

\[
(O\% \text{ calculated from the C1s peak}) = (C - O)\% + (C = O)\% + (O - C = O)\% \quad (5.2)
\]
5.3.3.3 Implications

The evaluated percentages of functional groups from the XPS measurement are summarized as a function of treatment time in table 5.3 and as a function of plasma power in table 5.4. The XPS measurement was taken on all samples at the same time, roughly four months after the samples were subjected to plasma treatment.

Several observations were made about the effect of plasma treatment time (see table 5.3). For these samples, the power was kept constant at the low setting (6.8 W). First, the hydrocarbon percentage increased with the 4 minutes sample, decreased close to zero with the 6 and 8 minutes treatment time, and then again increased with 10 minutes. This hydrocarbon (CHx) peak can be correlated to the carbon state of non-organized carbon or defects in the crystalline carbon structure. With plasma treatment, amorphous carbon on the CNT surface can be eliminated while defect sites of crystalline carbon structures increase with functional group attachment. Balancing between these two factors, CHx peak was minimized for the moderate treatment times (6 and 8 minutes). Meanwhile, carbonyl (C=O) and carboxyl (O-C=O) functional groups show a consistent increase with an increase in the treatment time. On the other hand, the ether (C-O) functional group showed a non-linear trend, unlike carbonyl and carboxyl groups. The sudden increase of ether groups with 10 minutes plasma treatment can be explained as more defect sites are generated, causing more functional groups to attach. The ether group percentage is slightly higher (by ~0.44 - 0.61%) with 4 minutes treatment time than the 6 and 8 minutes samples. This can be attributed to the measurement error or standard deviation (~7.6 - 14.5% among three measurements locations of data on the same sample). Another possible explanation is that the plasma treatment with very low power for a short time might have triggered unstable and unusual attachment of the ether functional groups. Based on theoretical calculation of interaction energy between CNTs (finite, open, single walled (5,5) carbon nanotubes with 150 carbon atoms) and functional groups, carbonyl functional group attachment requires the lowest interaction energy and thus results in the highest percentage [58]. This trend of favored attachment of carbonyl group was experimentally confirmed in the past [58, 87], and also in this thesis, with respect to the samples treated for 6, 8 and 10 minutes; the 4 minutes treated sample however did not show similar results. It should be noted that this plasma treatment condition (6.8 W for 4 min) resulted in the most dispersion and suspension of CNTs (see sections 5.3.1 and 5.3.2). More discussions on this result will follow later.

Several observations were made about the plasma power (see table 5.4). For these samples, the treatment time was kept constant at 4 minutes. Percentages of all the functional groups and hydrocarbons are observed to be the largest with the medium power setting (10.5 W). This trend can be explained considering that the lower power setting is not strong enough to attack the carbon structure, while the higher power setting is strong enough to eliminate amorphous carbon and defective crystalline carbon structures, and thus to reduce sites where the functional groups can be attached.

The above XPS measurement results were correlated with the results from CNT dispersion and
suspension observed in sections 5.3.1 and 5.3.2. In addition to the percentage of each functional group, the total percentage of oxygen in the sample was also calculated from the survey plot data (see table 5.5). Initially we expected the CNTs with higher oxygen percentage, and hence the most functional groups attached to show the best suspension and dispersion characteristics [65]. However, our experiments show that better dispersion and suspension is obtained for samples treated with 6.8 W plasma power for 4 minutes, which showed the least oxygen percentage among all tested samples in the XPS measurement. Conveniently, the same set of CNT samples were measured using XPS about one month prior to the final test, but taking data at only one location for each sample. As seen in tables 5.5 and 5.6, decrease of oxygen percentage (1.7 - 33.6%) was consistently observed with all samples regardless of the plasma treatment conditions, after one additional month of sample storage, indicating degradation of the functional group attachment over time. Among these samples, the most degradation (33.6%) was observed with the CNT samples treated with 6.8 W plasma power for 4 minutes. As noted above, this plasma treatment with very low power for short time might have triggered unstable and unusual attachment of ether functional groups which can be prone to degradation over time. Considering the CNT suspension and dispersion studies in sections 5.3.1 and 5.3.2 were conducted immediately after plasma treatment, most better dispersion and suspension can still be correlated to higher percentage of oxygen.

5.4 Future Work

Plasma treatment successfully exposed CNT tips for Ni coating deposition and also successfully attached oxygen containing functional groups to enhance CNT dispersion and suspension in IPA. XPS analysis of these CNTs have provided some insight on the specifics of this functionalization process, including the unstable, but effective hydroxyl group attachment with lower power for short time. More parametric studies to optimize plasma treatment can be performed in the future with larger power setting, longer treatment time, pressure control, and introduction of other gases such as ammonia for amine functional groups.

In the future, more scalable setups for plasma treatment than the Asher will be tried at Dr. Sean Knecht’s laboratory (School of Engineering Design, Technology and Professional Programs, PSU) as shown in figure 5.9. The Asher setup can only process samples in batches, and requires a vacuum environment. On the other hand, the low temperature setups in Dr. Knecht’s lab are capable of conducting continuous processes in a non-confined, atmospheric environment.

Parallel Plate Plasma Setup

The parallel plate plasma setup consists of two plate electrodes, separated by a small distance (0.075 inches). The CNT sample is placed between the electrodes as shown in figure 5.9(a). A very high electric voltage (~8 kV) applied between the plates ionizes the air between the plates and generates plasma. The parallel plate plasma treatment setup is susceptible to electrical
arcing at the edges of the substrate. Further studies are needed in order to have uniform spacing to avoid arcing.

**Plasma Jet Setup**

The plasma jet setup consists of a hollow quartz capillary, with an electrode running along the longitudinal axis of the capillary, as shown in figure 5.9(b). The electrode is connected to a high voltage electric supply (3-6 kV). At the open end of the capillary, a grounded electrode is present. Electric arcing between the electrode and the grounded terminal ionizes the gas passing through the capillary. The plasma is forced out of the capillary opening in the form of a plasma jet, which is directed on to the CNT surface for plasma treatment. The main advantage of this setup is its ability to control the plasma source gas. However, owing to the very small jet diameter, it is impractical to use this method for large scale applications. In future, the diameter of the jet can be increased, or the jet can be rasterized to cover a larger area to make this process scalable.
Figure 5.1: SEM images of (a) as-grown CNT forest with the top layer of entangled CNTs, and (b) plasma treated CNT sample with individual tips exposed.

Figure 5.2: Digital image of Harick Plasma PDC 32G basic plasma cleaner taken from the company website (http://harrickplasma.com/products/basic-plasma-cleaner)
Figure 5.3: Digital images of CNT suspensions in IPA. All CNT samples were treated with low power plasma (6.8 W). (The difference between suspension characteristics is not obvious as a result of undesirable vignetting of the digital photograph. However the difference is evident when observed with the naked eye.)

Figure 5.4: Digital image of CNT suspensions in IPA. All CNT samples were treated for 4 minutes.
Figure 5.5: SEM images of dispersed CNTs dried on Si substrates. The CNT samples were plasma-treated with low power (6.8 W) plasma treatment.
Figure 5.6: XPS measurement plots of a pristine CNT sample; (a) survey plot and (b) C 1s peak
Figure 5.7: XPS measurement plots of a plasma-treated CNT sample (4 minutes, low power, 6.8 W). (a) Survey plot and (b) C 1s peak that is peak-fitted with the CNT, CHx, C-O, C=O and O-C=O peaks.
Figure 5.8: Comparison of the oxygen percentage calculated from the survey plot vs. the oxygen calculated from the peak-fit C1s plots.
Figure 5.9: Schematic of the other plasma treatment setups: (a) parallel plate (b) plasma jet
Table 5.1: Experimental parameters for oxygen plasma treatment on MWCNTs

<table>
<thead>
<tr>
<th>Treatment time</th>
<th>Low (6.8 W)</th>
<th>Medium (10.5 W)</th>
<th>High (18 W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 minutes</td>
<td>32 J</td>
<td>32 L</td>
<td>32 P</td>
</tr>
<tr>
<td>6 minutes</td>
<td>32 O.2</td>
<td>32 N.2</td>
<td></td>
</tr>
<tr>
<td>8 minutes</td>
<td>32 O.1</td>
<td>32 N.1</td>
<td></td>
</tr>
<tr>
<td>10 minutes</td>
<td>32 K</td>
<td>32 M</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: Binding energy positions and position constraints for the functional groups used in peak fitting.

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Peak Position (eV)</th>
<th>Peak Constraint (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHx</td>
<td>284.7</td>
<td></td>
</tr>
<tr>
<td>C-O</td>
<td>286.0</td>
<td>± 0.1</td>
</tr>
<tr>
<td>C=O</td>
<td>287.2</td>
<td></td>
</tr>
<tr>
<td>O-C=O</td>
<td>288.7</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.3: Percentage of functional groups present in the samples as a result of the variation in functionalization time

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT %</th>
<th>CHx %</th>
<th>C-O %</th>
<th>C=O %</th>
<th>O-C=O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>99.97</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4 min Low</td>
<td>85.24</td>
<td>8.89</td>
<td>3.32</td>
<td>1.67</td>
<td>0.88</td>
</tr>
<tr>
<td>6 min Low</td>
<td>90.09</td>
<td>0.00</td>
<td>2.71</td>
<td>4.23</td>
<td>2.97</td>
</tr>
<tr>
<td>8 min Low</td>
<td>89.81</td>
<td>0.01</td>
<td>2.88</td>
<td>4.32</td>
<td>2.99</td>
</tr>
<tr>
<td>10 min Low</td>
<td>77.83</td>
<td>5.67</td>
<td>7.42</td>
<td>5.25</td>
<td>3.82</td>
</tr>
</tbody>
</table>

Table 5.4: Percentage of functional groups present in the samples as a result of the variation in functionalization power

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT %</th>
<th>CHx %</th>
<th>C-O %</th>
<th>C=O %</th>
<th>O-C=O %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>99.97</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4 min Low</td>
<td>85.24</td>
<td>8.89</td>
<td>3.32</td>
<td>1.67</td>
<td>0.88</td>
</tr>
<tr>
<td>4 min Med</td>
<td>65.07</td>
<td>18.72</td>
<td>7.90</td>
<td>4.97</td>
<td>3.35</td>
</tr>
<tr>
<td>4 min High</td>
<td>90.86</td>
<td>0.01</td>
<td>2.51</td>
<td>3.95</td>
<td>2.67</td>
</tr>
</tbody>
</table>
Table 5.5: Variation in percentage of carbon and oxygen in CNT samples as a result of different plasma treatment settings, as obtained from XPS survey results

<table>
<thead>
<tr>
<th>Reference</th>
<th>Sample Identifier</th>
<th>4 months after plasma treatment</th>
<th>3 months after plasma treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C%</td>
<td>O%</td>
</tr>
<tr>
<td>Reference</td>
<td>32 S.2</td>
<td>Pristine</td>
<td>97.5</td>
</tr>
<tr>
<td>Timevariation</td>
<td>32 J</td>
<td>4 min Low</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>32 O2</td>
<td>6 min Low</td>
<td>88.5</td>
</tr>
<tr>
<td></td>
<td>32 O1</td>
<td>8 min Low</td>
<td>88.9</td>
</tr>
<tr>
<td></td>
<td>32 K</td>
<td>10 min Low</td>
<td>89.6</td>
</tr>
<tr>
<td>Powervariation</td>
<td>32 J</td>
<td>4 min Low</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>32 P</td>
<td>4 min High</td>
<td>90.6</td>
</tr>
</tbody>
</table>

Table 5.6: Variation in percentage of carbon and oxygen in CNT samples as a result of sample storage time, as obtained from XPS survey results

<table>
<thead>
<tr>
<th>Sample</th>
<th>CNT%</th>
<th>CHx%</th>
<th>C-O%</th>
<th>C=O%</th>
<th>O-C=O%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 months</td>
<td>32 J</td>
<td>85.24</td>
<td>8.89</td>
<td>3.32</td>
<td>1.67</td>
</tr>
<tr>
<td>3 months</td>
<td>32 J</td>
<td>57.75</td>
<td>26.42</td>
<td>9.36</td>
<td>4.15</td>
</tr>
</tbody>
</table>
Chapter 6
Ferromagnetic Layer Deposition on CNTs and Assembly Using Magnetic Fields

Functionalized MWCNTs were coated with thin layers of nickel using e-beam evaporation, so that they can be assembled using magnetic fields. These magnetically responsive CNTs can be aligned to form CNT-polymer nanocomposites with organized CNT structures.

The use of magnetic fields for CNT alignment provides several advantages over other methods of CNT alignment, like electric field, acoustic, and fluidic alignment [32]. Unlike CNT assembly using electric field, when using magnetic field for CNT alignment, one does not have to deal with such as surface charging [88], movement of the CNTs towards the negative electrode [89], absorbed water [90] and field inhomogeneity [91]. With magnetically responsive CNTs, the orientation and spacing of the CNTs in a matrix can be controlled using external magnetic fields of the order of 10 G (which is the magnitude of magnetic induction of an ordinary fridge magnet), within a short time (~1 hour) [55, 92].

In this chapter, I evaluated the nickel coating with respect to deposition morphology, adhesion to CNT sidewalls and the magnetic properties. Ni was selected because it does not react with the MWCNTs to form carbides, unlike Fe or Co [93, 94]. The uniformity of deposition and adhesion was studied using SEM imaging and Energy Dispersive Spectroscopy (EDS). The degree of magnetization of nickel coated CNTs was studied using a Vibrating Sample Magnetometer (VSM). Further, the magnetic assembly of the synthesized magnetically responsive MWCNTs was demonstrated in the lab using direct and alternating magnetic fields of varying strengths.

6.1 Electron Beam Evaporation for Nickel Coating on CNTs

As noted in Chapter 3, e-beam evaporation was selected as the deposition method for synthesizing magnetically-responsive MWCNTs. The deposition was carried out on the Kurt J. Lesker AXXIS Multipurpose Physical Vapor Deposition System located in Dr. Suzanne Mohney’s lab in the Department of Materials Science and Engineering, PSU. The e-beam setup consists of an inverted stage for holding CNT samples. The stage is inverted directly above a crucible containing the
metal to be deposited (in this case, nickel). A filament focuses an electron beam on to the metal in the crucible. The electrons strike the metal in the crucible, causing it to heat up and evaporate. The evaporated metal rises up and gets deposited on the inverted substrate. The entire apparatus is enclosed in a high vacuum chamber, to prevent impurities, and to facilitate the deposition. Since e-beam evaporation is a line-of-sight process, if the CNT tips are closely packed together, the coating can form clusters of CNTs. This tendency to form clusters is reduced by plasma treatment of the CNTs.

After the samples were loaded into the deposition chamber, the chamber was pumped down to an operating pressure of less than ~0.8 µTorr. After pumping, the CNT samples were masked and Ti vapor was introduced into the chamber by focusing the electron beam on the crucible containing titanium. The Ti vapors react with any oxygen and water vapor that might have been introduced in the chamber while loading, to form titanium oxides. This process is known as gettering and is used to improve the vacuum inside the chamber. Thereafter, the CNT sample was unmasked and the Ni deposition was carried out by using the electron beam to evaporate nickel. The deposition rate used was ~1 Å/sec, and the deposition was conducted without stage rotation. Samples with Ni coating thicknesses of 20 nm, 40 nm, 60 nm, 80 nm and 100 nm were prepared.

6.2 Characterization of Ni Coating

The nickel coated samples were inspected visually using SEM imaging. EDS was used to understand the elemental composition of the samples. In addition, the magnetic property of the Ni-coated CNTs was characterized using VSM.

6.2.1 SEM and EDS Inspection for Morphology

Figure 6.1 shows the surface of the CNT forest for CNTs without coating, with 20 nm Ni coating and 100 nm Ni coating. Individual CNTs are clearly visible in figure 6.1(a). As the thickness of the Ni deposition increases, the CNTs get coated and the individual CNTs start forming clusters. With 100 nm of Ni coating (figure 6.1(c)), individual CNTs cannot be observed. The cross section of the CNT forests is seen in figure 6.2. With increasing Ni deposition, thickness of the coating around CNT sidewalls increases, but the coated length of CNTs remains almost the same. With 20 nm Ni coating, the amount of nickel deposited is not enough to evenly coat all the CNT tips. However with a 100 nm Ni deposition, the excessive Ni causes CNTs to clusters, with multiple CNTs bundles together because of the thick coating. The formation of CNT clusters has an adverse impact on the suspension properties. Clusters, being heavier particles tend to agglomerate quickly within a solution, reducing the settlement time for the Ni-coated CNT sample. With thicker Ni deposition, the Ni layer is highly likely to delaminate from the CNTs. This leads to non-uniform particle sizes when dispersed in a solution. Considering
these factors, the ideal Ni coating thickness would be one which evenly coats CNT tips, without causing large clusters, is somewhere between 20 nm and 100 nm. The coating thickness also affects the magnetic anisotropy, and hence the magnetic assembly of the CNTs. With lower deposition thickness, the coated CNTs will not possess sufficient magnetic anisotropy to cause a change in orientation. Further experiments will be carried out to ascertain the ideal thickness of Ni coating.

Energy dispersive X-ray spectroscopy (EDS) was used to map element distributions, particularly the Ni coating on the CNT surface. EDS is an analytical method which uses a high-energy incident beam of charged particles to excite electrons in the inner shell of an atom, which creates an electron hole. An outer layer electron loses energy to fill that hole, and the energy lost is released in the form of X-rays. Since the energy difference between outer and inner shells is characteristic of each element, this can be used for elemental analysis of samples. The location of each element present in the sample can be mapped and overlaid on an SEM image to understand the elemental positions on the sample surface. As seen in figure 6.3, presence of Ni was confirmed with 20 nm thick deposition, with EDS. With increasing thickness, more Ni intensity was observed around the CNT tip areas, indicating thicker Ni layers leading to the formation of CNT bundles.

6.2.2 Characterization of Magnetic Properties using VSM

The anisotropic magnetic properties of the Ni-coated CNTs were measured using MicroSense EZ VSM located in Dr. Paris von Lockette’s lab at the Department of Mechanical and Nuclear Engineering, PSU. VSM is used to measure the response of a magnetic sample to external magnetic field. This is done by oscillating a magnetic sample inside a controlled magnetic field, and measuring the change in the applied field as a result of the interference caused by the samples oscillations to the applied field. Samples coated with 20 nm and 100 nm of nickel were analyzed along with a reference sample. The reference sample was a silicon wafer with the catalyst (1 nm Fe, 30 nm Al₂O₃) deposited on it. It is important to subtract the effect of the substrate with Fe catalyst particles, from the VSM data of Ni-coated CNTs. All three samples were tested in the axial as well as transverse orientation against CNT alignment, as shown in figure 6.4 and the magnetization response of the sample to a change in the external magnetic field was analyzed. Figure 6.5(a) shows the magnetization response of 100 nm Ni coated sample after substraction of the magnetization due to catalyst-coated substrate. The VSM results (see table 6.1) show that there is higher remanent magnetization and lower coercivity in the axial orientation. Remanant magnetization, as the name suggests, is the magnetization left behind in a sample when the external field is removed, while coercivity is the strength of the external magnetic field needed to reverse the direction of magnetic domains in the sample (see figure 6.4(b)). This is expected as the aspect ratio of Ni coating is much higher in the axial orientation as compared to the transverse orientation which makes it is easier for the magnetic domains to realign with a change in the direction of magnetic field, leading to lower coercivity. With an increase in the Ni-coating thickness, the remanence increases and coercivity decreases.
6.3 Magnetic Assembly of Ni-coated CNTs

Preliminary magnetic assembly of Ni-coated CNTs (100 nm) was demonstrated with the small magnetic field (~100 G) after a short time (15 minutes). As shown in figure 6.6, the setup consists of an optical table with two solenoid coils. The sample is placed on a microscopic slide between the solenoids. The solenoids are connected to a variable power source and a function generator to control magnitude and type of magnetic field produced by the solenoids. A gaussmeter is introduced in the region between the solenoids to measure the magnetic field strength, and a digital microscope (Olympus BX51WI) is used for in-situ observation of magnetic assembly of the Ni-coated MWCNTs.

Samples for magnetic assembly were prepared by dispersing Ni-coated CNTs in DI water (~35 mg of MWCNTs in 750 µL of DI water). DI water was chosen as the solvent for this test, because unlike IPA, DI water does not evaporate quickly at room temperature, affecting the concentration of the dispersion. A few drops of this solution were placed on a microscopic slide and the slide is placed between the solenoid coils and under the microscope eyepiece. The solenoids are energized to the desired magnetic field strength (~100 G to 200 G) by controlling the power supply, and the function generator was used to control the frequency of the magnetic field. The effect of the external magnetic field on the CNTs in the CNT-DI water solution were observed using the microscope.

When subjected to an external field of 100 G DC, the CNTs with 100 nm thick Ni-coating showed alignment along the direction of applied magnetic field, in ~15 minutes, as seen in figure 6.7. But CNTs with 20 nm Ni-coating did not show any response to DC magnetic fields of up to 175 G. When subjected to an AC magnetic field of 175 G at 1 Hz frequency and 50% duty cycle, the 20 nm CNTs showed slight oscillation after 5 minutes. Definite magnetic assembly could not be obtained for 20 nm Ni-coated CNTs, as with smaller thickness, the coatings are not responsive to external magnetic field.

6.4 Future Work

To further improve the characteristics of magnetically responsive CNTs, the adhesion of Ni coating to the surface of CNTs should be studied. The plasma treatment parameters could possibly be altered to introduce different functional groups, to improve Ni adhesion. Possibly, a thin layer of Fe could also be deposited on the CNTs instead of Ni deposition to intentionally form carbides. This would cause chemical bonding of the coatings to the CNT surface and potentially improve adhesion. VSM analysis of 40 nm, 60 nm, and 80 nm Nickel coated samples can help in further characterization of the magnetic properties of Ni-coated CNTs. Other methods of metal deposition such as atomic layer deposition (ALD) or electroplating can also be considered for more conformal coating.

Further experiments with 40 nm, 60 nm, and 80 nm Nickel coated CNTs as well as with AC and
DC fields of different magnetic strengths need to be carried out to quantify the effects of field strength and frequency on the assembly of magnetically responsive CNTs. In addition to the frequency, the waveform shape and duty-cycle of the magnetic field can be varied to study their effects on magnetic assembly.
Figure 6.1: SEM images of CNT forest surface (a) without Ni coating, (b) with 20 nm Ni coating, and (c) with 100 nm Ni coating

Figure 6.2: SEM images of CNT forest cross section (a) without Ni coating, (b) with 20 nm Ni coating, and (c) with 100 nm Ni coating
Figure 6.3: EDS images of dispersed, Ni-coated MWCNTs (a) with 20 nm Ni coating, (b) with 40 nm Ni coating, (c) with 60 nm Ni coating, and (d) with 80 nm Ni coating. The green and red regions indicate presence of Ni coating.
Figure 6.4: Schematic showing (a) the orientation of CNTs in the magnetic field for VSM analysis, and (b) the typical hysteresis curve obtained from VSM analysis.
Figure 6.5: (a) Plot of magnetization vs external magnetic field for reference substrate and 100 nm Ni-coated CNT sample in both axial and transverse orientation (b) zoomed image showing region of interest for remanence and coercivity measurement
Figure 6.6: Setup for conducting magnetic assembly of magnetically responsive MWCNTs (a) schematic, and (b) digital image. Images prepared by Mychal Spencer.

Figure 6.7: Digital microscope images of 100nm Ni-coated MWCNTs dispersed in DI water (a) before, and (b) after application of 100 G DC magnetic field.
Table 6.1: Variation of remanence and coercivity as a function of coating thickness and test orientation

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Remanence (emu)</th>
<th>Coercivity (Orsted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Axial</td>
<td>$84.28 \times 10^{-6}$</td>
<td>253.69</td>
</tr>
<tr>
<td>Transverse</td>
<td>$71.79 \times 10^{-6}$</td>
<td>203.78</td>
</tr>
<tr>
<td>100 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Axial</td>
<td>$422.92 \times 10^{-6}$</td>
<td>129.71</td>
</tr>
<tr>
<td>Transverse</td>
<td>$234.13 \times 10^{-6}$</td>
<td>189.39</td>
</tr>
</tbody>
</table>
Chapter 7
Conclusions and Recommendations for Future Work

A summary of results from this thesis are presented in this chapter. Suggestions for future work to improve CNT dispersion and suspension, to optimize magnetization and anisotropy, and to enhance magnetic assembly will follow. Contributions from this thesis will be listed. Future work suggested based on this thesis work will follow.

7.1 Summary of Results and Contributions

In this work, the following four tasks were accomplished to demonstrate effective magnetic assembly of MWCNTs as the first step to achieve scalable manufacturing of CNT-polymer nanocomposites. Magnetic assembly is a promising scalable method to bulk organize CNTs within polymer matrix solutions, and CNTs need to be processed to suspend within matrix solution and to have anisotropic magnetic properties. First, in-house synthesis of MWCNTs was accomplished by apparatus and recipe development. Second, CNTs were successfully functionalized using scalable, dry, non-polluting air plasma treatment. Dispersion degree was investigated through settlement studies and SEM inspection. The results were compared with chemical states information measured using XPS. Best dispersion and suspension was correlated with oxygen containing functional groups. Third, CNTs were successfully processed to have anisotropic magnetic properties by conformal thin Ni coating with high aspect ratio. Balancing between magnetization strength and anisotropy was confirmed with varying Ni coating thickness. Fourth, effective alignment of Ni-coated CNTs was demonstrated with application of weak magnetic field (~100 G) in a short time (~15 min). The major contributions through this thesis work are listed below.

Synthesis of MWCNTs using CVD:

- Chemical vapor deposition system to synthesize MWCNTs was designed and built consisting
of an atmospheric growth chamber, controlled supply of carbon source, reduction, and diffusion gases, and exhaust system.

- A CVD recipe was developed (see table 4.1) to achieve repeatable and consistent deposition of carbon with multi-walled tube structure, through parametric growth studies with varying substrate preparation (catalyst layer thickness, diffusion barrier thickness, and moisture control) and reduction gas treatment. As for substrate preparation, the Al$_2$O$_3$ diffusion barrier layer needs to be thick (~30 nm) for robustness, and the Fe catalyst layer needed to be very thin (~1 nm) to form distributed nanoparticles. Small amount of moisture precipitation significantly mitigated uniform growth of CNTs, and thus need to be carefully controlled. Application of hydrogen gas treatment was also the key to reduce the catalyst layer to nucleate nanoparticles to form distributed and vertically aligned MWCNTs.

- Vertically aligned MWCNTs (~200 µm in length and 35±10 nm in diameter, with an average of 20 to 30 walls) were successfully fabricated to be processed to become magnetically-responsive through functionalization and Ni-coating deposition.

**Air plasma treatment of MWCNTs:**

- The top layer of entangled CNTs were eliminated through oxygen plasma. The CNT tips were exposed to be conformally coated with ferromagnetic Ni layers.

- Parametric studies of air plasma treatment was conducted to enhance dispersion and suspension of CNTs within IPA solution, by varying treatment time (4, 6, 8, and 10 mins) and power setting (6.8, 10.5, and 18.0 W). Settlement study identified that plasma treatment with low power setting (6.8 W) with moderate time (4 min) most improved CNT suspension. SEM inspection of dispersed CNTs showed comparable results with the settlement study: the CNTs treated with the above condition (6.8 W for 4 min) were most loosely packed with small clusters.

- Functional group attachment due to air plasma treatment was measured using XPS, and correlated with CNT suspension results. Measured C1s peaks were peak-fit to quantitatively evaluate hydroxyl, carbonyl, and carboxyl function groups, using pristine CNT measurement as a reference. Decency of peak-fitting was confirmed by comparing the oxygen percentage calculated from peak-fit results and the oxygen percentage directly calculated from the survey oxygen peak. The XPS analysis on these plasma treated CNTs have provided some insights on the specifics of this functionalization process, including the unstable but effective ether (C-O) functional group attachment with low power (6.8 W) for short time (4 minutes). Effective CNT dispersion and suspension was correlated with the largest oxygen percentage and thus higher attachment of oxygen containing functional groups, if the hypothesis of this functional group degradation was to be accepted.
Conformal nickel coating using e-beam evaporation:

- Relatively conformal Ni coating was demonstrated by directional e-beam evaporation on vertically aligned CNTs, and their coating morphology was inspected with SEM and EDX. With increasing thickness (~100 nm), Ni coating filled in the spacing between CNTs, forming clusters and preventing dispersion.

- Anisotropic magnetic properties of Ni-coated CNTs were measured using vibrating sample magnetometer. Magnetization strength and anisotropy were observed to change with Ni coating thickness. With the smaller thickness (~20 nm), remanence and coercivity in the axial direction were larger than those in the transverse direction; these results are compatible with the previous results, indicating coating is thin enough to form a collection of small magnetic domains aligned along the CNT direction. Meanwhile, with the larger thickness (~100 nm), remanence is larger but coercivity is smaller in the axial direction than in the transverse direction; this change can be attributed to magnetic domain changes due to increased coating thickness or decreased aspect ratio of the Ni coating.

Alignment of magnetically responsive CNTs using magnetic fields:

- Preliminary study confirmed effective magnetic alignment of MWCNTs with ~100-nm-thick Ni coating dispersed in IPA when applied with weak magnetic fields of ~100 G in 15 min.

7.2 Recommendations for Future Work

Further investigation will be necessary for the following tasks in future.

CVD synthesis of CNTs:

- Improve consistency and cleanliness of as-grown MWCNT samples with moisture control and debris elimination from substrate
- Increase MWCNT quantity that can be grown at one time for more scalability

Plasma treatment:

- Investigate plasma treatment with more parameters and their range, such as higher power setting, longer treatment time, and different gas type, using settlement and XPS analysis
- Evaluate degradation of function group attachment over time
- Conduct more dispersion and settlement study: more intensive CNT dispersion and dispersion in polymer matrix solution
Ferromagnetic coating on CNTs:

- Finish VSM characterization of MWCNTs coated with Ni layer of 40, 60, and 80 nm to observe transition of anisotropic magnetic properties
- Evaluate adhesion of metal coating to CNTs during dispersion and assembly processes
- Try other, more conformal coating methods on CNTs such as electroplating or atomic layer deposition

Magnetic assembly:

- Study behavior of magnetic assembly with varying parameters of magnetic fields (magnitude and oscillating frequency) and polymer viscosity
- Fabrication and characterization of CNT-polymer nanocomposites with varying CNT structures
Bibliography


