Property Control of Single Walled Carbon Nanotubes and Their Devices

by

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

2008
ABSTRACT

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Abstract

Controlling the properties of single walled carbon nanotubes (SWNTs) is the major challenge toward their future applications. This dissertation describes several contributions to this challenge.

This dissertation begins with the brief review on carbon nanotubes (CNTs), including discovery, structure, properties, challenges, synthesis and applications. The remaining parts can be divided into three sections. They demonstrate the control of SWNT properties as well as their devices by direct synthesis and metal decoration.

Two studies are described on the control of SWNT properties by direct synthesis. The first demonstrates the controlled synthesis of SWNTs in terms of their diameter, uniformity, and density by the chemical vapor deposition (CVD) method. The approaches employed include using uniform nanoparticles with specific sizes as catalysts to grow different diameter SWNTs, specially small diameter tubes less than 1 nm; using laser irradiation to grow uniform and high quality SWNTs; and changing the gas flow pattern to obtain different density. The second study demonstrates the growth of aligned SWNTs by flow and substrate guidance. Horizontally aligned ultralong nanotubes are synthesized on Si substrate by both high flow and low flow. The guided growth by the quartz substrate is shown by a large variety of metal catalysts to further the understanding of the growth mechanism. Moreover, top gated FETs have been explored for the selective growth of purely semiconducting, horizontally aligned SWNTs grown on quartz by a ethanol/methanol mixture.
The control of SWNT device performance is also described, in particular, the correlation between the SWNT field effect transistor (FET) configuration and its gate dependence response. The effects of FET channel length, nanotube density and diameter on the device performance are demonstrated. A model has been constructed in order to simulate the electronic behavior. An interesting metallic behavior has been observed.

Finally, control of SWNT properties by Palladium decoration after growth is used to manipulate their properties. Moreover, two novel applications including improvement of carbon nanotube film conductivity and catalysis of nanostructure growth are developed.
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<th>Description</th>
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<tbody>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotube</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionized</td>
</tr>
<tr>
<td>DOS</td>
<td>Density of states</td>
</tr>
<tr>
<td>DWNT</td>
<td>Double walled carbon nanotube</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectrometer</td>
</tr>
<tr>
<td>FET</td>
<td>Field effect transistor</td>
</tr>
<tr>
<td>FWNT</td>
<td>Few walled carbon nanotube</td>
</tr>
<tr>
<td>HiPco</td>
<td>High-pressure carbon monoxide</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High resolution electron microscopy</td>
</tr>
<tr>
<td>MWNT</td>
<td>Multi walled carbon nanotube</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma enhanced vapor deposition</td>
</tr>
<tr>
<td>PS-P4VP</td>
<td>Poly(styrene-b-4-vinylpyridine)</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimeter</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single walled carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-liquid-solid</td>
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Chapter 1: Introduction to Carbon Nanotubes

1.1 Discovery of Carbon Nanotubes

The carbon nanotube (CNT) is one of the most intensively studied nano-materials. CNTs are an allotrope of carbon, a high aspect ratio nanostructure, a member of the fullerene structural family, and a cylindrical carbon molecule of entirely sp² bonds. The novel properties of CNTs have led to useful applications in nanotechnology, electronics, optics and other fields.

Although most of the academic community attributes the discovery of CNTs to Sumio Iijima at NEC in 1991, the observation of the hollow carbon structure actually can be traced back decades before that date. In 1952, two soviet scientists, L.V. Radushkevich and V. M. Lukyanovich showed the images of 50 nm diameter carbon tubes.¹ This discovery was published in a Russian language Journal and not noticed, probably due to the Cold War. Oberlin, Endo, and Koyama demonstrated hollow nanometer-scale carbon fibers using a vapor growth technique in 1976.² Significantly, a transmission electron microscope (TEM) image showed a single wall nanotube. In 1979, John Abrahamson presented carbon nanotubes produced by arc discharge at the 14th Biennial Conference of Carbon.³ In 1981, Soviet scientists showed the chemical and structural characterization of carbon nanotubes produced by carbon monoxide thermal decomposition. They proposed that the nanotube was formed by rolling a graphene layer into a cylinder. In addition, they hypothesized the different carbon atom arrangement of the armchair and chiral nanotube.¹ Howard G Tennent of Hyperion Catalysis was issued a patent for the production of “cylindrical discrete carbon fibrils” in 1987.⁴

Although CNTs have been produced and observed prior to 1991, Iijima’s discovery⁵ is of particular importance because the carbon nanotube research was drastically popularized among the science and engineering community after the observation of multi-walled carbon nanotubes
(MWNTs) under high resolution transmission electron microscope (HRTEM) on the cathode of a carbon arc. Since then, numerous methods have been developed to synthesize and characterize carbon nanotubes. Various applications have bloomed in the last fifteen years and carbon nanotubes have emerged as one of the hottest topics in nanotechnology and may trigger the nanotechnology revolution in the future.

1.2 Structures of Carbon Nanotubes

A CNT can be described as a rolled up graphene sheet that is closed at each end with half of a fullerene, as shown in Figure 1. However, this is purely an intuitive description, and CNTs are actually not formed in this way. CNTs are simply classified as single-walled and multi-walled tubes according to the number of sidewall layers. Single-walled carbon nanotubes (SWNTs) which have only one layer or sidewall are one-dimensional molecular wires with a diameter from 1 to 2 nm, exhibiting special structural features and unique electronic properties that have attracted great interest in their applications. MWNTs consist of more than one and up to dozens of walls. Among them, a subset of MWNTs containing 2-6 layers of graphene sheets and with a diameter less than 5 nm have been named as few-walled carbon nanotubes (FWNTs). They have attracted significant interest because of the high quality and high yield with which they can be produced.

![Figure 1: Schematic illustration of a 2D single layer graphene sheet rolling into a SWNT. The figure is adapted from ref[6].](image)
The unique structure of CNTs leads to their distinctive properties. The construction of a SWNT from a single layer of graphene sheet is demonstrated in Figure 2. The relation between the hexagonal carbon lattice and the chirality of a CNT is determined by the wrapping vector $\mathbf{C}$, which is defined with the two integers $(n, m)$ and the basis vectors of the graphite sheet as $\mathbf{C} = na_1 + ma_2$. The chiral angle $\theta$ (between 0° to 30°) is the angle between the chiral vector $\mathbf{C}$ and the so-called “zigzag” direction $(n, 0)$. The integers $(n, m)$ determine the diameter of the tube and $\theta$. The graphite sheet is rolled up in the direction of the chiral vector $\mathbf{C}$ to get a $(n, m)$ nanotube. The direction perpendicular to $\mathbf{C}$ is called translation vector $\mathbf{T}$, which is the direction along the SWNT axis. As shown in Figure 3, special classes of nanotubes are the so-called “armchair” nanotubes $(n, n)$ and the “zigzag” nanotubes $(n, 0)$. All the others are “chiral” nanotubes $(n, m)$ with $n \neq m$ and $m \neq 0$. Whether a nanotube is a conductor or a semiconductor is determined by its chirality. If $(n-m)/3$ is an integer, the nanotube is a metal and otherwise a semiconductor. In a bulk sample, the SWNTs are often found in bundles that are formed by a triangular arrangement of individual SWNTs, with nanotubes held together by Van der Waals forces.
Figure 2: Schematic illustration of a SWNT atomic structure. The figure is adapted from ref[8].

Figure 3: Molecular models of SWNTs with different chiralities. (a) armchair, (b) zig-zag, and (c) chiral. The figure is adapted from ref[9].
1.3 Properties of Carbon Nanotubes

CNTs have an array of unique structural, mechanical, and electronic properties, such as a high length/diameter ratio, chemical inertness, high mechanical strength but low density, high thermal stability and conductivity, 1D ballistic transport, biocompatibility and the close relation to graphene. Here, we present some selected properties.

1.3.1 Electronic Properties

The electronic properties of CNTs are derived from the graphene electronic structure and affected by their carbon atom arrangement – helicity. SWNTs can be either metallic or semiconducting depending on the \((n, m)\) wrapping vector. Theoretically, SWNTs possess several unique properties. For example, a metallic SWNT can have an electrical current density more than 1000 times greater than copper. As a 1D structure, electron transport in the SWNT takes place through quantum effects and propagates along the tube axis.

1.3.1.1 Band Structure of Single Walled Carbon Nanotubes

The distinct electronic properties of SWNTs formed by carbon sp\(^2\) hybridization can be discussed starting from the 2D energy dispersion of graphene. Graphene is a semimetal whose valence and conduction bands degenerate at only six \(K\) corners, defining the first Brillouin zone as shown in Figure 4a. These six points form the Fermi surface of the graphene sheet. After rolling this 2D sheet into a 1D SWNT, the wave vector \(K\) becomes quantized due to the periodic boundary conditions: \(K \cdot C = 2\pi q\), where \(q\) is an integer and \(C\) is the chiral vector. By this constraint, only a set of discrete states are allowed. As shown in Figure 4, if the wave vector passes thought the \(K\) points, the nanotube will be metallic (Figure 4b) and if not, it will be semiconducting (Figure 4c). It is clear that the (9, 0) tube contains a \(K\) point but (10, 0) tube has none. However, the curvature of the tubes causes the mixing of the \(\pi/\pi^*\) bonding and \(\pi/\pi^*\) antibonding orbitals on carbon. Then the wave vector shifts away from the \(K\) point so as to produce small gaps in \((n, 0)\) and \((n, m)\) metallic tubes with the band gap depending inversely on
the square of the tube diameter. Armchair (n, n) tubes are truly metallic because there is no such shift. Therefore, (n, 0) or chiral (n, m) SWNTs are small band gap metallic tubes when \((n-m)/3\) is an integer and otherwise semiconducting.

Figure 4: Band structure of graphene and its relationship to the SWNTs. (a) Three-dimensional view of the graphene \(\pi/\pi^*\) bands and their 2D projection. (b) Example of the allowed 1D subbands for a metallic tube. Schematic depicts \((9, 0)\). (c) Example of the quantized 1D subbands for a semiconducting tube. Schematic depicts \((10, 0)\). The white hexagon defines the first Brillouin zone of graphene, and the black dots in the corners are the graphene \(K\) points. The graph is adapted from ref[6].
The density of states (DOS) of SWNTs is shown in Figure 5. The left plot a is the DOS of a metallic SWNT and the right plot b is the DOS of a semiconducting tube. Near the Fermi level $E_F$, the possibility of electron occupation for a metallic SWNT is non-zero, while it is zero for a semiconducting tube. The DOS plots of both kinds of tubes are symmetric with very high density mirrored spikes in both conduction and valence bands, called von Hove singularities (VHS), that result from the 1D structure and the curvature of the SWNTs.

According the above description of a SWNT band structure, the energy gaps of the semiconducting tubes are theoretically inversely dependent on the tube diameter as shown in Figure 6. This inverse dependence is reasoned from the semiconducting energy gap corresponding to the vertical separation between $\pi$ and $\pi^*$ bands. Because of this dependence, larger semiconducting tubes should have smaller energy gaps. For application of SWNTs as transistors, small diameter or large band gap tubes are highly desired for minimizing the off-stage current leakage and increasing the on/off ratio.
Figure 5: Schematic diagram of electronic density of states. (a) metallic and (b) semiconducting SWNTs. The graph is adapted from ref[12].

Figure 6: Calculated band gaps of semiconducting SWNTs inversely proportional to their diameters. The graph is adapted from ref[13]. $E_g$ is 2.5 eV.
1.3.1.2 Electrical Transport Properties of Single Walled Carbon Nanotubes

The unique electronic transport properties of SWNTs come from the confinement of the electrons in its 1D structure.

Metallic SWNTs can hold current densities up to $10^9 \text{A/cm}^2$. This large value is more than 100 times of metals such as Cu. The strong carbon-carbon bonds and the small scattering effects both contribute to this property. Because of this property, SWNTs are highly resistive to the electron migration. In addition, metallic SWNTs have a Fermi velocity similar to the metals and higher hole-mobility than silicon.

A semiconducting SWNT FET behaves like a p-type transistor because of oxygen adsorption on the tubes. The conductance will decrease as the electric gate bias increases. The on stage is the state at the negative gate bias and the off stage is at the positive bias. However, the Schottky barrier at the tube-metal junction can dominate the overall device performance because of the poor coupling between a SWNT and the metal electrode due to their different energy structure. Therefore, the electrode metal should be carefully selected to match the tube band structure in order to limit this effect; as such, Pd is a good choice for electrodes.

1.3.2 Optical Properties

The optical properties of SWNTs are a consequence of the 1D confinement of their electronic structure. This unique electronic structure results from the VHS of SWNTs. All the optical techniques used to characterize SWNTs are based on this property. Such optical methods, including absorption, Raman, infrared spectroscopy, and others, are simple, quick, and nondestructive. Moreover, individual nanotubes can be characterized using such methods. The basis of all the techniques can be understood by the so-called Kataura plot as shown in Figure 7. Each point in the plot shows one optical transition energy $E_{ii}$, which determines the energy of the light absorption by the nanotube, for a specific $(n, m)$ nanotube with a diameter $d_t$. 
In this section, only Raman spectroscopy is discussed because it is relevant to the research presented in the following chapters.

1.3.2.1 Raman Spectroscopy of Single Walled Carbon Nanotubes

Raman spectroscopy is widely used to characterize SWNTs. The method is simple, sensitive, and requires no sample preparation. As shown in Figure 8, the Raman spectra of SWNTs have many characteristic features. Herein, we will discuss three of them, the radial breathing mode (RBM), D mode and G mode, because these three will be used in the next chapters and are the primary modes by which nanotube samples are characterized. The Raman signal is strongly dependent on the excitation laser wavelength (energy) and in particular, matching the excited energy to the optical transition energy can greatly enhance the Raman signal, termed as resonance Raman spectroscopy (RRS). In addition, the Raman intensity is
dependent on the orientation between the excited light polarization and the tube direction. Only a tube with the axis along the polarized direction results in the strongest intensity.

![Raman spectra from a metallic and a semiconducting SWNT at the single-nanotube level. The graph is adapted from ref[17].](image)

Figure 8: Raman spectra from a metallic and a semiconducting SWNT at the single-nanotube level. The graph is adapted from ref[17].

The RBM is one of the most important regions in SWNT Raman Spectra. The RBM peak position and intensity can be used to determine the diameter, \((n, m)\), and other properties of SWNTs. Herein, we demonstrate the relationship of the diameter to the RBM frequency which is relevant in the following chapters. Calculations from the RBM are the most accurate method to measure the diameter of a SWNT. Numerous experiments and theoretical calculation have concluded that the diameter of a SWNT is inversely proportional to its RBM peak frequency, although many different relation equations have been published in the literature.\(^{17}\) The RBM results is from the radial vibration of the tube, and is dependent on the environment around the tubes such as the substrate, surfactant, outer-force, etc.
The G mode is derived from the G band in graphite at a single-peak of 1582 cm\(^{-1}\). The G band in a SWNT is in the range between 1565 and 1590 cm\(^{-1}\) because of the tube curvature. The G band has very important information about the tube type, with metallic and semiconducting tubes having different line-shapes as shown in Figure 8. A metallic tube generally has a broader shoulder. This feature can be used to distinguish the tube type.

The D mode appears in the range between 1350 and 1370 cm\(^{-1}\). It represents the disordered sp\(^2\) bonding such as sp\(^1\) and sp\(^3\) carbon. Amorphous carbon and MWNTs often show strong D band, and the D band indicates the defect and impurity level of a SWNT sample.

1.3.3 Mechanical Properties

Carbon nanotubes have unique mechanical properties because of their structure and chemical bonding. The carbon-carbon bond is the strongest bond known in nature. The cylindrical structures of CNTs further enhance the mechanical strength. Some strong materials are listed in Table 1 with their Young’s modulus, showing that CNTs are the strongest. However, the mechanical properties are dependent on the structural quality; thus, high quality tubes are desired for mechanical applications.
Table 1: Young’s modulus for SWNTs, MWNTs and other materials. The table is adapted from ref[18].

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Alloys</td>
<td>72 GPa</td>
</tr>
<tr>
<td>Steel</td>
<td>200 GPa</td>
</tr>
<tr>
<td>Tungsten</td>
<td>400 GPa</td>
</tr>
<tr>
<td>Carbon Fibers</td>
<td>800 GPa</td>
</tr>
<tr>
<td>SWNTs</td>
<td>1.25 TPa</td>
</tr>
<tr>
<td>MWNTs</td>
<td>1.28 TPa</td>
</tr>
</tbody>
</table>

1.4 Synthesis of Carbon Nanotubes

High quality, high yield, and controllable synthesis techniques of CNTs, especially SWNTs are necessary for many research applications. Several techniques have been developed to synthesize CNTs in large scale or on various substrate surfaces for different applications. Current synthesis techniques include arc discharge, laser ablation, high pressure carbon monoxide (HiPCO), and chemical vapor deposition (CVD). Among them, the CVD method is the most popular due to its scalability and versatility; it includes various deposition techniques in industry such as low pressure, plasma enhanced, etc.

1.4.1 Arc discharge and Laser ablation

Arc discharge and laser ablation were the first methods used to produce CNTs and SWNTs.\textsuperscript{19-21} CNT research became a hot topic after Iijima synthesized CNTs by arc discharge method at NEC Lab in Japan.\textsuperscript{5} In the arc discharge method, carbon atoms are evaporated by the inert gas plasma induced as high currents are passed through two graphite rods, as seen in Figure 9. The growth conditions are normally at a pressure around 500 Torr and a high
temperature of 3000-4000 K with high DC current across the electrodes. CNTs are formed in the cathode and the chamber inside-wall as the anode is consumed. For MWNTs, no catalysts are needed but they are required for SWNT synthesis. Common catalysts are transition metals such as Fe, Co, Ni or their alloys, which are stored inside a hollow graphite anode. The arc discharge method can produce high quality MWNTs and SWNTs because of the high temperature and other features.\textsuperscript{22} The laser ablation method is similar to arc discharge, except that the carbon atoms are evaporated from the solid carbon source target ablated by a high energy pulsed laser. The target is heated to a high temperature above 1200 \textdegree C inside a furnace under a flow of inert gas. The CNTs are collected in the trap by water cooling in the downstream. To obtain SWNTs, catalysts are added to the target as the arc discharge method. Similarly, the quality of the synthesized CNTs is high.

The above two methods were the first methods to synthesize SWNT in relatively large amounts.\textsuperscript{23} However, both methods employ hot gaseous carbon atoms generated from the evaporation of solid carbon; as such, the equipment requires a large amount of energy. Thus the yield compared to the energy consumption is low. In addition, the CNTs synthesized are powder sample in bundles.\textsuperscript{21} Also, controlled, well organized synthesis on substrates is impossible by these two methods. Interestingly, a variation of the laser ablation method, laser assisted heating growth shows promising potential in controlled surface synthesis and is discussed in this dissertation.
Figure 9: Arc discharge method for carbon nanotube synthesis. (a) Schematics of the arc-discharge setup for carbon nanotube production. (b) Image of the arc experiment between two graphite rods. The extreme temperature reached during the experiment is located between the rods (~3000-4000 K). The figure is adapted from ref[9].
1.4.2 Chemical Vapor Deposition

CVD is a chemical process, normally used to produce high-purity, high-performance solid materials. In the semiconductor industry, CVD is a typical process for synthesizing thin films on substrates (wafers) by the chemical decomposition of the reaction gases. CVD methods have many variations. According to the chamber pressure during the process, it can be classified as atmospheric pressure CVD (APCVD), Low-pressure CVD (LPCVD), etc. The CVD can be assisted by plasma, microwave, etc. In this thesis, we focus on the most common and simplest APCVD because CVD synthesis of CNTs is still in an early stage.

1.4.2.1 Description of SWNT CVD Setup

Figure 11 shows a typical CVD system setup for CNT growth. The carbon feeding gases, such as methane, ethane, etc, are introduced into the system when the substrate with the catalysts is heated up to a desired temperature. The carbon containing gases are decomposed to provide the carbon source for CNT growth. The temperature, carbon feeding gases, catalysts, and other parameters can be tuned in order to control the growth results. For this reason, along...
with the simple setup and low cost, CVD is the most widely used methods for CNT synthesis. Figure 12 shows a photograph of a CVD system in our lab.

Figure 11: Schematic illustration of a typical CVD system for SWNT surface growth.

![Schematic illustration of a typical CVD system for SWNT surface growth.](image)

Figure 12: The photograph of a typical CVD system in our lab. It has the computer controlled gas flow system to feed the gases, the tube furnace to heat the reaction chamber and the quartz tube reactor to hold the CVD synthesis.

![Photograph of a typical CVD system in our lab.](image)
1.4.2.2 Mechanism of Single Walled Carbon Nanotube CVD Synthesis

Much research has been done on the mechanism of SNWT synthesis. However, no final conclusion or systematic model has been achieved. Researchers generally agree on the base-growth and tip-growth models within the so-called vapor-liquid-solid (VLS) growth mechanism adopted from the nanowire growth.

As shown in Figure 13, when the catalysts are heated up to an elevated temperature, the solid metal catalysts will become liquid or semi-liquid nanoparticles, depending on their melting points. The hydrocarbon decomposition occurs on the surface of these metal droplets, producing carbon and other species, and the carbon atoms dissolve into these metal droplets. When the carbon concentration inside reaches a certain level (we assume the saturation level), carbon atoms start to precipitate from the metal droplets on the outer shell of the catalysts. The formation of tubular carbon solids with sp² structure from the catalyst surface results into the carbon nanotube growth. The growth terminates when growth conditions are no longer favorable, for example due to the carbon feeding change, temperature change and catalyst aggregation.

The above mechanism implies the nanotube diameter is clearly related to the nanoparticle diameter. As shown in Figure 14, the SEM image proves the model as well as...
indicates the relationship between the tube and the catalyst for a base growth model. The tip-model is similar except that the catalyst nanoparticle drags the growing CNT. Moreover, by selecting different size catalysts, corresponding diameters of carbon nanotubes were grown as shown in Figure 15. Consequently, the diameter of the CNTs can be easily controlled by the size of the catalysts. However, many other parameters can affect the growth so that the overall effect should be considered.

Figure 14: SWNT growth mechanism. (a-f) TEM images of SWNTs grown from nanoparticles. (g) A schematic model for nanotube growth. (h) AFM image of SWNT grown from a particle. The figure is adapted from ref[25].
1.5 Challenges of Single Walled Carbon Nanotubes - “Control”

Although numerous potential applications of SWNTs have been discussed, none have led to the real products so they are limited in the research laboratories. SWNT synthesis remains a central focus of CNT research. Reliable control over the synthesis, or manipulation after synthesis to produce the specific (n, m) carbon nanotube or desired diameter at a given location, or growing in a desired direction over a controlled length are all still goals although each of them can be obtained partially. Up to now, simultaneously controlling the type, diameter and length of SWNT’s is still a challenging problem awaiting a solution. There are four major challenges in the production of SWNTs.

1. Controlling the chirality to obtain pure semiconducting and metallic SWNTs selectively.
2. Controlling the diameter to grow specific bandgapped semiconducting SWNTs.
3. Controlling the placement and orientation of SWNTs for scalable electronic devices.
4. Determining the growth mechanism of SWNTs.

In the next sections, two specific topics, purification and chemical functionalization of semiconducting SWNTs will be discussed in detail because they are closely related to the control of SWNT properties.

1.6 Purification of Semiconducting Single Walled Carbon Nanotubes

So far, all carbon nanotube synthesis inevitably yields a mixture of both semiconducting and metallic nanotubes, which are different in their structure and properties. This mixture is difficult to separate has blocked the practical use of carbon nanotubes in electronic devices and other applications.

1.6.1 Introduction

CNTs are cylindrical carbon molecular structures and can be either semiconducting or metallic depending on their helicities. For example, the different electronic behavior of semiconducting and metallic CNTs significantly limits the application of CNTs in molecular electronics, which normally demands electric field gating effects for the function of FETs, in order to surpass the modern silicon devices. Extensive studies have devoted to selectively synthesizing semiconducting CNTs or post-growth separation using various approaches.

1.6.2 Existing Separation Methods

In order to use CNTs in large-scale circuits, various efforts have been developed trying to obtain high quality, purely semiconducting, and narrow diameter distribution CNTs. One approach is the selective synthesis of semiconducting CNTs, however, pure semiconducting yield is not guaranteed. Most of the methods are based on post treatment after CNT growth to separate the mixture. Solution-phase approaches have been developed but are only applicable to suspended
nanotubes in solvents.\textsuperscript{28-32} In addition, electrical breakdown can selectively remove metallic nanotubes on the substrate after fabricating electrodes on CNTs.\textsuperscript{33} However, this approach cannot be scaled up. Moreover, selective chemical modification\textsuperscript{34-36} can be applied to large scale fabrication and used for surface samples. Among them, the simple chemical reaction with diazonium reagents developed by Jie Liu's group can selectively remove metallic nanotubes. As a result, CNTs can be easily obtained without gating or preconditioning.

1.6.3 Highlight of the Methane Plasma Method

Beside the above methods, the finely tuned methane plasma reaction developed recently by Hongjie Dai and coworkers selectively etches and eliminates the metallic CNTs from a substrate without damaging semiconducting CNTs with large diameter more than 1.4 nm.\textsuperscript{37} This process is a great breakthrough for the potential scalable manufacturing of high performance nanotube-based electronic devices. This dissertation is mostly focused on the surface-grown SWNTs so this method is highlighted here.

In their study, Hongjie Dai and coworkers demonstrated that semiconducting CNTs could be purified to retain electrical properties similar to pristine materials after a selective hydrocarbonation reaction to remove metallic carbon nanotubes using the methane plasma followed by an annealing step. After the CNTs with diameter distribution 1-2.8 nm were treated with methane plasma at 400 °C and followed by 600 °C annealing in vacuum, the diameter was narrowed down to 1.3-1.6 nm. The CNTs of diameter less than 1.4 nm were all removed as shown in Figure 16 because both metallic and semiconducting CNTs are reactive due to the higher radius of curvature and resulting strain in the C-C bonding.\textsuperscript{37} In the medium diameter range 1.4 nm to 2 nm, only metallic CNTs were removed, leaving semiconducting CNTs without damage. Dai explained that semiconducting CNTs are less reactive because of lower formation energies due to the electronic energy gain in opening the band gap and the higher chemical
reactivity of metallic CNTs with more abundant delocalized electronic states, supported by a theoretical study. For large diameter CNTs, both metallic and semiconducting CNTs survived after the treatment. This indiscrimination is due to the slighter differences when the diameter of the semiconducting CNTs becomes larger. Notably, hydrogen-generated plasma does not purify semiconducting CNTs because of the hash treatment. Interestingly, an annealing step that eliminates covalently bound groups through demethylation and dehydrogenation is necessary because covalent chemical group formed during methane plasma degrades electrical properties of CNTs. In addition, CNTs with controlled diameter 1 to 1.8 nm, have reproducibly resulted in a 100% yield of metallic CNTs electronic devices.

This gas phase purification approach represents a breakthrough in large scale fabrication of semiconducting carbon nanotube based devices. It overdoes chemical purification and electrical breakdown methods in full semiconductor yield, high scalability, reproducibility and process compatibility with semiconducting processes. As long as the diameter of the CNTs is less than 1.6 nm, 100% yield of semiconducting CNTs after treatment is obtained. The gas phase treatment can be done even for an entire large wafer fit to the plasma reaction chamber or tube system. By finely tuning the power, temperature, and reaction time, different purification results can be achieved. In addition, the narrow distribution of diameters improves the consistency of the device performance.
Figure 16: Chemical and structural evolutions of SWNTs and diameter and metallicity dependence. (A) Illustrations of the fate of metallic and semiconducting SWNTs in different diameter regimes. In all cases, the annealing step reverses covalent functionalization (represented by species drawn on the tubes after the plasma step) on the retained SWNTs. (B) Infrared transmittance spectra of a film of SWNTs after plasma and annealing, respectively. IR absorption peaks (blue curve) at 2960 cm\(^{-1}\), 2920 cm\(^{-1}\), and 2850 cm\(^{-1}\) are assigned to C–CH\(_3\), C–H or C–H\(_2\), and C–H\(_2\), respectively, covalently attached to the C atoms on nanotube ends and/or sidewalls. These peaks vanish after annealing. (C) A schematic of the possible chemical groups on a SWNT after the plasma step. The figure is adapted from ref [37].

Despite of the advantages of the gas phase reaction, the reasons for the selective purification remain unproven and the reactivity difference between semiconducting and metallic nanotubes at high temperature (400 °C) is still not clear. A deep understanding of the selectivity mechanism is necessary to advance this technique in obtaining purely semiconducting CNTs. In addition, the current procedure is only appropriate for nanotubes with diameter from 1.3 to 1.6 nm in order to gain pure semiconducting nanotubes. This restriction limits the use of this approach to small diameter nanotubes less than 1.3 nm and large diameter nanotubes more than 1.6 nm. In addition, purification of bulk sample is not shown in Dai’s paper. Compared with Dai’s method,
Liu’s approach\textsuperscript{38,39} is fully understood and well controlled, but does not share the irreversibility of the gas phase purification.

An efficient and effective approach approach to purify semiconducting CNTs by gas phase plasma reaction compatible with microfabrication technology is demonstrated by Dai. This approach not only narrows down the nanotube size distribution but also completely removes metallic tubes in the diameter range of 1.3 nm to 1.6 nm. Most importantly, it is scalable, and yields high-performance devices. However, for real applications and the manufacture of CNTs based devices, other problems need be solved such as synthesis of dense aligned arrays of nanotubes. This nanotube synthesis will be shown in the following chapter.

1.7 Chemical Functionalization of Single Walled Carbon Nanotubes

Chemical strategies have been developed to modify SWNTs for specific purposes. For example, selective functionalization and their attachment to pre-organized surfaces allow SWNT assembly. By functionalization, SWNTs will find applications in the novel nanoscale devices such as biosensors, fuel cells, and molecular electronics.\textsuperscript{40} SWNTs are easier to handle for chemical functionalization and gain especially interesting properties because of their monomolecular character and simpler structure.

1.7.1 Introduction

SWNTs are inert in chemical reactivity and their solubility in solvents can not be controlled. Functionalization of SWNT surfaces by specific materials such as proteins and antibodies can enable solubility, specific interactions and selective binding.

The approaches to functionalizing SWNTs are generally divided into two groups, covalent and noncovalent functionalization of the sidewalls. As shown in Figure 17, defect groups on the
sidewall are commonly used functionalization sites. In addition, covalent sidewall functionalization, noncovalent exohedral functionalization by surfactants or polymers, and endohedral functionalization are also the general approaches.\textsuperscript{40}

Figure 17: Chemical functionalization of SWNTs. (A) Typical defects in a SWNT: a) five- or seven-membered rings in the carbon framework, instead of the normal six-membered ring, lead to a bend in the tube; b) sp\textsuperscript{3}-hybridized defects (R=H and OH); c) carbon framework damaged by oxidative conditions, which leaves a hole lined with -COOH groups; and d) open end of the SWNT terminated with –COOH groups. Besides the carboxy termini shown, other terminal groups such as -NO\textsubscript{2}, OH, H, and =O are possible. (B) Functionalization possibilities for SWNTs: a) defect-group functionalization; b) covalent sidewall functionalization; c) noncovalent exohedral functionalization with surfactants; d) noncovalent exohedral functionalization with polymers; and e) endohedral functionalization. The figure is adapted from ref [40].
1.7.2 Covalent Functionalization

Typically, SWNTs have no caps at the two ends, and consist of only one graphitic sidewall, usually with defects. Since SWNTs show low solubility or dispersability, and occur in bundles, functionalization of the sidewall by covalent bonding will only be successful if a highly reactive reagent is used.

Carboxylic groups can be covalently attached by oxidizing sidewall defects and can be used to build architectures that include nanoparticles covalently bound to carbon nanotubes. For example, SWNTs have been controllably oxidized along their lengths, and the generated carboxylic groups utilized to tether gold nanoparticles via 2-aminoethanethiol (7) linkages as shown in Figure 18A.\(^{41,42}\) Figure 18B shows a three-dimensional topographic representation of a single SWNT covalently decorated with 2-3 nm gold nanoparticles.\(^ {41,42}\) Similarly, the carboxylic groups on the SWNTs have been used to introduce starburst polyamideamine (PAMAM) dendrimers to the SWNT surface via carbodiimide coupling.\(^ {41,42}\)

The ends of SWNTs are more reactive than their sidewalls, thus allowing the attachment of functional groups to the nanotube ends. Selective activation at the ends allows elongation on solid supports. For example, SWNTs have been elongated by the formation of biomolecule junctions that interconnect the ends of SWNTs.\(^ {43}\) Amino-terminated β-galactoside (8) was covalently bound to the carboxylic groups at the ends of oxidized SWNTs yielding sugar-unintended SWNTs as shown in Figure 19A. The β-galactoside-specific lectin from Peanut arachis hypogaera was then used as a bioaffinity linker to couple two sugar-functionalized ends of SWNTs, resulting in long wires of end-to-end interconnected SWNTs as seen in Figure 19B.
Figure 18: Covalent functionalization of SWNTs with gold nanoparticles. (A) Carbodiimide coupling reaction used to tether gold nanoparticles covalently to oxidized sites along SWNTs. (DCC=dicyclohexylcarbodiimide). (B) AFM three-dimensional topographic representation of a single SWNT covalently decorated with gold nanoparticles 2-3 nm in diameter. The AFM image is approximately 50x150 nm² in size (z scale 0-3.5 nm). The figure is adapted from ref [41, 42].

Figure 19: Noncovalent functionalization of SWNTs. (A) Formation of the biomolecule junction between the sugar-functionalized ends of SWNTs. (B) Scanning electron micrograph of the end-to-end interconnected SWNTs generated in the presence of β-galactoside-specific lectin, 60 mm. The figure is adapted from ref [43].
1.7.3 Noncovalent Functionalization

Covalent functionalization of the SWNTs damages the sidewalls, thereby diminishing the mechanical and electronic properties of the SWNTs. SWNTs can be functionalized without their covalent coupling. Noncovalent functionalization of the SWNTs, by inserting the molecules into the cavity of SWNT or by careful selection and application of a polymer wrapping around the SWNT, have been obtained.

Open-end carbon nanotubes provide internal cavities (1-2 nm in diameter), which can store organic molecules and biomolecules of respective sizes. DNA has been encapsulated inside SWNTs in a water-solute environment via an extremely rapid dynamic interaction process, provided that the tube size exceeds a certain critical value as shown in Figure 20, indicated by molecular dynamics simulations. Van der Waals and hydrophobic forces were found to play a dominant role on the DNA-CNT interaction.44

![Figure 20: DNA entering an SWNT cavity. Simulation snapshots of an oligonucleotide (eight adenine bases) interacting with a (10, 10) carbon nanotube at 0, 30, 100, and 500 ps. The graph is adapted from ref [44].](image)

The noncovalent association of polymers with nanotubes provides an electrical non-interaction with the nanotubes; reactive groups of the polymers allow for interaction with specific
molecules. When specific molecules interact with the polymers coating the SWNT, the electrical properties of the nanotubes are altered, enabling detection of the molecules. Multilayer polymeric shells surrounding CNTs have been generated by the layer-by-layer deposition of oppositely charged polyelectrolytes. The CNTs were functionalized as shown in Figure 21A by the adsorption of cationic species (1-pyrenepropylamine, 1), followed by the stepwise deposition of the negatively charged polystyrene sulfonate (PSS, 2) and positively charged poly(diallyldimethylammonium chloride) (PDDA, 3). The TEM images of the uncoated CNTs as seen in Figure 21B and the polymer-modified CNTs as seen in Figure 21C show the formation of nanometer-thick amorphous polymer nanoshells around the nanotubes. Several alternating PSS and PDDA layers form this amorphous region, as shown in Figure 21C. Element mapping using energy-filtered TEM confirmed the presence of both polyelectrolytes in the organic shell around the CNTs. Nitrogen appears in both PDDA and 1, whereas PSS is the only source of sulfur. Moreover, nitrogen from 1 should be confined to the nanotube surface because the pyrene moieties lie flat on the nanotube. On the other hand, sulfur from PSS and nitrogen from PDDA should be distributed uniformly throughout the coating, a property that was indeed imaged by the element maps as shown in Figure 21D, E. These multilayer polyelectrolyte shells on individual CNTs introduce nearly unlimited opportunities for the incorporation of different functionalities into nanotube-based devices, which, in turn, opens up the possibility of building complex multicomponent structures.
1.8 Applications of Carbon Nanotubes

Since their discovery by Iijima in 1991, CNTs have attracted great interest in chemistry, physics, electronics and materials science. Because of their amazing properties, CNTs show a wide range of current and potential applications such as FETs, sensors, light emitters, logic circuits, etc. In terms of the timeline, applications of CNTs were grouped as seen in Table 2 based on the manufacture scale, bulk and limited volume.
Table 2: Applications of CNTs grouped as present (existing), near term (to appear in the market within ten years) and long term (beyond ten-year horizon) and as categories belonging to bulk (requiring large amounts of material) and limited volume (small volume and organized nanotube structure) applications. The table is adapted from ref[50].

<table>
<thead>
<tr>
<th>Present</th>
<th>Large-volume applications</th>
<th>Limited-volume applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Battery electrode additives (MWNT)</td>
<td>- Scanning probe tips (MWNT)</td>
</tr>
<tr>
<td></td>
<td>Composites (sporting goods; MWNT)</td>
<td>- Specialized medical appliances (catheters) (MWNT)</td>
</tr>
<tr>
<td></td>
<td>Composites (ESD* applications; MWNT)</td>
<td></td>
</tr>
<tr>
<td>Near term</td>
<td>Battery and supercapacitor electrodes</td>
<td>- Single-tip electron guns</td>
</tr>
<tr>
<td>(less than ten years)</td>
<td>Multifunctional composites (3D, damping)</td>
<td>- Multiplex array X-ray sources</td>
</tr>
<tr>
<td></td>
<td>Fuel-cell electrodes (catalyst support)</td>
<td>- Probe array test systems</td>
</tr>
<tr>
<td></td>
<td>Transparent conducting films</td>
<td>- CNT brush contacts</td>
</tr>
<tr>
<td></td>
<td>Field emission displays/lighting - CNT-based inks for printing</td>
<td>- CNT sensor devices</td>
</tr>
<tr>
<td></td>
<td>Power transmission cables</td>
<td>- Electromechanical memory device</td>
</tr>
<tr>
<td>Long term</td>
<td>Structural composites (aerospace and automobile, etc.)</td>
<td>- Thermal-management systems</td>
</tr>
<tr>
<td>(beyond ten years)</td>
<td>CNT in photovoltaic devices</td>
<td></td>
</tr>
</tbody>
</table>

* ESD stands for electrostatic discharge

Although numerous applications have been commercialized, many challenges have slowed down the CNT revolution. Among these challenges, production in high volume for industrial needs is essentially the hardest, especially for SWNTs. Presently, MWNTs can be manufactured in a relatively reasonably large scale,\textsuperscript{50} and therefore, all the current commercial applications are based on MWNTs. SWNT manufacturing is far not enough advanced for true demands, which is at least tons per day. Moreover, controlled assembly and integration for limited scale applications such as nanoelectronics hinder the advancement of CNT. Specific chirality or
diameter, controlled length, precise alignment, and control of location are necessary to match the current silicon industry. CNT science and engineering are just at the very beginning. The next decade will be the time of nanotechnology, boosted by the CNT research.

1.8.1 Electronics

CNTs emerge as a substitute or competitor of current silicon-based devices because of their outstanding properties and nanoscale dimension. CNTs are found to possess long electron mean-free path, ballistic transportation of electrons and holes, resistance to electronmigration, and other unique properties which give them potential as the building blocks of future electronic circuits. Recent advances in the separation of SWNTs may help provide the potential to develop high performance FETs and interconnects for the IC industry. However, the integration of CNTs into electronic devices is just at very beginning and still a long term application although the market is huge.

Silicon transistors can be shrunk to nanosize but no less than 10 nm. The tiny CNT with a diameter around 1 nm has been demonstrated to be the choice to speed up the nanoscale electronics revolution. A decade ago, research groups at Delft and IBM developed a SWNT FET, a p-type semiconducting transistor which showed orders of magnitude change in the channel conductance by the gate bias as shown in Figure 22. The gate modulation is basically from the Schottky barrier height at the contact of the electrode and nanotube. After that, more complicated circuits have been shown as in Figure 23, such as the logic NOR, static random-access memory cell, ring oscillator, Y-junction switches, etc.
Figure 22: SWNT or MWNT FET transistor. (A) Schematic cross section of the FET device. (B) I-V \(_g\) curves. The inset is the conductance modulation by gate. The figure is adapted from ref[54].

Figure 23: Demonstration of one-, two-, and three-transistor logic circuits with carbon nanotube FETs. (A) inverter. (B) NOR. (C) SRAM. (D) Ring oscillator. The graph is adapted from ref[49].
The metallic properties of the nanotubes can lead to their application in interconnects. The interconnect material used at present is Cu which suffers from the electron migration, low current density, and resistance scattering problems as size shrinks. Because of the high current density, resistance to electron migration, long electron free length, chemical inertness and other unique properties, the nanotube is a promising candidate to replace Cu in future nanoelectronics.56

1.8.2 Energy Applications

Carbon nanotubes, especially bulk samples, have great potential in supercapacitors, Li-ion batteries (LIBs), solar cells and fuel cells because of their unique electrical properties, electrochemical stability, and high surface area.

The carbon nanotubes have a high reversible capacity57 so that they can be used as electrodes in LIBs.58, 59 In addition, the anode materials in LIBs can employ carbon nanotubes.60 Carbon nanotubes dispersed in synthetic graphite make a continuous network and a mechanically strong electrode, which has doubled energy efficiency of LIBs as shown in Figure 24.61

Moreover, carbon nanotube supercapacitors have been studied because they can store high energy density62 and deliver energy rapidly63. Organic solar cells can also benefit from the properties of the carbon nanotubes as the bulk supporting materials for the organic polymers. Carbon nanotubes can also be ideal materials for electron transport.64-66
Figure 24: The cyclic efficiency of synthetic graphite as a function of added weight percent of graphitized s-VGCFs. The graph is adapted from ref[61].

1.8.3 Mechanical Applications

Carbon nanotubes have potential in mechanical applications because of their unique mechanical and structure properties. Nanotubes hold fifty times the specific strength (strength/density) of steel so that they are considered as the excellent fibers for mixing with the polymers to enhance the mechanical properties. The reported individual tube strength is 100 GPa, better than all the other known materials.

By loading carbon nanotubes into a epoxy composite, the polymer fracture surface showed stretched nanotubes in the crack (Figure 25) which reinforces the mechanical properties of the epoxy. Although carbon nanotubes are good candidate to enhance the mechanical
strength due to their stiffness and high aspect ratio, the non-uniform tube loading is still a big challenge. The interaction between the polymer and the nanotubes is weak because the tubes are chemically inert although the interaction can be improved by modification of the CNTs.

![SEM image of SWNT bundles stretched across cracks observed in a nanotube-epoxy composite. The graph is adapted from ref[69].](image)

**1.8.4 Sensors**

Carbon nanotubes are effective sensing elements because of their 1D electronic structure, all their atoms on the surface, and their high aspect ratio. The above characteristics combined with the unique electrical, electrochemical and optical properties, provide potential for detecting low or ultra low gas, especially toxic gas in the environment.

One of the first sensors based on CNTs to be demonstrated is an individual semiconducting SWNT gas sensor as shown in Figure 26. The conductance changed by orders of magnitude upon gas exposure. The sensing mechanism is still a controversy. People argued between a Fermi level shift of the tube and the Schottky barrier of the tube-electrode contact after several researches. Even if the mechanism is unclear, many methods have been suggested to
improve the sensitivity and selectivity of CNT gas sensors. One of them is binding specific ligands to CNTs through which the selectivity and sensitivity can be greatly improved by utilizing the affinity of the ligand to the gas molecules.\textsuperscript{70}

Figure 26: Electrical response of a semiconducting SWNT to gas molecules. (A) Conductance vs time in NO\textsubscript{2} flow. (B) Data for different concentration of NO\textsubscript{2}. (C) Conductance vs time in NH\textsubscript{3} flow. (D) Data for different concentration of NH\textsubscript{3}. The graph is adapted from ref\cite{47}.

In addition to the gas sensor, the glucose sensor,\textsuperscript{71, 72} the DNA sensor,\textsuperscript{73-75} and other biosensors have been fabricated.

The above sensors are based on FET devices of CNTs. A novel capacitance sensor has also been developed.\textsuperscript{76} A transparent SWNT network with the electrodes patterned on the substrate was used as the sensing element shown in Figure 27A. This sensor is highly sensitive,
fast and reversible. The capacitance is changed either up or down depending on the analyte as shown in Figure 27B. SWNT functionalization can increase the sensitivity.

![Figure 27: SWNT chemicapacitor sensor. (A) Optical image of the sensor. (B) Relative capacitance change in response to DMF. The graph is adapted from ref[76].](image)

### 1.8.5 Other Applications

CNTs are good field emission materials because of their low threshold voltage, stable emission ability and long emission time.\(^7^7, \, 7^8\) In addition, CNTs are biocompatible with human tissue, nanometer size, cylindrical shape and chemically stable so that they can be used in various biological applications.\(^7^9, \, 8^0\) Moreover, due to their high mechanical strength, and high electrical/thermal conductivity, the formation of strong, transparent, electrically and thermally conductive composites is promising, including electromagnetic shielding of cables and conductive coating of aircraft.

However, the CNT is not an all-purpose material. For example, hydrogen storage by CNTs has been proven to be impractical after several years’ study.\(^5^0\)
Chapter 2: Controllable Synthesis of Single Walled Carbon Nanotube Thin Film

2.1 Introduction

CNTs have attracted great interest in chemistry, physics, electronics and materials science because of their unique structural, mechanical, and electronic properties. Among CNTs, SWNTs are especially interesting. SWNTs are 1D molecular wires, either semiconducting or metallic depending on their helicity and diameter. Because of their chemical and mechanical stability, high conductivity, high surface-to-volume ratio and other unique properties, SWNTs have various potential applications such as FETs, sensors, light emitters, logic circuits, etc.

However, technological hurdles in device assembly in the nano-scale have hampered the development of individual-SWNT device applications. Moreover, the behavior of individual-SWNT devices varies due to lack of control over the diameter and chirality. One promising solution is to use a SWNT thin film (or random network). Combined with the current state-of-the-art microelectronic processing techniques, SWNT thin film devices can be fabricated easily in micro or sub-micro scale for real applications. Because the properties are ensemble averaged, SWNT thin film devices provide relatively uniformity from device to device. Thus, high quality SWNT thin films have been used to build FETs, chemical sensors, and other applicable devices.

In this section, we explore the synthesis of a SWNT thin film with controlled diameter of individual SWNTs by CVD. Uniform small diameter (<1.1 nm) SWNT thin films have been grown from the nanoparticles formed using Co diblock copolymer micelles. In addition, a novel laser irradiation CVD is demonstrated to synthesize highly uniform diameter and less defective SWNT thin films. Moreover, the density or yield of the SWNT thin film can be controlled by the flow...
pattern, which was observed for the first time. These achievements will further improve the understanding of SWNT thin film synthesis, and guide the controllable growth of SWNTs.

### 2.2 Small- and Uniform Diameter Single Walled Carbon Nanotube Synthesis

Small diameter SWNTs are interesting because they provide larger band gaps to minimize off-state leakage, and increase the transistor on/off current ratio in device applications. Moreover, small diameter carbon nanotubes provide fewer chiral arrangements so that more uniform performance in SWNT thin film devices can be achieved. For example, a carbon nanotube thin film with all the tubes less than 1nm in diameter definitely contains only single-walled tubes with fewer chiral arrangements. Those small diameter SWNTs limit the band gap range and, if the diameter range is small enough, can be exclusively either metallic or semiconducting. As a result, producing SWNTs with small diameters can improve uniform performance in SWNT thin film devices and guide the bulk synthesis of small diameter SWNTs in large scale as well. However, no uniformly distributed SWNT thin films with diameter all less than 1nm have been demonstrated by catalytic CVD on a large surface area.

Growth of small diameter and narrowly distributed SWNTs is highly desired in order to control the nanotube chiral arrangement which varies with its diameter. In the CVD growth of SWNTs, the diameter of SWNTs is mainly determined by the size of catalyst particles. In this project, small diameter SWNTs were produced by small diameter catalyst nanoparticles formed from diblock copolymer micelles loaded by Co salt.

### 2.2.1 Experimental Section

Preparation and transfer of Co diblock copolymer micelles as catalysts. The catalyst solution was prepared by adding 10mg (53800)-block-poly(2-vinylpyridine) (8800) (PS-PVP) (Polymer Source, Inc.) diblock copolymer to 10ml toluene. The solution was stirred at room
temperature for 24 h, after which 0.333mg Co(CH₃COO)₂·4H₂O (Co²⁺: PVP=0.1) dissolved in methanol was then added to obtain the final solution. The substrates were spin-coated with the solution at 4000 rpm with a spin coater (KW-4, Chemat Technology) for 40s. Then the substrates were annealed at 140°C for 3 h in the oven. After cooling down to room temperature, the substrates were treated with oxygen plasma (PDC-32G, Harrison) for 15mins.

SWNT thin film CVD synthesis using nanoparticles formed by Co diblock copolymer micelles. The substrate with nanoparticles from oxidizing Co diblock copolymer micelles on its surface was first put into a 1-inch quartz tube heated by a thermal furnace and annealed at 700°C in air for 10 min. After cooling down to room temperature, the substrate was heated to 900°C in 500 sccm (standard cubic centimeter) H₂. 800 sccm of CH₄ and 20 sccm of C₂H₄ were added to the gas flow and maintained for 10mins at 900°C. All the carbon source flows were then switched off and the furnace was cooled down to room temperature under the protection of H₂.

SEM, AFM, and Raman measurement of SWNT thin film. Scanning electron microscopy (SEM) characterization was carried out with a XL30 scanning electron microscope (FEI) with accelerating voltage of 1KV. The atomic force microscopy (AFM) characterization was performed on a Nanoscope IIIa atomic force microscope (Digital Instrument) with tapping mode in ambient conditions. The Raman instrument was a Renishaw Raman microscope equipped with 3 laser wavelengths (780 nm, 633 nm and 514 nm).

2.2.2 Results and Discussion

After removing the organic components with oxygen plasma, Co oxide nanoparticles were generated on the surface by the Co diblock copolymer micelles synthesized in our group. Figure 28A shows the AFM image of Co oxide nanoparticles on the surface. The nanoparticles were distributed on the surface with a density about 23/μm² and an average diameter about 3.7
nm, as determined by height measurement using AFM and analyzed by the particle analysis function in Nanoscope III software. As can be seen in the diameter distribution histogram (Figure 28B), the majority of the particles have a diameter less than 2 nm, with a minority having a larger diameter of 5~10 nm. With this catalyst, a SWNT thin film was grown on the surface as shown in Figure 29A. The tube density can be controlled from very low to ultra high by controlling the density of the catalysts and the growth conditions. Figure 29B shows an AFM image of SWNTs on a clean surface free of amorphous carbon. The diameters of the formed SWNTs are all smaller than 1 nm and are in a narrow range according to the measurement as shown in Figure 29C. The average diameter of the SWNTs is about 0.63 nm, which might be slightly lower than the real value due to compression caused by the AFM tip force during the measurement. This result was supported in Figure 29D by Raman data with three different laser wavelengths. The tube diameters are estimated using the relationship $d(\text{nm}) = \frac{248}{\omega_{\text{RBM}}}$. ($\omega_{\text{RBM}}$ is the wavenumber of the SWNT radial breathing mode.) From the data in Figure 29D, the diameter range is calculated to be 0.8-1.1 nm and no larger diameter tubes (>1.1 nm) were identified.

Figure 28: Cobalt oxide nanoparticles prepared on a Si surface. (a) A tapping-mode AFM image (5μm x 5μm). (b) A histogram of size distribution.
Figure 29: Small diameter SWNT thin film grown on surface. (a) A SEM image of the SWNT network. (b) A taping-mode AFM image (3μmx3μm) of the SWNT thin film. (c) A histogram of diameter distribution with statistic analysis of the SWNTs. (d) Raman of the SWNT thin film by 3 different laser wavelengths.

Another Co diblock copolymer micelle donated by Jennifer Lu at Agilent, which has the same composition as ours but a different Co to polymer ratio and polymer chain length, was used in a synthesis analogous to the above. Figure 30A shows that the nanoparticles formed were uniformly distributed on the surface with a very high density (about 550/μm²). The average diameter of these particles is about 1.6 nm by the AFM measurement and statistical analysis (Figure 30B). The formed SWNT thin film is a highly dense tube mat as shown in Figure 31A. As can be seen in Figure 31B and C, the diameters of the formed SWNTs are all smaller than 1nm in a narrow range, with the average diameter about 0.6nm as measured by AFM. Raman data also show the similar results, a diameter range from 0.8nm to 1.1nm. Although the diameter
distribution of the catalysts is more uniform than the one we prepared, the two sets of SWNTs obtained have a similar diameter distribution because only small size nanoparticles (in a similar size range) in both catalysts can grow tubes, probably affected by the growth condition.85

Figure 30: Cobalt oxide nanoparticles prepared on a Si surface. (a) A tapping-mode AFM image (2µmx2µm) of cobalt oxides nanoparticles prepared on surface. (b) A histogram of diameter distribution for the cobalt nanoparticles.
Figure 31: Small diameter SWNT thin film grown on surface. (a) A SEM image of high-density SWNT network on surface. (b) A tapping-mode AFM image (3μmx3μm) of SWNT grown on surface. (c) A histogram of diameter distribution with statistic analysis of SWNTs. (d) Raman plot of SWNT thin film by 3 different laser wavelengths (514nm, 633nm and 780nm)

From the above results and discussion, we have established that Co diblock copolymer micelles are effective catalysts for small diameter, uniform, and clean SWNT growth. The small diameter and narrow distribution are apparently due to the uniformity of the catalysts which confine the diameter of SWNTs.
2.3 Uniform Diameter Single Walled Carbon Nanotube Synthesis by Laser Assisted CVD

The usual heating systems for CVD are tube furnaces, which take several minutes to reach the desired temperature (such as 900°C). SWNTs synthesized at temperatures higher than 900°C will have fewer defects, and the catalysts’ aggregation can be reduced by using a short preheating time before SWNTs start to grow, resulting in a narrower diameter distribution. Collaborating with researchers at Oak Ridge National Laboratory (ORNL), a novel laser-irradiated CVD technique to synthesize SWNTs was developed using laser irradiation to heat the substrates to a high temperature in a short time which could be precisely controlled by choosing the proper laser power, repetition rate, pulse width and numbers of laser pulse. With this system, as seen in Figure 32, the Si (with 1000nm SiO₂) wafer surface can reach above 1100°C in 5 to 6 seconds, and if an extremely high pulse is used, it takes just for about half a second because of the extreme energy focusing ability.

Figure 32: Laser assisted CVD system setup at ORNL.
2.3.1 Experimental Section

SWNT thin film synthesis by laser-irradiated CVD at ORNL using nanoparticles formed by Fe diblock copolymer micelles. The substrate with nanoparticles on its surface was first put into a chamber and the chamber was vacuumed. Then 60 sccm of H₂, 2000 sccm of Ar, 800 sccm of CH₄ and 60 sccm of C₂H₄ were flushed into the chamber. The substrate was heated by laser-irradiation to 1100 °C (5s) and maintained for 3mins with the temperature measured and controlled by an optical pyrometry. The carbon sources were switched off and the substrate was cooled down to room temperature under the protection of Ar.

SEM and Raman analysis of SWNT thin film. SEM characterization was carried out with a XL30 scanning electron microscope (FEI) with an accelerating voltage of 1KV. The Raman instrument is a Renishaw Raman microscope equipped with 3 laser wavelengths (780 nm, 633 nm and 514 nm).

2.3.2 Results and Discussion

Inverted micelles formed by polystyrene-block-poly(2-vinyl-pyridine) in toluene loaded with FeCl₃ were used as catalysts to synthesize SWNTs due to their uniform diameter distribution. A network of SWNTs was grown forming a ring-like pattern with an obvious boundary imaged by SEM in Figure 33A. As can be seen in Figure 33B and C, the tubes were cleaner and denser farther from the center. In Figure 34A, Raman excitation (wavelength of 633nm) spectrum shows a G band at 1590cm⁻¹ and no distinguishable D band, indicating high quality SWNTs. The RBM peaks are at 195cm⁻¹ at every spot studied and a peak of 184cm⁻¹ in some spots, which shows tubes highly uniform by 248/195=1.27nm and 248/184 = 1.35nm (1.27nm and 1.35nm tubes are metallic nanotubes analyzed by Kataura plot). These highly uniform SWNTs may be due to the extremely high temperature and rapid heating speed, resulting into the most stable tube structures.
Figure 33. SEM images of the sample by laser heating in ORNL with FeNP as catalysts. (A) Wide view. (B) Area A is the outer area of the heating zone. (C) Area B is the inner area of the heating zone.
Figure 34: Raman data of SWNTs grown by laser heating. (A) One typical Raman data in one spot (RBM and G band are highlighted). (B) Detailed RBMs in 5 spots.
The laser-assisted catalytic chemical vapor deposition method has three potential advantages over other conventional CVD techniques.

1. Fast heating: The laser with high power can instantly heat up the substrate, leading to the less aggregation of catalysts, resulting into a uniform growth of SWNTs if uniform catalysts are used.

2. Location control: The local heating feature of laser-assisted CVD confines the catalytic chemical vapor deposition only occurring within the heating zone. This feature reduces the formation of amorphous carbon (impurities) by the thermal deposition of carbon feeding gases inside the chamber, which normally happens in the conventional thermal CVD.

3. Heating area control: The laser spot size can be tuned. Therefore, the temperature profile of the wafer can be tuned with the tunable spot size.

This laser-assisted CVD process, generally creating a local hot spot on the substrate surface, has emerged in other publications as well.\textsuperscript{86, 87} Uniform and high quality SWNT thin film has not been shown; however, it is shown here for the first time. Our experiments also show pure metallic tubes in the as-grown SWNTs by laser-assisted CVD, although the mechanism is unclear. Therefore, a set of systematic experiments and a further study of the growth mechanism are necessary.

Interestingly, another study of SWNTs grown by laser-assisted CVD shows predominantly semiconducting characteristics. That author explained that the laser can potentially affect the chiralities by resonant absorptions of SWNTs at specific Van Hove singularities, when the wavelength of the incident laser matches the resonant absorption wavelength of the SWNTs.\textsuperscript{88}
2.4 Density Control of Single Walled Carbon Nanotube Thin Film by Flow Pattern

CVD is a classic method to produce SWNTs on a surface, and can tune the growth by temperature, catalysts, feeding gas, and other parameters. Normally, either a quartz tubing (widely used in labs due to its simplicity) or a chamber (either cold wall or hot wall) are used to synthesize SWNTs. All the above systems have a circular cross section. If the diameter of the quartz tube is not much larger than the size of the substrate, according to gas flow dynamics, the gas flow velocity above the CNT growth substrate is nonuniform in different positions as seen in Figure 35, and can not be quite low (nearly zero) whatever the gas flow is. Gas flow is important because it determines the transport of the various chemical species and plays a significant role in the temperature distribution inside the gas in many reactions. In this study, we use square quartz tubing to grow SWNTs, which provides nearly zero gas flow velocity and a uniform boundary layer above the substrate as seen in Figure 35. Some prototype results show the different growth behavior from the circular tubing system. This study will lead to a better understanding of the gas flow effect and the super low flow growth, in order to improve the controllable SWNT growth.

Figure 35: Sketch of circular tubing and square tubing with a substrate of comparable size to the tubing inside.
2.4.1 Experimental Section

Two sets of experiments were done for initial characterization of the SWNT growth in the square tubing furnace. One is to compare circular and square tubing growth under the same growth conditions. The other one is to grow SWNTs with different carbon feeding rates using two kinds of tubing. The substrates in each set of the experiment are from the same big piece of wafer to avoid the catalyst differences and the two sets are from the wafer with different catalysts concentration. The square tubing is 1 foot long (long enough for tube flow) and 13mmX13mm in cross section (just fit for the 1 inch round tubing), positioned in the middle of the square tubing to regulate the gas flow.

2.4.2 Results and Discussion

Figure 36 shows three circular tubing growths and three square tubing ones grown under the same condition but separated runs. Additionally, the results are quite consistent. As seen in Figure 36, the density of the SWNTs grown in circular tubing is lower than the square tubing under the same condition. The lower density from the circular tubing is probably due to the difference of the actual carbon feeding in the two different flow pattern systems, which varies the yield of the SWNTs.85

Figure 37 shows results for the square tubing growth by varying the ethylene flow rate, which normally changes the growth result dramatically in the circular system as seen in Figure 38. For the circular system as shown in Figure 38, by reducing the ethylene, the density becomes lower and only few tubes can be found without any ethylene. However, as seen in Figure 37, for the square tubing growth, the density of the tubes varies little.
Figure 36: Comparison between the circular tubing growth (three samples) and square tubing growth (three samples). Growth condition is 900°C; 800sccm CH₄, 700sccm H₂, and 20sccm C₂H₄; 10mins growth for all the samples in separated growth.

Figure 37: Comparison of growth by different C₂H₄ flow rare in square tubing. Growth condition is 900°C; 800sccm CH₄, 700sccm H₂, and 20, 15, 10, 5, 0 sccm C₂H₄ (respectively); 10mins growth for all the samples.
Figure 38: Comparison of growth by different C\textsubscript{2}H\textsubscript{4} flow rare in circular tubing. Growth condition is 900\textdegree C; 800sccm CH\textsubscript{4}, 700sccm H\textsubscript{2}, and 20, 15, 10, 5, 0 sccm C\textsubscript{2}H\textsubscript{4} (respectively); 10mins growth for all the samples.

The only difference between square and circular tubing growth is the gas flow velocity above the substrates. The square tubing can give almost zero flow velocity while the circular tubing can not for a substrate comparable to the dimension of the tubing. The deposition gasses must diffuse through the stagnant boundary layer whose thickness is inversely proportional to the gas flow velocity. The boundary layer thickness, therefore, may play a critical role in determining the deposition rate. Carbon species were assumed to be self-decomposed in the boundary layer when the flow velocity is low. Alternatively, the gas could probably be heated sufficiently in the boundary layer, and the temperature of the gas is higher in the bulk gas flow above the substrate. Further experiments will be necessary to better understand the square tubing growth, the gas velocity effect, and modeling the flow in the tubing may also help.
2.5 Summary

In brief, a uniformly distributed, small diameter (<1 nm) SWNT thin film has been produced from Co diblock copolymer micelles. In addition, laser-irradiated CVD provides high quality and highly uniform SWNTs, or even a high proportion of metallic tubes, although the mechanism is not clear and the results are not fully conclusive. More studies are needed to control and improve the growth. Furthermore, flow pattern was found to affect the SWNT growth for the first time. However, further investigations are needed to elucidate the mechanism.
Chapter 3: Horizontally Aligned and Ultra-long Single Walled Carbon Nanotubes

3.1 Introduction

Since their discovery by Iijima,\(^5\) SWNTs have displayed potential in a variety of promising applications such as FETs,\(^46\) sensors,\(^47\) light emitters,\(^48\) logic circuits,\(^49\) and so forth. To fulfill their potential in these applications in large scale, the location and orientation of SWNTs must be controlled; specifically, horizontally aligned organization on a flat substrate is in high demand. Post growth alignment methods such as the novel “blown bubble films”\(^89\) are excellent for large scale and flexible substrates; however, the nanotubes used are generally short and exposed to strong acid during purification. Direct growth\(^90\) by CVD with an external force has emerged as the most attractive approach for meeting this demand.

Such aligning external forces can originate from an electric field,\(^91\) the gas flow,\(^38\) or interactions with the substrate surface.\(^92\)\(^-\)\(^95\) The gas flow and substrate guidance are the major focus in this dissertation because of their respective advantages. The gas flow method is simple, compatible with any kind of substrate, suitable to the current FET fabrication and can provide ultra long tube in centimeters. The surface-guided growth on single crystal substrates such as sapphire\(^92\) or quartz\(^93\)\(^-\)\(^95\) surpasses all the others in the high density and perfect alignment.\(^96\)

3.2 Horizontally Aligned Single Walled Carbon Nanotubes on Si Substrate

Fast heating method\(^38\) was developed in our group to grow horizontally aligned and ultra long SWNT on surface. The mechanism is a lifting-up of the catalysts which can then be carried by the gas flow like a kite to grow long tubes. The key is the fast heating process to lift up the catalysts from the substrate surface. However, the process is not easy to control in the fast
heating step by the current available furnace. Here, we show that if the gas flow is dramatically increased, the fast heating process is unnecessary to obtain same results. Surprisingly, if the gas flow is tremendously decreased, ultra long and aligned tubes can be also obtained. This study will further our understanding of horizontally aligned SWNT growth and the SWNT allocation control. Moreover, a novel 3D SWNT structure with isolated tubes across and suspended mostly orientated orthogonal to the trench is shown for the first time. This structure is useful for the intrinsic property study of CNTs and CNT based devices without the influence of the substrates but with known orientation.

### 3.2.1 Horizontally Aligned Single Walled Carbon Nanotube by Ultra-high Flow Growth

The Fe/Mo nanoparticles were patterned on the substrate which was then put into the quartz tube heated by a thermal furnace and annealed at 700 °C in air for 10 min. After cooling down to room temperature, the substrate was heated to 900 °C in 1000 sccm H₂. 1500 sccm of CH₄ and 30 sccm of C₂H₄ were added to the gas flow and maintained for 30mins at 900°C. All the carbon source flows were then switched off and the furnace was cooled down to room temperature under the protection of H₂.

Figure 39 shows the millimeter long horizontally aligned SWNTs grown by the ultra high gas flow. The tube orientation is along the gas flow although some curved tubes are observed and the alignment is not perfect. However, the curvature can confirm the gas flow effect which also introduces the local gas turbulence to regulate the tubes. In addition, such “turn” and suspended structure is interesting to study. To further confirm the gas flow regulation, a substrate with trench was used to grow the aligned tubes, Figure 40 shows that the tubes can grow over the trench. The tubes must fly off the surface in order to grow over the trench and the carrying force is the high gas flow. This structure is useful to analyze the intrinsic property of an individual SWNT without the substrate influence. Figure 41 shows the AFM measurement of the
tube diameters which are mostly less than 2 nm in order to demonstrate that the majority of the tubes are single walled.

Figure 39: SEM images of the horizontally aligned SWNTs grown by ultra high flow. (A) Low magnification. (B) High magnification.

Figure 40: SEM images of the horizontally aligned SWNTs grown over the trench by ultra high flow rate. (A) Low magnification. (B) High magnification.
3.2.2 Horizontally Aligned Single Walled Carbon Nanotubes by Ultra-low Flow Growth

0.01M FeCl$_3$ in ethanol was used as the catalysts patterned on the substrate. Then the substrate was put into the quartz tube heated by a thermal furnace and annealed at 950°C in 100 sccm Ar and 30 sccm H$_2$ for 50 min. Ar was turned off and 40 sccm CH$_4$ was turned on, maintaining for 3 hours at 950°C to grow tubes. The CH$_4$ was then switched off and 100 sccm Ar was turned on. The furnace was cooled down to room temperature under the protection of Ar and H$_2$.

Figure 42 shows the SEM image of the horizontally aligned tubes grown by the low gas flow rate, which is only 4% of the high flow growth in the total flow. The tubes are along the flow direction and even some tubes turned into the flow direction after their initial non-orientated growth. As we can see, most of the tubes are millimeters and centimeters long. The longest one is around 5 centimeters. However, if the medium flow rate is used, no such aligned growth was obviously observed.
The aligned tubes from the high flow or low flow growth is not very high in density (around -3 tubes/10μm locally in maximum), not perfect aligned (some curvature or even turns), and not clean on the surface (high carbon feeding and long time growth). However, this isolated morphology, turned structure and ultra long length can provide various applications and properties which the perfect aligned but not ultra long (not centimeter long) CNTs grown on quartz can not give. One of the examples is the nanoscale dipole antenna based on the centimeter long isolated SWNTs.
Figure 42. A series of SEM images of horizontally aligned ultralong SWNTs by low flow rate.
3.2.2.1 Application: Carbon Nanotube Based Nanoscale Dipole Antenna

Up to now, most of the explored CNT devices are wired electronics. The wireless devices are rare due to the mismatch between the nanometer scale devices and the microwave wavelength. The microwave wavelength (centimeters) is much larger than the normal CNT device size (nanometers or micrometers). Such huge size difference prevented exploiting the unique electronic properties of these nanomaterials. Carbon nanotubes with length comparable to the wavelength of microwaves and RF waves are highly desired. Through our development of several millimeters and several centimeters long SWNT, many promising applications can be studied.

Over 50 years ago, Hallen found one of the only analytical solutions to the current distribution on a radiating system. This solution was exact only in the limit that the length/diameter ratio was infinite. SWNTs might be the only known material which can provide such ideal geometry. In this project, the feasibility of using such long nanotubes as nanoscale antennas is presented.

To fabricate such antenna structure, well isolated aligned SWNT (centimeters long) was used. The length of nanotubes can be precisely controlled by the chemical etching. Dipoles were fabricated on individual long nanotubes using photolithography method. As shown in Figure 43, after the growth of the aligned SWNT, metal electrodes was patterned onto the individual tube. Then the middle part of the tube will be removed by using oxygen plasma treatment after a second aligned photolithography. Figure 44 shows the SEM image of the fabricated antenna structure before removing the tube between the electrode pair. Finally, the length of the tube on each electrode can be controlled by a third step lithography and plasma treatment. Therefore, the nanoscale dipole antenna structure by the aligned SWNTs can be achieved.
3.2.3 3D Single Walled Carbon Nanotube Structure

The above section shows the horizontally aligned SWNTs grown on Si wafer surface or over the trench on the substrate. This 2D alignment structure can be the object to study the intrinsic tube properties; however the density of the tubes is normally low due to the low yield of flow aligned growth. Herein, we demonstrate a suspended and distributed SWNT 3D
configuration grown between the “V” shape walls in the trenches on Si substrate. The tubes are more or less aligned by their orientation orthogonal to the trench direction probably because of the geometry effect. Importantly, the as-grown SWNTs are extremely uniform and controllable in diameter by the uniform catalysts generated from block copolymers templates. This 3D structure is useful for the CNT-based unified devices for electronic and optoelectronic applications without the substrate impact.

The catalysts preparation is similar as the previous study by Jennifer Lu.101 “V” Shape sloped sidewalls were formed by using a patterning processing. AZ 1512 was spin coated on (100) Si wafers with 100 nm of thermal silicon oxide and then exposed using a Karl-Suss MA-6 mask aligner. Wafers were then subsequently developed by a 0.26N TMAH developer. Wet etching of the SiO₂ was followed in a hot KOH bath to form sloped trenches. After resist stripping by acetone, buffered HF was employed to remove the 100 nm thermal SiO₂, a layer of 50 nm silicon oxide was subsequently deposited using PECVD. Finally, iron(II) loaded PS323-b-P4VP78 micelles were deposited. After stripping the block copolymer template by UV ozonation, catalyst nanoparticles were formed on the sidewalls of the trenches. (The process was performed by Jennifer Lu.)

The substrate was then treated with oxygen plasma for 15 min followed by CVD growth of SWNTs at 900 °C. First the reduction to Iron (0) to activate nanocatalyst was carried out in the home-built growth chamber with a flow of 700 sccm H₂ for 20 min at 700 °C. The temperature was ramped up to 900 °C and hold for 5 min before introducing the carbon precursor which composes of 800 sccm CH₄ and and 20 sccm C₂H₄. After 1 min, 20 sccm C₂H₄ was turned off and the growth continued for 9 min before switch off 800 sccm CH₄. The samples were then cooled to room temperature under the protection of H₂ and inspected in a Hitachi S-4500
scanning electron microscope. CNT Raman spectra were obtained with a Jobin-Yvon T64000 triple spectrometer with microprobe sampling (100x objective) at UC Merced.

Figure 45 shows the SEM image of the as-grown SWNTs suspended across the two sidewalls of the trench. For a more clear view, Figure 46 is a representative set of tilted SEM images showing that SWNTs have been synthesized in between sloped sidewalls. It seems that majority of tubes are aligned orthogonally to the orientation of the trenches, independent of the gas flow direction because two close fields with trench orientation perpendicular to each other as shown in Figure 48 have the similar growth aligned properties. It is proposed that the topography can induce alignment of SWNTs. Most of the tubes grew almost orthogonal to the trench probably because such suspended length is the shortest and thus it is the highest yield and most mechanically stable. The tubes by other angles might be bended or bumped to other tubes. When tubes touch the sidewall or other tubes, the growth might be stopped in high possibility. More systematic work is underway to understand this phenomenon.

Figure 45: SEM image of the as-grown SWNTs across the trench.
Figure 46: Tilted SEM images of substrates after CNT growth. (a) Representative tilted 3D SEM images of substrates. (b) Representative x-section SEM images of substrates after CNT growth. Black arrows used for highlighting anchoring points of CNTs on the sidewalls. The image was taken by Jennifer Lu.

Figure 47: Tilted SEM images (3 μm by 2 μm field of view) of suspended CNTs across trenches oriented 90 degree with respect to each other (left and right). The optical image (center) shows that this set of trenches with two different orientations are in close proximity to each other. Arrows in the Figures indicate tubes are more or less oriented perpendicularly to trench sidewalls. The SEM image was taken by Jennifer Lu.
These suspended SWNTs are high in quality and uniform in diameter. Figure 48 shows the Raman spectra of several nanotubes. As seen, the RBM bands are between 210 and 230 nm indicating that the majority of tubes are around 1 nm. Such uniform tube diameter is obviously attributed to the highly uniform nanocatalysts form the polymer micelles and is possible derived from the topography as well. The absence of D band clearly shows high quality of SWNTs free of amorphous carbon and defects.

Figure 48: Typical Raman spectra of suspended CNTs at Radial breathing region (left) and in-plane graphene oscillation region (right). The inset is top-down SEM of suspended CNTs used for Raman analysis. The Raman was taken by Jennifer Lu.

3.3 Horizontally Aligned Single Walled Carbon Nanotubes on Quartz

Horizontally aligned SWNTs are highly desired for SWNT device applications. In this section, a large variety of metals including Fe, Co, Ni, Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, and Al successfully catalyzed the growth of such tubes on stable temperature (ST)-cut quartz by lattice guidance. In addition, Mg and Al were presented to produce random and aligned SWNTs for the
first time. A hypothesis is proposed in which the precipitated carbon shell on the outer surface of the metal catalysts guides the alignment along the crystal lattice but not the catalysts themselves. By elucidating the role of the catalysts, an understanding of the aligned growth mechanism on quartz is further improved. Moreover, a simple “scratch” method by a razor blade such as the carbon steel and tungsten carbide (with 9% cobalt) is presented to pattern the “catalysts” without any complex processing steps such as lithography for the aligned SWNT growth.

3.3.1 Introduction and motivation

The horizontal aligned SWNTs on quartz are highly desired for silicon-on-insulator devices because of the high density, perfect alignment and good control. However, the basic alignment mechanism is still unclear. Atomic steps, nanofacets, crystallographic lattice, or a mix of these are assumed to be the guidance force without further clarification. Moreover, the alignment driving force either from the tube-substrate or catalyst-substrate has not been distinguished because the evidence of either tip or base growth is lacking.

Recently, our group has proved the crystal-lattice-guided growth on ST-cut quartz and demonstrated the tip-growth mechanism. Thus, the catalysts play the major role during the crystal guided growth and will be the research focus in order to explore the full mechanism. Up to date, the catalysts have been limited to Fe and Cu (recently used by our group). It is important to know whether some metals could catalyze the aligned growth and some could not, and more importantly, whether different catalysts could grow nanotubes with different helicities. Narrow (n, m) distribution of SWNTs by Co-Mo has been reported, indicating that the chirality is related to the types of catalysts. By exploring new catalysts for SWNT aligned growth on quartz, the guidance mechanism might be further understood; it is hoped that this will lead to type-controlled and orientation-controlled SWNTs synthesis. These goals motivate this report, in which 13 kinds of metals show horizontally lattice-aligned growth of carbon nanotubes on quartz.
substrates. The growth mechanism is discussed. In addition, Mg and Al are reported to grow SWNTs for the first time. Moreover, an easy blade “cut” method without any additional processing steps for the formation of patterned catalysts is demonstrated.

3.3.2 Experiment Methods

In this research, SWNTs were all grown by catalytic CVD using methane and hydrogen under the same growth process as following to avoid any effect by the changing of growth conditions. Besides the commonly used iron-family metal catalysts such as Fe, Co, and Ni, other less common catalysts like Au, Pt, Pd, and Cu\textsuperscript{106-108} and some rarely used metals such as Mn, Mo, Cr, and Sn were employed. Most of them have never been shown to grow horizontally lattice-aligned SWNTs on quartz. Additionally, Mg and Al were chosen because they have never been demonstrated as catalysts for carbon nanotubes and researchers commonly believe they are not able to grow carbon nanotubes. To our best knowledge, it is also the first time to show such a large variety of metals catalyzing SWNTs growth under the same growth conditions.

Single crystal ST-cut quartz wafers from Hoffman Materials Inc. with no further treatment except solvent rinsing, were used as the substrate for all of the growth experiments. 1mM metal salts in alcohol were used as the catalyst solution, which was patterned, spin coated, or dip-coated on quartz. Then the substrates were treated with oxygen plasma for 20 mins and heated to 700 °C in air for 10 mins. The growth was done in a horizontal CVD system under atmospheric pressure. The system was first flushed with H\textsubscript{2} to remove air and heated to 900 °C. Next, the growths were carried under 100 sccm H\textsubscript{2} and 800 sccm CH\textsubscript{4} for 10 mins. After the growth, the system was cooled to room temperature with H\textsubscript{2} protection. The samples were inspected with scanning electron microscopy (SEM, FEI XL30 SEM-FEG) at a voltage of 1 kV, tapping mode atomic force microscopy (AFM, Digital Instruments Nanoscope IIIa, Vecco), and Raman spectroscopy (LabRam ARAMIS, Horiba Jobin Yvon).
3.3.3 Horizontally Aligned Single Walled Carbon Nanotubes on Quartz from a Large Variety of Metals

As shown in Figure 49, horizontally aligned SWNTs along the X direction of quartz surface can be seen, catalyzed by Co (Figure 49A), Ni (Figure 49B), Pt (Figure 49C), Pd (Figure 49D), Mn (Figure 49E), Mo (Figure 49F), Cr (Figure 49G), Sn (Figure 49H), and Au (Figure 49I). Fe and Cu can also produce such result under the same condition as shown in Figure 50. The tubular structures grown by Cu were shown to be SWNTs according to the less than 2.8 nm diameter measured by AFM shown in Figure 51C and Raman spectroscopy shown in Figure 52. The samples by Co and Au were also confirmed to be SWNTs by AFM measurement with diameter less than 2 nm (shown in Figure 51A) and 3 nm (shown in Figure 51B), respectively. The degree of alignment and yield vary for different metals probably because the fixed growth conditions used here are not the optimal conditions for every metal catalyst. The gas flow rate was found not to affect the alignment direction and the surface is free of steps measurable by AFM as demonstrated previously.103
Figure 49: SEM images of horizontally aligned SWNTs growth by (A) Co, (B) Ni, (C) Pt, (D) Pd, (E) Mn, (F) Mo, (G) Cr, (H) Sn, and (I) Au. The alignment direction is the X direction on ST-cut quartz.

Figure 50: SEM images of horizontally aligned SWNTs on quartz grown by (A) Fe; (B) Cu. The alignment direction is the X direction on ST-cut quartz.
Figure 51: AFM images and diameter distribution of aligned SWNTs on quartz grown by (A) Co; (B) Au; (C) Cu. The diameters of SWNTs are less than 2nm and 3nm for Co and Au, respectively.
Figure 52: Raman spectroscopy of aligned SWNTs by Cu on quartz. The insert is the corresponding SEM image. Excitation laser wavelength is 633nm. Peak at 148 cm\(^{-1}\) corresponds to SWNTs with diameter in 1.68nm. The diameter of SWNTs are characterized by radial breathing modes of Raman spectroscopy using \(d = \frac{248}{\omega}\), where \(\omega\) is the radial breathing mode peak position and \(d\) is the diameter in nm.\(^\text{17}\)

From these results, horizontally aligned SWNTs along the X direction on ST-sut quartz can be synthesized from many metal catalysts, some of which were previously believed to be inactive for SWNT growth. Similar experiments on Si wafers with a 1 \(\mu\)m thermal oxide layer were also performed; they show random SWNTs networks obtained for each metal under the same treatment and growth conditions as shown in Figure 53. The only difference is that the nanotubes grown on the crystal SiO\(_2\) surface of quartz are aligned and those grown on the amorphous thermal SiO\(_2\) on top of Si wafer are random.
Figure 53: SEM images of random SWNTs on Si wafer grown by (A) Fe; (B) Cu; (C) Co; (D) Ni; (E) Pt; (F) Pd; (G) Mn; (H) Mo; (I) Cr; (J) Sn; (K) Au; (L) Mg; (M) Al. SWNT network were obtained for each metal.
The origin of the alignment is still not well-understood. In previous publications, Rogers et al. attributed the alignment to the atomic steps formed on ST-cut quartz. In their reports, atomic steps are formed by thermal annealing of the substrates under high temperature for an extended period of time, and the steps are easily observable under AFM measurements. However, in all of the results reported here, AFM measurements showed no obvious steps; no thermal annealing was performed on the substrates. Additionally, the degrees of alignment for different growth experiments are different as shown in Figure 49. For example, tubes synthesized from Pd have relatively poor alignment under the same growth condition as other metals; however, it can be greatly improved when the growth is changed to the optimal condition. If the alignment is caused by the atomic steps, such differences are not expected since all experiments are performed on the same wafer. Another possibility is that the alignment is caused by the lattice of the substrates. The X direction on the ST-cut quartz is the direction where the motion of the metal catalyst is preferred. However, it has been reported that different metals have different interaction with the substrates. But the alignment trend of the nanotubes shows no obvious preference for different metal catalysts although the alignment degrees are not exactly the same. All of the metals can provide aligned SWNTs. In order to study the movement of the catalysts, Co nanoparticles formed by diblock copolymer method was deposited on quartz. AFM shows no movement of the particles when the substrate was heated to 900 °C without introducing any carbon precursor. However, after introducing the carbon precursor, the catalysts moved wildly to form aligned SWNTs. (as shown in Figure 54) Thus, the introduction of a carbon source seems to be an important factor for the movement of the metal catalyst and the alignment. As a result, we propose a new hypothesis to explain our experimental results. In this hypothesis, the direction of alignment is determined by the crystal lattice of the substrate. However, it is not the lattice of the metal nanoparticles that is interacting with the surface lattice to dominate the motion and the alignment. The carbon shell precipitated on the outer surface of the catalysts is more likely to be the lattice that interacts with the substrate lattice and leads the growth along the direction of
alignment. The differences in the density, yield, and degree of alignment for different metal catalysts can be explained to be from the different carbon solubility in different metal under the same temperature and carbon feeding. Metal particles only provide a platform for the decomposition of the carbon precursor and dissolution of carbon. This hypothesis can explain the growth of aligned nanotubes from so many different metals, but more experimental and theoretical work will be needed to confirm it.

![AFM images of nanoparticles](image)

Figure 54: AFM images of nanoparticles (A) without introducing carbon source; (B) after introducing carbon. The insertion is the corresponding SEM image of aligned SWNTs. The particles only move and aggregate after introducing carbon source at 900°C.

### 3.3.4 Single Walled Carbon Nanotube Growth from Mg and Al

Additionally, Mg (Figure 55A) and Al (Figure 55B) were able to catalyze the growth of horizontally aligned SWNTs along the X direction of quartz. Highly pure salt (99.995% magnesium chloride hexahydrate and 99.999% aluminum chloride from Sigma Aldrich) and ethanol (>99.5% from Sigma Aldrich) were used to avoid any complication by possible impurity inside the salt or solvent. Furthermore, control experiments on a bare quartz or a bare Si wafer (as shown in Figure 56B) and another wafer with only ethanol washing (as shown in Figure 56C)
were done together with the substrates which had Mg or Al catalysts (as shown in Figure 56A). No tubes were found on those substrates without Mg or Al but tubes were observed on the substrate with catalysts. Therefore, the SWNTs are confirmed to be from the Mg and Al. However, the growth mechanism is not fully understood and will be studied further as a new topic in the future.

![Figure 55: SEM images of horizontally aligned SWNTs growth by (A) Mg and (B) Al. The alignment direction is the X direction on ST-cut quartz.](image)

![Figure 56: SEM images of the control experiments to confirm SWNT growth from Mg on Si wafer. (A) Si substrate with Mg catalysts; (B) Si substrate without Mg catalysts; (C) Si substrate with EtOH solvent only. The three samples were done by the same CVD run.](image)
3.3.5 Simple “Cut” Catalyst Pattern Method

Moreover, we also demonstrate a very simple but novel patterning method for the formation of catalyst islands used to grow these aligned SWNTs. A blade such as steel or tungsten carbide (WC, with 9% Co) can be used to scratch a line on top of the quartz. Metal particles will be generated on the surface because of the hardness of quartz. Aligned SWNTs can be grown from the scratches formed by steel (Figure 57A) and WC (Figure 57B) blades. This easy process does not require any complex patterning process such as lithography.

![Figure 57: SEM images of horizontally aligned SWNTs growth by the blade patterning with (A) carbon steel and (B) WC (with 9% Co). The alignment direction is the X direction on ST-cut quartz.](image)

3.3.6 Alignment Control on Quartz by Plasma Treatment

To further demonstrate the substrate guidance and control the SWNT alignment, oxygen plasma treatment was applied onto the substrate so as to change the quartz surface. By the plasma ashing, the quartz surface crystal structure was probably damaged. As seen in Figure 58, under the same growth condition and by the same catalyst on quartz, aligned SWNTs were observed for without plasma treatment and random network were shown for with oxygen plasma treatment. Therefore, the alignment can be controlled by the surface manipulation and the quartz surface guided alignment was clearly indicated.
3.4 Top Gated FET of Purely Semiconducting Single Walled Carbon Nanotubes on quartz by EtOH/MeOH Mixture Growth

High-density and perfectly aligned SWNT arrays were grown on ST-cut quartz substrates by EtOH/MeOH mixture. Raman spectroscopy showed that the samples consist of almost 100% semiconducting tubes. The methanol in the growth process combined with the interaction between the SWNTs and the quartz lattice leads to the selective growth of semiconducting nanotubes. Such high density and horizontally aligned semiconducting SWNTs can be used in FETs and sensors. In this section, we mainly demonstrate that the fabrication of SOI devices and the electrical measurement of such top gated FETs to support and confirm the Raman observation. The on/off ratio of the FETs can be as high as $10^3$. This study demonstrates a possibility to solve the metallic and semiconducting nanotubes mixture problem which limits application of carbon nanotubes in nanoelectronics.

3.4.1 Selective Growth of Aligned Semiconducting Single Walled Carbon Nanotubes

The selective growth of aligned semiconducting SWNTs was mainly developed by Lei in our group. The dense arrays of aligned SWNTs were grown on single-crystal ST-cut quartz...
substrates using an ethanol/methanol mixture as the carbon source and Cu nanoparticles as catalysts as shown in Figure 59A and B. Nanotubes within the arrays revealed a narrow diameter distribution from 1.55 nm to 1.78 nm as shown in Figure 59C and D. The SWNTs are nearly all semiconducting by Raman analysis as shown in Figure 59E and F. To further confirm a high percentage of semiconducting nanotubes in these SWNT arrays, electrical characterization of the FETs fabricated from as-grown aligned nanotube arrays directly on quartz substrates was first done by the conducting polymer top gated FETs fabricated by e-beam lithography as shown in Figure 60. The on/off is obviously more than 3 but not high enough to show pure semiconducting containing probably because of the gate leakage from the conducting polymer gate, low gate bias, and the long device channel length configuration (0.5 mm). Therefore, another top gated FET is important for this study.
Figure 59: Arrays of SWNTs of almost exclusively of semiconducting nanotubes. (A and B) SEM images. The bright and parallel horizontal lines visible in the images are catalyst lines. (C) AFM image. (D) Diameter distribution of 200 SWNTs of an array measured by AFM. (E and F) Raman spectra of SWNTs transferred onto the SiOx/Si substrates. The spectra were obtained using 488- and 633-nm excitation laser lines at 10 different spots over the substrate for each laser line. Each curve in a panel shows spectrum at a spot on the substrate. Peaks within the rectangles marked with S correspond to the semiconducting SWNTs. The rectangles marked with M denote the frequency range where RBM peaks of metallic SWNTs are expected. The graph is from Lei Ding.
Figure 60: High on/off ratio FETs fabricated with as-grown aligned CNT arrays top-gated by solid electrolyte polymer films. (A) Large magnification view of the set of electrodes of a test device. The widths of the gaps between the 40 nm-thick gold contact lines correspond to the channel lengths of FETs (from top to bottom): 4 μm, 3 μm, 2 μm, 1 μm, and 5 μm. To break possible current paths through the nanotube array past the transistor channels, the tubes were partially removed by reactive ion etching (RIE) in oxygen plasma. (B) Family of transfer characteristics (drain current, I_d, versus top gate voltage, V_g) of one of the test devices under a bias voltage V_{ds} = 80 mV. The parameter of the family is the transistor channel length L. The channel width is 0.5 mm. (Inset) The on/off ratios obtained for the device as a function of the channel length, L. The graph is from Alexander Tselev.

3.4.2 Top Gated FET Device Fabrication on Quartz

Figure 61 shows the schematic illustration of the top gate FET. Four major steps were used to complete the devices. The method to integrate the SWNTs arrays into transistors began with photolithography and e-beam evaporation to define source and drain electrodes (Cr, 5nm/Au, 30 nm) on SWNTs/quartz surface as shown in step 1 of Figure 63. The mask is the Mask1 as shown in Figure 62. The measurement regions were in between the catalyst lines. After that, we used aligned photo-lithography to cover the device region and burned the nanotubes outside by oxygen plasma as shown in step 2 of Figure 63. The mask is the Mask2 as shown in Figure 62.
Thirdly, a uniform film (600 nm) of epoxy (SU-8) was spin-casted on the surface followed by aligned photo-lithography to pattern the gate dielectric layer as shown in step 3 of Figure 63. The mask is the Mask3 as shown in Figure 62. Lastly, aligned photo-lithography and e-beam evaporation were used to form the gate electrodes (Cr, 5nm/Au, 30 nm) as shown in step 4 of Figure 63. The mask is the Mask4 as shown in Figure 62. Figure 64 shows a typical top gated FET fabricated on quartz.

Figure 61: Schematic illustration of the top gate FET. (A) Side view. (B) Top view.
Figure 62: The mask design for the top gate FET. (A) Overview of the four patterns overlapped. (B) Four individual mask patterns. The mask patterns contain the alignment markers.
Figure 63: The optical microscope and SEM image of the four fabrication steps for the top gate FET.

Figure 64: SEM image of a typical fabricated top gate FET.
3.4.3 Results and Discussion

In the large channel width devices with a large number of nanotubes, the on/off ratios stabilize around 20 due to small percentage of metallic nanotubes in the samples. In particular, the on/off ratio of 20 is expected if 95% of tubes are semiconducting assuming all nanotubes have similar resistances in their ON-state. We have estimated from these measurements that the samples consisted of 95 to 98% semiconducting nanotubes. (from Lei Ding and Alexander Tselev)

The shorter channel width top-gate FETs were fabricated with SU-8 epoxy as the dielectric layer. It shows that the on/off ratio can be up to 5000 (as shown in Figure 65) when the number of nanotubes in each device is smaller, which further proved the enhanced fraction of semiconducting SWNTs in the arrays. This better performance of the devices can be explained by the fact that there are smaller numbers of nanotubes (10-20) in each of the FETs, meaning a smaller probability of having metallic nanotubes in the device. Assuming that 98% of the nanotubes are semiconducting, if each device consists of 5 aligned nanotubes, 90% (0.985 ≈ 0.9) of the devices will have only semiconducting nanotubes and will give very low OFF current and high on/off ratio.
Figure 65: Gate dependence measurement of the top gate FET. Drain current vs. gate voltage curve measured from a typical device with a bias voltage $V_{sd} = 0.5 \text{ V}$. The channel length and width were 10 $\mu\text{m}$ and 50 $\mu\text{m}$, respectively. A 600-nm-thick SU-8 epoxy layer was used as a gate dielectric. The on-current and off-current are estimated to be about $1 \times 10^{-6} \text{ A}$ and $2 \times 10^{-10} \text{ A}$, respectively. The on/off ratio is calculated as 5000.

### 3.5 Summary

In this chapter, we primarily focus on the allocation control of SWNT synthesis. Aligned growth either on Si wafer, “V” shape trench, or quartz was demonstrated. Importantly, selective growth of purely semiconducting SWNT arrays on quartz by EtOH/MeOH mixture is shown.

Horizontally aligned SWNTs were grown by the high and low gas flow. This study can improve our understanding of the aligned growth by gas flow. In addition, such ultra long tube can be the template for the nanoscale antenna. Moreover, 3D uniform diameter and high quality SWNT structure inside trenches were shown and proposed due to the topography effect.
Horizontally lattice-aligned SWNTs were synthesized on ST-cut quartz by a large variety of metals. We proposed that the alignment is promoted by the carbon atoms on the outside of the metal nanoparticles. Moreover, Mg and Al are first shown to produce SWNTs. A simple pattern scratch method is introduced. Those studies will improve our understanding of the horizontal lattice-alignment growth on quartz, provide new catalyst candidates for SWNT synthesis, and offer an easy patterning method.

The selective growth of pure semiconducting SWNT arrays on quartz leads to orientation plus property-controlled SWNTs for numerous applications. A method was developed to grow high density, perfectly aligned SWNT arrays with a highly pure semiconducting SWNTs on ST-cut quartz using an ethanol/methanol mixture. The top gate FETs fabricated on such SWNTs support the Raman analysis showing pure semiconducting tubes. Moreover, such devices are readily to be used for real applications.
Chapter 4: Single Walled Carbon Nanotube Device Property Control

4.1 Introduction

Despite the averaged performance of SWNT thin films, a number of parameters including: nanotube diameter, density, length, orientation, and device channel length can affect the behaviors of the thin film devices. Some studies have been done on SWNT thin film synthesis and devices. For example, Snow et al. reported the density effect of a thin film grown on a surface. Shim et al. examined the channel effects. However, the diameter effect, density effect, tube length effect, and channel length effect have not been fully studied, especially for a small diameter SWNT thin film (partly because of the lack in such kind of SWNT thin films), which provides pure SWNTs and narrows the tube performance variances. Moreover, a mathematical model of a SWNT thin film FET device matching the experimental data has not yet been shown.

In this section, the parameters affecting the performance of SWNT thin film FET devices such as the channel effect, diameter effect, and density effect have been examined experimentally. Moreover, a mathematical model that considers density, tube length, orientation, and channel length has been constructed to simulate the electronic behaviors (on/off ratio) of SWNT thin film devices. Interestingly, a SWNT thin film of metal behavior has been observed in some Co catalyzed grown samples. These achievements will further improve the understanding of SWNT thin film devices, and probably provide the metallic SWNT thin film as a candidate in many applications such as for interconnects in integrated circuits (IC).
4.2 On/off Ratio vs. Gap Length in Single Walled Carbon Nanotube Thin Film FET (Experiment)

For SWNT thin film FETs, the length of the device channel, the density of the network, and the diameter of the SWNTs determine their electronic performance. In this study, we focus on the current-gate voltage (I-Vg) characteristics and on-to-off current ratio of SWNT FET devices under the above effects because those properties determine the application of SWNT thin film FETs.

4.2.1 Experimental Section

SWNT thin film device fabrication with different channel lengths. The SWNT devices were fabricated using the thin film grown on surface to form a set of different channel lengths (5, 10, 20, 40, 80, 150 µm) as shown in Figure 66A. Metal electrodes, Au (30nm) with Cr (5nm) adhesion layer, were deposited by electron beam evaporation. After lift-off, SWNT thin film devices with different channel lengths were obtained by a second photolithography step combined with O₂/plasma etch. This step was used to confine SWNTs only in the device region and prevent current leakage to silicon back gate.

SEM, AFM, Raman, electronic characterizations of SWNT thin film and devices. SEM characterization was carried out with a XL30 scanning electron microscope (FEI) with accelerating voltage of 1kV. The AFM characterization was performed on a Nanoscope IIIa atomic force microscope (Digital Instrument) with taping mode in ambient conditions. The Raman instrument is a Renishaw Raman microscope equipped with 3 laser wavelengths (780 nm, 633 nm and 514 nm). The electronic behaviors of the devices were measured on a probe station with Keithley Model 2400 (resolution 10 pA) as sourcemeters.
4.2.2 Results and Discussion

First, the thin film (as shown in Figure 66B; with average diameter 1.6nm) grown by Fe diblock copolymer micelles\textsuperscript{24} was used to fabricate FET devices with different channel lengths. Figure 67 shows the I-V characteristics under gate bias for different channel lengths. As can be seen, the off current can not reach zero, indicating the device can not be completely turned off because of the electrical contribution of the small band gap and metallic tubes. In Figure 67, the on-to-off ratio increases with the channel length because the off current drops faster than the on current when the channel length increases (less conduction paths).

Figure 66: SEM images of SWNT thin films and their FET devices. (A) A typical SWNT thin film FET device with different channel length. (B) Large diameter (average diameter ~1.6 nm) SWNT thin film (high density). (C) Small diameter (less than 1 nm) SWNT thin film (high density). (D) Small diameter (less than 1 nm) SWNT thin film (low density).
Figure 67: SWNT thin film FET (large diameter) electronic performance: (Left) I-V characteristics at bias of 10mV between source and drain for different channel length; (Right) On-to-off ratio for different channel length.

Second, small diameter SWNTs (< 1 nm) from Co diblock copolymer micelles (our group) were used to fabricate SWNT thin film FETs. As can be seen in Figure 68, for a high density thin film device as shown in Figure 66C, the off current can not reach to zero as the film grown from Fe catalysts because the metallic tubes can form continuous paths in the channel for a high density thin film. A low density thin film as shown in Figure 66D was used for device fabrication and Figure 69 shows that the device can be completely turned off when the channel length is above 40 μm due to a lack of conducting paths. The on-to-off ratio is much larger than the high density thin film grown by Co and the thin film grown by Fe, but they all follow the same increasing trend for the on-to-off ratio.
Figure 68: High density SWNT thin film FET (small diameter) electronic performance: (Left) I-V characteristics at bias of 10 mV between source and drain for different channel length; (Right) On-to-off ratio for different channel length.

Figure 69: Low density SWNT thin film FET (small diameter) electronic performance: (Left) I-V characteristics at bias of 10 mV between source and drain for different channel length; (Right) On-to-off ratio for different channel length.
From the above results and discussion we can generally conclude that the on-off-ratio generally increases as the channel length gets wider for the same SWNT thin film FET. In addition, the wider the channel length is, the lower the off current because there are fewer and longer conducting paths (higher resistance) in larger channel length under the same tube length distribution. Moreover, the tube diameter seems having no obvious effect on the on/off ratio as shown in Figure 70 although the two thin films may be different. The diameter effect could be difficult to define. The density of thin film changes the on/off ratio much as shown in Figure 71 because the off current drops dramatically as the tube density gets lower. The low density and small diameter thin film can produce the high on/off ratio FETs.

![On/off ratio vs channel length for large D and Small D SWNTs](image)

Figure 70: Comparison of on/off ratio v.s. channel length between large diameter and small diameter SWNT thin film FETs.
Figure 71: Comparison of on/off ratio v.s. channel length between low and high density SWNT thin film (small diameter) FETs.

**4.3 On/off Ratio vs. Gap Length in Single Walled Carbon Nanotube Thin Film FET (Modeling)**

In order to simulate the electronic behaviors of SWNT thin film FET devices and support the experimental results, a mathematical model considering density, tube length, orientation and channel length has been constructed and programmed in Matlab as shown in Figure 72.
4.3.1 Modeling Method

The basic mechanism of simulating and calculating the on/off ratio of the SWNT thin film FET is to solve a 3-D resistor network incorporating the existence of the tube-tube contact resistance and the two types of the tubes. The general process is as following.

1. Set a pool of nanotubes by density, tube length, orientation and etc.
2. Find tubes in the device region with a channel length and width.
3. Form 3-D resistance network and solve the linear system with resistance parameters. (Figure 73 shows how to solve the 3-D network.)
4. Collect the current from electrode and obtain the on state current.
5. Eliminate all the semiconducting tubes and replay step 2 – 4 for off state current.
4.3.2 Results and Discussion

A SWNT thin film FET as seen in Figure 66C was used to show the simulation. The density of the SWNTs was estimated as 1 tube/4 $\mu$m$^2$. The average SWNT length was assumed 10$\mu$m with a normal distribution. The tube orientation was set to be an average distribution from 0 to $2\pi$. Figure 74 shows the channel length effect on the on/off ratio between the experimental and simulated data. As we can see, the calculated on/off ratio almost agrees with the experimental result and the trend is the same. Therefore, the modeling is successful for calculating on/off ratio of a SWNT thin film FET with consideration of the density, orientation, length, and other factors.

With a more robust program and algorithm, the model could be widely used in studying SWNT thin film devices in the future. Importantly, this simple program can be run even on a normal PC so that it can be used without requiring a computer cluster.
4.4 Metallic Behaved Single Walled Carbon Nanotube Thin Film FET

SWNT thin film FET devices are widely studied because of ensemble average properties. The devices behave more like semiconductors although they can not be turned off completely. To date, metallic SWNT FET thin film has never been grown directly on a surface without any treatment due to the mixture of semiconducting and metallic tubes after growth. Here, we report a SWNT thin film FET with metallic behavior for the first time.

4.4.1 Experimental Section

The Co catalysts from Agilent were used to grow the tubes and fabricate FETs. Figure 31A shows the SEM image of the small diameter SWNT with tubes less than 1 nm in high density. The device fabrication and measurement follow up the last section.
4.4.2 Results and Discussion

As can be seen in Figure 75, no gate effect is observed and the current between source and drain drops slightly under gate bias. Figure 75 shows that the resistance of thin film is linearly proportional to the channel length and the thin film behaves like a metal (Sheet resistance is 25 kΩ/square.). In addition, the contact resistance (380 Ω) does not dominate the overall resistance of the device.

The origin of the metallic behavior is still not fully clear. First, the density of the thin film is not the dominant factor because both high and low density samples show this phenomenon. The metallic behavior can be observed as well by the low tube density sample from 10 time diluted catalysts as shown in Figure 76. Second, the length of the tubes is not the main reason because the metallic behavior was seen for different channel lengths, even up to 160 μm. Moreover, if the gate bias was applied from -100 V to 100 V, the metallic behavior was still observed for both high and low density samples. This special observation of metallic behavior provides an opportunity for SWNT thin film devices in various applications which require metallic behavior, such as the interconnector of IC and also improves our understanding of SWNT growth and devices.
Figure 75: SWNT thin film FET (from Co diblock copolymer micelles donated by Jennifer Lu) electronic performance: (Left) I-V characteristics at bias of 10 mV between source and drain for different channel length; (Right) Device resistance vs different channel length at 0 gate and 10mV bias between source and drain.

Figure 76: Low density SWNT thin film FET (from Co diblock copolymer micelles donated by Jennifer Lu) electronic performance: (A) I-V characteristics at bias of 10 mV between source and drain for different channel length; (B) SEM image of the small diameter SWNT thin film in low density by diluted catalysts.
4.5 Summary

In brief, the experimental studies and the simulation work further improve the understanding of SWNT thin film FET devices. The alignment effect of the SWNT thin film FET devices needs to be examined experimentally. A more robust mathematical model, requiring less computing power and less time, needs to be achieved. The metallic SWNT thin film may lead to more useful applications of SWNT devices.
Chapter 5: Palladium Decoration on Carbon Nanotubes by Versatile Electroless Method

5.1 Introduction

Since their description by Iijima, CNTs have displayed potential in a large variety of applications due to their properties including high surface area, unique physical properties, high electrical conductivity, etc. Another type of nanostructure, metal NP, is an attractive nanomaterial in catalysis and materials science. With the CNTs serving as the template, hybridization of metal NPs and CNTs is an extremely promising nanostructure for the use of catalyst, storage, sensor, electronics, optics, etc. The combination of these two nano-materials can bring the integrated or unique properties in the new hybrid materials. Importantly, properties of CNTs can be manipulated after tube synthesis by such metal decoration.

The hybridizing approaches can be generally divided into two groups. One is the direct formation of metal NPs on the CNT surface. The other one is the connection of chemically modified NPs to CNTs or to modified CNTs. The former is more attractive because it is simple and has less negative effect on the properties of NPs and CNTs although few well-controlled methods have been developed.

So far, research in Metal/CNT composites are mostly focused on noble metals such as Pd, Pt, Au, Ag, and Ru. Among them, palladium (Pd), is widely used in electronics, gas purification, catalysis, hydrogen storage, etc. Pd/C, denoted as palladium metal supported on charcoal, is an efficient catalyst widely used for hydrogenation, hydrogenolysis and hydrodechlorination. Calculations show that the curvature of the nanotube seems to provide a stronger interaction and more suitable than a flat surface such as graphite. The most common approaches to functionalizing CNTs with Pd NPs involve electrochemical methods, physical
evaporation,\textsuperscript{117} or electroless deposition.\textsuperscript{118-120} Most of them are usually tedious and time-consuming treatments. Electrochemical methods are limited to small scale samples. Evaporation requires vacuum and is not suitable for large scale synthesis. Among them, electroless method is the most attractive. Pd NPs can electrolessly decorate CNTs by linker connection,\textsuperscript{118} substrate enhancement,\textsuperscript{120} oxidation assistance,\textsuperscript{119} etc. However, those methods involve multi-steps, substrate assistance, quality degradation, or other inconveniences. Most importantly, the morphology of the resulting NPs lacks consistency and control. Highly dispersed Pd NPs with well controlled size, uniformity and oxidation state on CNTs by a versatile and simple method have not been shown. Dai and coworkers reported a spontaneous method to form Au and Pt NPs reduced by CNTs.\textsuperscript{121} Unfortunately, Pd$^2+$ cannot theoretically be reduced by CNTs because of the lower redox potential. However, by other mechanism, we accomplished the desired Pd decoration by a similar experiment.

Due to the high surface area, chemical inertness and thermal stability of CNTs, Pd/CNTs has been reported in several specific applications such as Heck coupling reaction,\textsuperscript{122} hydrogen sensor,\textsuperscript{123} etc. However, most of them are limited to organic synthesis or hydrogen related, which can also be accomplished by Pd/C. Novel and special applications are necessary to show the unique properties of Pd/CNTs.

In this study, a versatile electroless Pd decoration method is demonstrated to be suitable for various kinds of CNTs such as SWNTs, DWNTs, and FWNTs, both surface-grown on Si wafers and bulk-synthesized in large scale. This approach is uniquely suitable for both pre and post deposition. CNTs were decorated by Pd NPs with controllable size tuned by decoration time and controllable oxidation state by decoration condition. In addition, the decoration is selective on CNTs with a higher efficiency than other noble metals like Pt and Au. The mechanism is explored that Pd NPs are reduced by ethanol not by CNTs, which only serve as nucleation sites.
rather than the reducing agent. Small size and well dispersed PdCl₂ NPs (further reduced to form Pd NPs by hydrogen) can decorate without use of ethanol. Importantly, two novel applications are introduced. One is electrical conductivity improvement by Pd decoration on both bulk and surface-grown CNTs. Electronic behavior change on the surface SWNT device is first shown to be combined effect of contact (tube to electrode) and doping (Pd NPs on tube). Pre and post deposition of Pd on bulk CNTs lowered the sheet resistance and enhanced the conductivity by up to 10 and 5 fold, respectively. The second is nanostructure growth catalyzed by the Pd NPs supported on CNTs. Au NPs were grown using the Pd NPs supported on the SWNTs as the “seed” nuclei, more efficient than the non-seeded growth. In addition, uniform diameter carbon nanofibers (CNFs) were grown by such hybrid and the growth efficiency is much higher than the naked Pd NPs without support because the immobility of NPs by the SWNTs limits the aggregation at high temperature.

5.2 Experimental Section

5.2.1 Chemicals

Sodium tetrachloropalladate(II) (Na₂PdCl₄; 99.998% pure), tetrachloroauric(III) acid (HAuCl₄·3H₂O; ≥99.9% pure), sodium tetrachloroplatinate(II) hydrate (NaPtCl₄·4H₂O; ≥40% Pt basis), and ethanol (99.5% pure) were purchased from Aldrich. All chemicals were used as received.

5.2.2 Bulk Tube Sample Preparation and the Pd Decoration

*Growth of bulk CNTs and purification.* FWNTs were synthesized and then purified by the gas-phase oxidation method.⁷,¹²⁴ H₂O₂ purification method was also used to obtain low quality defective FWNTs. DWNTs were obtained by a similar method. Hipco tubes after gas-phase oxidation purification were used as the SWNTs. All the purified CNTs contain impurity less than 1%.
Pd Pre-deposition on bulk CNTs. Purified CNTs were dispersed in ethanol by probe ultrasonication (Sonics VC 750; 50% power) for one hour. 5 mM Na$_2$PdCl$_4$ was dissolved in nanopure-water first and then mixed with equal volume of ethanol. (Ethanol was used in the decoration if not specified.) The above two solutions (CNT and Pd salt) were mixed together and stirred at room temperature. The CNT buckypaper was formed by vacuum filtration and baked in an oven at 110 $^\circ$C for 12 hours. Four-probe measurements were taken to determine the sheet resistance.

Pd Post-deposition on bulk CNTs. The CNT buckypaper without Pd decoration was formed as above and then the sheet resistance was measured. A typical 50 ml 5 mM Na$_2$PdCl$_4$ nanopure-water/ethanol (half/half) solution was poured onto the buckypaper which served as the filter paper. After the Pd salt solution was filtered through it, the buckypaper was baked at 110 $^\circ$C for 12 hours and another sheet resistance measurement was taken.

5.2.3 Surface Tube Sample Preparation and the Pd Decoration

SWNT surface growth. Iron nanoparticles were prepared by inversed micelles loaded with iron salt to obtain uniform size catalysts.$^{24}$ The treatment on the substrate and the random SWNT thin film growth procedure were demonstrated in our previous publication.$^{24}$ Aligned SWNTs were grown as described in our earlier publication.$^{103}$

Pd decoration on surface-grown SWNTs. Random SWNT thin film or aligned SWNTs were used after growth without further treatment. They were soaked in Na$_2$PdCl$_4$ nanopure-water/ethanol (half/half) solution. Then the sample was rinsed by nanopure-water and dried by an air gun.
Surface-grown SWNT thin film devices fabricated by shadow mask. The metal electrodes (Cr/Au: 5 nm/30 nm) were evaporated by a homemade plastic shadow mask (500 μm in length and 2 mm in width) and a 100 mesh TEM grid (Ted Pella, Inc.) used as the shadow mask. The electrodes from the TEM grid are 204×204 μm² and the gap between the adjacent electrodes is 50 μm. The Pd decoration process was done before or after the device fabrication.

5.2.4 Characterization

SEM characterization of SWNTs on the surface. The samples were inspected with scanning electron microscopy (SEM, FEI XL30 SEM-FEG) at a voltage of 1 kV.

AFM characterization of the nanoparticles and SWNTs on the surface. The substrates with nanoparticles and SWNTs were characterized by tapping mode atomic force microscopy (TPAFM) (Digital Instruments Nanoscope IIIa, Vecco). The diameters of the nanoparticles and nanotubes were determined by height measurements.

TEM characterization of bulk CNTs. The CNTs with and without Pd decoration were characterized by a transmission electron microscope (Philips 301 integrated with EDS or FEI Tecnai G² Twin).

XPS characterization of the Pd decorated on CNTs. X-ray photoelectron microscope spectra were recorded on a Kratos Axis Ultra system with monochromatic Al Kα X-rays. Sample charging during the measurements was compensated by an electron flood gun.

Raman spectroscopy characterization of CNTs with and without Pd decoration. Raman spectroscopy (LabRam ARAMIS, Horiba Jobin Yvon) was taken by the excitation laser of 633 nm.
**UV-vis-NIR absorption characterization of CNTs with and without Pd decoration.**

Absorption spectrum was taken on a Varian Cary 500 Scan system.

**Electrical characterization of CNT buckypaper and SWNT devices.** Four-probe measurement was applied to measure the sheet resistance of the CNT buckypaper. 5 data points were taken and the average value was used for each sample. SWNT devices were measured with a probe station (Signatone S-1160A-5) and parameter analyzer (Keithley 4200-SCS).

**TGA characterization of Pd loading in the Pd/CNTs hybrid.** Thermogravimetric analysis was done in air heated from room temperature to 900 °C by a TA instrument (SDT2960). Because the purified CNTs in this study were all over 99% pure, the residues were palladium oxide after burning in air at 900°C. The palladium loading percentage was calculated according to the residual weight percentage.

**NMR characterization of chemical content in the solution.** The Nuclear magnetic resonance (NMR) was taken on a Varian 400 system to characterize the chemical components of the solution after Pd decoration.

**5.3 The Electroless Pd Decoration Method and Its Mechanism**

The morphology and nanostructure of supports are the main factor in determining the dispersion of metal NP. CNTs are competitive support materials because of their high surface area and chemical inertness, particularly in strong basic and acid environments. In addition, their high thermal stability leads to gas-phase applications at elevated temperature. Precious metal catalysts can be easily reclaimed by burning the carbon away.
5.3.1 A Versatile, Controllable, and Effective Electroless Pd Decoration Method

The structure and nature of the resulting Pd/CNTs were characterized by TEM and AFM. Highly purified bulk CNTs including SWNTs (Figure 77A), DWNTs (Figure 77C), and FWNTs (Figure 77E) and surface-grown SWNTs (Figure 77G) were decorated by Pd NPs, as shown in Figure 77B, D, F and H, respectively. (Ethanol was used in the decoration if not specified.) As seen in Figure 77A, C and E, the bulk CNTs before decoration are free from impurities such as catalysts. Thus the particles after decoration are Pd and the crystal lattices were observed by the high resolution TEM as seen in Figure 78. The decoration time is one day, one hour and one day for SWNTs, DWNTs and FWNTs, respectively. The NPs were bonded sufficiently strongly on the CNTs because long time ultrasonication could not obviously break the adhesion. The shape of the NPs seemed not regular. The diameter distributions of the NPs are roughly 5-50 nm (few more than 50 nm), 5-15 nm, 5-50 nm (few more than 50 nm) for SWNTs, DWNTs and FWNTs. The decoration time for surface-grown SWNTs is 10 seconds and the isolated NPs are roughly 3-15 nm (The NP size were estimated by the height measurement subtracted by the tube diameter.). In addition, the decoration was mostly selective on SWNTs and few NPs were formed on the substrate.
Figure 77: TEM images of bulk CNTs and AFM images of surface-grown SWNTs before and after Pd decoration. (A) TEM image of purified SWNTs (Hipco). The scale bar is 200 nm. (B) TEM image of SWNTs (Hipco) after Pd decoration for one day. The scale bar is 400 nm. (C) TEM image of purified DWNTs. The scale bar is 500 nm. (D) TEM image of DWNTs after Pd decoration for one hour. The scale bar is 40 nm. (E) TEM image of purified FWNTs. The scale bar is 500 nm. (F) TEM image of FWNTs after Pd decoration for one day. The scale bar is 300 nm. (G) AFM image of surface-grown SWNTs. The scale bar is 500 nm. (H) AFM image of SWNTs after Pd decoration for 10 seconds. The scale bar is 500 nm.
In order to examine if the Pd NPs directly decorated CNTs or were physically adsorbed after NP pre-formation, CNT samples were stirred in the preformed Pd NP suspension for one day. For the bulk sample, NP clusters were found on only a few sites along the tube sidewall as shown in Figure 79D. This is obviously different from the isolated Pd NP decoration in Figure 77. For the surface sample, only a few particles can be seen in Figure 79F either on the substrate or perhaps on the tubes. Therefore, the decorating NPs were started from the nucleation on the sidewall of CNTs not in the solution.
Figure 79. TEM images of bulk FWNTs and AFM images of surface-grown SWNTs before, after Pd decoration, and stirred with preformed Pd NPs. (A) Purified FWNTs. (B) FWNTs with Pd decoration for one hour. (C) FWNTs stirred with preformed Pd NPs for one day. (D) SWNTs grown on surface. (E) Surface-grown SWNTs with Pd decoration for 10 seconds. The inset is high resolution AFM image. (F) Surface-grown SWNTs stirred with preformed Pd NPs for one day. The inset is high resolution AFM image. The strip lines in AFM images are due to the large particles on the substrate during the measurement. The scale bars of all the TEM images are 40 nm. The scale bars of all the AFM images are 2 μm. The scale bars of all the inset AFM images are 500 nm.

As shown above, the Pd NPs decorating on either bulk or surface-grown CNTs have relatively large size and broad distribution. The properties of NPs are tuned by their size and distribution. In some cases, finer NPs may be highly desired. For example, the deactivation of Pd
catalysts occurs by an increase of crystallite size in some organic reactions.\textsuperscript{113} In addition, denser decoration than shown above is demanded for higher NP yield. Here, such NPs decorated without ethanol as demonstrated in Figure 80. The experimental procedure is exactly the same as above except without ethanol. As seen in Figure 80A and B, uniform (2-3 nm) NPs decorated the bulk DWNTs for 1 hour decoration time. Moreover, the NPs are dramatically dense and almost evenly formed with a regular shape. Similar to as shown in Figure 80C and D, surface-grown SWNTs were decorated by 2-5 nm diameter Pd NPs with much higher coverage than with ethanol as shown in Figure 77H for the same decoration time. The better uniformity, higher coverage, and smaller size without ethanol are discussed in the next section. As shown below, the NPs are actually PdCl\textsubscript{2}, but they can be reduced to Pd.

![Figure 80. TEM images of bulk DWNTs and AFM images of surface-grown SWNTs decorated by fine-size and highly-dispersed PdCl\textsubscript{2} NPs. (A) Bulk DWNTs decorated by small-size and high-density PdCl\textsubscript{2} NPs for one hour. The scale bar is 20 nm. (B) PdCl\textsubscript{2} NPs (The diameter of the NP shown in the figure is 2.5 nm) decorating on DWNT. The scale bar is 5 nm. (C) Surface-grown SWNTs decorated by PdCl\textsubscript{2} NPs for 10 seconds. The scale bar is 500 nm. (D) Zoomed-in AFM image of Pd NPs (The average size of the NPs is estimated to be 3 nm.) decorating surface-grown SWNTs. The scale bar is 200 nm.](image-url)
5.3.2 Mechanism of Palladium Decoration

Dai and coworkers applied a similar method to decorate surface-grown SWNTs with Pt and Au NPs but the ethanol was used only as the solvent (better wetting to CNT than water).\textsuperscript{121} They claimed that the NPs were formed after the reduction of metal ions by CNTs. However, $\text{PdCl}_4^{2-}$ can not be reduced by SWNTs according to their theory. The work function of SWNTs is $\sim$5 eV.\textsuperscript{126} The Fermi level of a SWNT is about +0.5 V above the potential of a standard hydrogen electrode (SHE),\textsuperscript{121} very close to the reduction potential of $\text{PdCl}_4^{2-}$, which is +0.591 V vs SHE.\textsuperscript{127} Therefore, the redox process can not happen easily. However, we discovered that ethanol can be used as the reducing agent to assist Pd NP formation on CNTs.

The existence and the oxidation state of Pd were characterized by high resolution XPS spectrum of Pd 3d binding energy on surface-grown SWNTs. (The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.\textsuperscript{128}) For NPs formed with ethanol, the binding energy peak (335.5 eV) showed metallic Pd as seen in Figure 81A and Cl was not obviously presenting as shown in Figure 81B. In contrast, for the NPs formed without ethanol, Pd halide binding energy peak (337.3 eV) was seen in Figure 81A and Cl (198.5 eV) was obviously shown in Figure 81B. EDS on the NP decorating bulk sample without ethanol further supported the present of Pd and Cl, as shown in Figure 82. Therefore, the NPs formed on CNTs without ethanol are $\text{PdCl}_2$. Pd NPs can be obtained easily after hydrogen reduction of those $\text{PdCl}_2$ NPs in $\text{H}_2$ for 20 mins at 500$^\circ$C. As seen in Figure 81A and B, the binding energy (335.5 eV) showed the change to metallic Pd and the diminishing of Cl. NMR indicated the formation of acetate acid (formed from aldehyde) in the solution after Pd decoration with ethanol, which confirmed the redox reaction during decoration with ethanol. From the above analysis, Pd NPs were reduced by ethanol not by SWNTs, which only serve as the nucleation sites rather than the reducing agent. Furthermore, spontaneous reduction was confirmed by post ethanol soak. The $\text{PdCl}_2$ decorating SWNT sample was stirred in ethanol at room temperature or 60$^\circ$C for 5 hours. The $\text{PdCl}_2$ NPs
were not reduced to metallic Pd as shown in Figure 81C (binding energy peak at 337.4 eV) and Cl (binding energy peak at 198.7 eV) was still detectable as seen in Figure 81D. Consequently, the Pd NPs were not formed by post-reduction but only during the growth. In brief, Pd NP formation process is nucleation and growth, both going with reduction. The PdCl₂ formation process is nucleation and growth. Though the NPs supported on the CNTs have different oxidation states in each mechanism, they may have the similar properties as between Pd⁰/C and Pd²⁺/C because no evident differences of them in catalytic activity were observed.¹¹³ For example, they were both able to catalyze the Suzuki-Miyaura reactions.¹¹³

Figure 81. XPS spectrum of Pd and Cl on surface sample for decoration mechanism. (A) XPS spectra of Pd 3d binding energy after decoration in ethanol/H₂O, in H₂O, and post-reduction after decoration in H₂O. (B) XPS spectra of Cl 2p binding energy after decoration in ethanol/H₂O, in H₂O, and post-reduction after decoration in H₂O. (C) XPS spectra of Pd 3d binding energy after soaking the decoration sample (by H₂O) in ethanol. (D) XPS spectra of Cl 2p binding energy after soaking the decoration sample (by H₂O) in ethanol. The binding energy was calibrated using the C 1s photoelectron peak at 284.6 eV as the reference.
As shown above, the Pd NPs are larger, broader in distribution and grow faster with reducing agent (ethanol) assistance than the PdCl₂ NPs without reducing agent. Those differences between Pd and PdCl₂ NPs decorated CNTs are similar to the decoration to the activated carbon. Uniform Pd²⁺/C (covering entire surface) can be prepared through adsorption of Pd²⁺ salts onto activated carbon. On the other hand, spontaneous reduction of metallic Pd particles leads to a broad size distribution.

The chemical inertness of CNTs can be a disadvantage. The low reactive surface makes it difficult to deposit metals, leading to low decoration efficiency. Pretreatment by oxidation processes, although degrading to the CNT properties by damaging the tubes, is generally used to introduce surface groups, thus enhancing the interaction with the metal. However, Pd NPs decoration by our method does not necessarily require the chemical modification and has a higher efficiency than Pt and Au. Three commonly used noble metals, Pd, Pt and Au were done by the same decoration treatment on the same as-grown SWNTs both in ethanol/H₂O and H₂O. As seen in Figure 83, the decoration (Figure 83A) efficiency is higher than Pt (Figure 83C) and Au
(Figure 83) in water solution. In addition, the decoration (Figure 83B) efficiency is higher than Pt (Figure 83D) and Au (Figure 83F) in the mixture solution. If NPs only interact with the oxygen group (normally present on surface-grown SNWTs), the decoration efficiencies of the three metals should be similar because same SWNTs were used. However, Pd and PdCl₂ have much higher efficiency than the other two. Therefore, the nucleation of Pd or PdCl₂ could prefer to the oxygen groups on the sidewall but not only to them. In addition, the adsorption of PdCl₂ NPs is even and highly cover the sidewall without preference to the reactive group, similar to as with the activated carbon.¹³⁰ The reason for the high efficiency is probably due to the strong Pd-C interaction. Because the yield of Pd NPs is so high, direct decoration of Pd or post reduction of PdCl₂ can save precious metal and is commercially valuable.
Figure 83. AFM images of surface-grown SWNTs decorated by Pd, Pt and Au in H₂O and ethanol/H₂O for 1min. (A) Pd in H₂O. (B) Pd in ethanol/H₂O. (C) Pt in H₂O. (D) Pt in ethanol/H₂O. (E) Au in H₂O. (F) Au in ethanol/H₂O. All the scale bars of the AFM images are 500 nm.

5.3.3 Controllable Size Decoration

Pd NPs with controllable size can be obtained by varying the decoration time. For the bulk sample, as shown in Figure 77, NP size can be controlled by varying the decorating period from 1 hour to 1 day. For the surface sample, as in Figure 84, different size PdCl₂ NPs can decorate for 3 seconds (Figure 84A; ~2 nm), 1 minute (Figure 84B; ~3-6 nm), and 1 hour (Figure 84C; ~3-10 nm), respectively. After one day decoration, thickly dotted NPs on SWNTs can be seen in Figure 85 even by SEM, indicating very large NPs.
Figure 84. AFM images of surface-grown SWNTs decorated by different size of PdCl$_2$ NPs by controlling the decoration time. (A) 3 s (~2 nm). (B) 1 min (~3-6 nm). (C) 1 hr (~3-10 nm). The bottom images are corresponding zoom-in AFM images. The size is estimated by the height measurement subtracted by the tube diameter. The scale bars of all the AFM images on the top are 1 μm. The scale bars of all the AFM images at the bottom are 250 nm.

Figure 85. SEM image of PdCl$_2$ NPs on surface-grown SWNTs after 1 day decoration.
5.4 Applications of Palladium Decoration on Carbon Nanotubes

The Pd/CNTs can provide a variety of known applications of Palladium such as sensing, organic reaction catalysts, and hydrogen storage. For example, the catalytic properties of Pd can be enhanced when CNTs are employed as support materials. However, those applications are not the only ones. The versatile decoration method discussed here has many advantages such as high efficiency, controllability, electroless, no chemical modification, etc. Those benefits lead to two novel applications.

CNTs are ideal candidates as an electrode material in devices such as capacitors, batteries, solar cell, etc. However, the electrical conductivity is not high enough to replace the commercial materials such as amorphous carbon and ITO (indium tin oxide). Several strategies generally divided into two groups as direct linking and chemical functionalization have been developed to improve the conductivity, however, they both have their own disadvantages. The method should ideally not degrade the individual CNT properties while improving the bulk conductivity and must be suitable for pre and post deposition on large-scaled bulk CNTs and surface CNT devices. The direct cross-shell linking between individual CNTs requires irradiation with electrons, UV light, and electrical current, which all cause the structural changes, are not workable for surface devices and are not proper for pre deposition (Linking will agglomerate the CNTs to prevent well-dispersed suspension.). The chemical functionalization approaches include adsorption of molecules with functional groups, covalent bonding of functional groups, and metal NP decoration. The first one can block the individual tube conduction and raise the electrode-tube contact barrier on CNT device. The second one is tedious and damages the CNT structure via exposure to strong acid. The last one is a more suitable approach. So far, Au is the only metal which has shown a conductivity improvement on CNTs. However, the weak Au-SWNT interaction due to the small binding energy and the correlated low activation barrier for diffusion can decrease decoration efficiency and might limit the enhancement. Pd can
be firmly welded to CNTs due to the strong Pd-C bond and the Fermi level of Pd is close to CNTs so as to limit the contact barrier. As a result, Pd can theoretically give better improvements but this has never been shown. For surface devices, the improvement can be from both the doping of tubes by decoration and by the electrode-tube contact. However, separated contact and doping effect has never been shown on the metal NPs decorating CNT thin film device.

Pd/C is an important catalyst material, broadly used in inorganic and organic reactions. Pd/CNT has similar catalytic properties but has never been shown to catalyze nanostructure growth. It is interesting to show Pd/CNT catalyzed growth to further understanding of nanostructure synthesis.

5.4.1 Electronic Behavior Change and Conductivity Improvement

Au coating on CNTs only forms isolated particles on the nanotubes. Although Au decoration has been shown to improve the conductivity of CNT film, the Au NP size is not controllable, not uniform and the efficiency is low. Some NPs are even more than 1 μm, which can cause photon scattering and worsen the transparency. On the other hand, Pd clusters coating individual CNTs have shown the CNT electronic behavior change from semiconducting to metallic. In addition, Pd electrodes give much lower tube-electrode contact resistance. Pd NPs decorating CNTs might demonstrate similar effects as an evaporated Pd layer, which is not well sticky to the Si substrate. Using with the decoration method described in this study, Pd decoration may be able to change the electronic properties of CNT device and film.

5.4.1.1 Electronic Behavior Change by Pd Decoration

The electronic change of CNTs by Pd decoration was studied first on surface-grown SWNTs. Devices were fabricated by the shadow mask in order to avoid contamination from photoresist. (Two devices with and without Pd were from the same as-grown SWNT sample.) Relatively large gap FETs show distinct increase in both on and off current after Pd decoration,
as seen in Figure 86. The on/off current ratio changed from 7.4 to 1.3. The more metallic behavior and higher pass current were believed due to both the contact (Tube-electrode contact was improved by lowering the Schottky barrier.) and doping effect (Tubes were doped by the Pd NPs), but not separated by this experiment.

Figure 86. The gate-dependence of SWNT FET fabricated with and without Pd decoration. Device is made without Pd and after Pd decoration. The insert is the dimension of the SWNT FET fabricated by E-beam evaporation using a homemade shadow mask. The source-drain bias is 10 mV.

Next, the separation of contact and doping effect were studied on smaller gap devices using a TEM grid as the shadow mask. In each set of experiment, the SWNTs were from the same big chip. Three kinds of devices were made as shown in Figure 87. The first one is without Pd (intrinsic behavior), the second is a device fabricated after Pd decoration (overall effect including contact and doping), and the third is a device with Pd decoration after device fabrication.
(doping effect only). With zero gate bias, the average resistance between two adjacent electrodes was evaluated. As seen in Figure 88A-D and Table 3, for the low tube density sample, the overall resistance decreased by 33% after Pd decoration and the contribution from the contact (68% in total improvement) is weighted more than the doping effect (32% in total improvement) probably because the contact conductance dominates the total passing current (Tube network resistance weights more in the overall resistance.). Therefore, high density sample was employed because the tube network conductance dominates the total passing current in such case (Contact resistance weights more in the overall resistance.). As seen in Figure 88E-H and Table 3, for the high density tubes, the overall resistance decreased up to 2 fold after Pd decoration and the contribution from the doping (63%) is weighted more than the contact (37%) as expected. The device gap is 50 μm, still far longer than the tubes. If the device gap can be even smaller and comparable to the tube length, the doping effect proportion will be further enhanced as well as the overall conductivity.

![Figure 87. SWNT device fabrication steps to separate contact and doping effect of Pd decoration.](image)

(A) Device fabrication steps to separate contact and doping effect of Pd decoration. (I) is without Pd (Intrinsic behavior). (II) is device fabrication after Pd decoration (overall effect including contact and doping). (III) is Pd decoration after device fabrication (tube doping effect only). (B) SEM image of device after fabrication. The SWNTs between the electrodes are uniform to ensure the ensemble average. The inset is the SEM image of the SWNTs between the electrodes.
Figure 88. Resistance change of the surface-grown SWNT devices (low density and high density).
(A) SEM image of low density SWNT thin film. The scale bar is 5 μm. (B) Resistance histogram of SWNT (in A) device without Pd decoration. (no Pd effect) (C) Resistance histogram of SWNT (in A) device fabricated after Pd decoration. (overall Pd effect in both contact and doping) (D) Resistance histogram of SWNT (in A) device with Pd decoration after fabrication. (Pd effect in doping only) (E) SEM image of high density SWNT thin film. The scale bar is 5 μm. (F) Resistance histogram of SWNT (in E) device without Pd decoration. (no Pd effect) (G) Resistance histogram of SWNT (in E) device fabricated after Pd decoration. (overall Pd effect in both contact and doping) (H) Resistance histogram of SWNT (in E) device with Pd decoration after fabrication. (Pd effect in doping only)
Table 3. Decrease in overall, contact and tube network resistance of low and high density SWNT device by Pd decoration. Let the resistance of the device without Pd decoration is $R$, the resistance of the device with Pd decoration only on the tube network is $R_t$, and the resistance of the device with Pd decoration both on the contact and the tubes is $R_o$. 

\[ \begin{align*} 
\text{tube contact decrease}^a & \quad \text{contact/overall}^b & \quad \text{doping decrease}^c & \quad \text{doping/overall}^d & \quad \text{overall decrease}^e \\
\text{low} & \quad 22.7\% & \quad 68.1\% & \quad 10.7\% & \quad 31.9\% & \quad 33.4\% \\
\text{high} & \quad 19.1\% & \quad 37.3\% & \quad 32.1\% & \quad 62.7\% & \quad 51.2\% 
\end{align*} \]

5.4.1.2 Carbon Nanotube Buckypaper Conductivity Improvement by Pd Decoration

As with surface SWNTs, conductivity of CNT buckypaper can be improved by decorating with Pd NPs. Importantly, the method described in this study is suitable for both pre and post deposition. In pre-deposition, Pd NPs decorated first and then the buckypaper was formed. As seen in Table 4, the sheet resistance decreased by 2 fold for high quality FWNTs (FWNT1(a) in Table 4) and 10 for low quality FWNTs (FWNT2(b) in Table 4) by pre-deposition. However, the film thickness was increased compared to the film formed without Pd under the same process. (The thickness can be reduced by high compression.) This observation is probably due to the repulsion in bundling after the sidewall decoration, which was indirectly supported by the better stability of Pd-decorated FWNT ethanol suspension (The FWNT ethanol suspension without Pd decoration is easy to aggregate but becomes more stable with Pd.). Therefore, post-deposition was used to keep the film thickness unchanged. The decorating Pd has no effect in the film thickness because even if all the Pd was reduced (75 mg Na$_2$PdCl$_4$ salt), the thickness of this Pd film is estimated to be only $\sim$1.37 um (for 46 mm diameter). The percentage loading of Pd on CNTs was verified to be 5% to 25% by TGA, As seen in Table 4, the conductivities of Hipco (HIPCO(f) in Table 4), DWNTs (DWNT(g) in Table 4) and FWNTs (FWNT1(c), 1(d), 3(e) in Table 4) were improved by 2 to 4 fold.
Table 4. Sheet resistance decrease and conductivity improvement in Hipco (SWNTs), DWNTs and FWNTs by pre and post deposition of Pd. \(^{a,c,d}\)High quality and air-phase oxidation purified FWNT sample No.1. \(^{b}\)Low quality and H\(_2\)O\(_2\) purification purified FWNT No.2. \(^{e}\)High quality and air-phase oxidation purified FWNT No. 3. \(^{f}\)High quality and air-phase oxidation purified Hipco tubes. \(^{g}\)High quality and air-phase oxidation purified DWNT. \(^{h}\)CNTs suspended in 1% SDS. All the others are CNTs suspended in ethanol.

<table>
<thead>
<tr>
<th>CNT type</th>
<th>mass (mg)</th>
<th>sheet resistance ((\Omega/\square))</th>
<th>conductivity (S/cm)</th>
<th>thickness ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no Pd</td>
<td>Pd</td>
<td>R1</td>
<td>no Pd</td>
</tr>
<tr>
<td>FWNT 1(^a)</td>
<td>5.0</td>
<td>1.45</td>
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<td>81.86</td>
<td>36.00</td>
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Because the outer wall of CNTs dominates the electronic behaviors, any surface interaction which takes place is sensitively reflected in the electronic properties. Calculation also reveals a geometrical distortion of CNTs occurring in the Pd NPs supported on CNTs, which is caused by strong Pd-C interactions.\(^{114}\) The UV-vis-NIR absorption showed the absorption peak shift in the semiconducting region and the diminishing of the absorption peak in the metallic region, as seen in Figure 89. This shift was also observed in other conductivity improvement methods such as doping by chemical treatment.\(^{135}\) The doping effect is hypothesized to change the electronic structure and the surface plasmons leading to the above change. Additionally, Raman spectrum (D band) as shown in Figure 90 showed no more defects created by the Pd
decoration process, which can beat other enhancement methods which relay on introducing defects by exposure to the strong acid. Besides the doping effect, the Pd NPs can probably fill the interspaces in the buckypaper to improve tube-tube contact but no photon scattering will be caused because the small Pd NPs size is far less than the visible wavelength, which is considerably useful for transparent films. More importantly, the sheet resistance of the low quality bulk (FWNT 2(b) in Table 4) sample which normally is easily obtained in higher yield than high quality sample can be enhanced by one order of magnitude. The decoration process can save precious high quality CNTs. Metal color (silver) can be seen after 20 times post-deposition on FWNT buckypaper, as seen in Figure 91.

Figure 89. UV-vis-NIR absorption of FWNTs (A) and Hipco (B) with and without Pd decoration. The Absorption peak is shifted in the semiconducting region (in A and B) and is diminished in the metallic region (in B).
Figure 90. Raman Spectrum of FWNTs before and after Pd decoration. D band (no change by decoration) indicates no more defects created by the Pd decoration process.

Figure 91. FWNT buckypaper with and without post Pd decoration. (A) No Pd decoration. (B) One time post Pd decoration. (C) 20 times post Pd decoration. Silver metal color can be seen.
5.4.2 Nanostructure Synthesis Catalysts

Figure 92. Au NPs growth by Pd “seed”s and its higher efficiency compared to non-seeded growth. (A) AFM image of Pd decorating on the aligned SWNTs. The scale bar is 500 nm. (B) AFM image of Au NPs grown by the Pd seeds. The scale bar is 2 μm. (C) SEM image of Au NPs grown by the Pd seeds. The scale bar is 2 μm. (D) AFM image of the same SWNT without Pd under same Au growth process. The scale bar is 500 nm. Only few small Au NPs can been seen on the tubes without Pd. Aligned SWNT were used in order to avoid interfering effects from the catalysts around the tube after SWNT synthesis.

Seeded growth of Au NPs was made possible by the Pd NPs supported on SWNTs. As discussed above, the inert surface of CNTs makes it difficult for Au NP nucleation. However, the
Pd decoration efficiency is high and Au\(^{3+}\) can be theoretically reduced by Pd. Based on these two points, as seen in Figure 92B and C, Au NPs were grown by Pd NPs (on SWNTs) as the “seed”. This efficiency is much higher than without Pd seeds as shown in Figure 92D under the same solution growth condition. Moreover, bimetallic NPs (core-shell structure) can be obtained by this method for specific studies.

Additionally, CNFs can be catalyzed by the Pd NPs supported on the CNTs. PdCl\(_2\) NPs around 2 nm decorated on SWNTs (3 seconds decoration) were used as the catalysts, which were reduced by H\(_2\) at growth temperature before the CNF growth. As seen in Figure 93A-E, uniform CNFs (shown in Figure 93C) were synthesized starting from or wrapping around the SWNTs after 3 seconds growth (Figure 93A; low density) and 10 mins growth (Figure 93B; high density). Fishbone structure of CNFs was observed in Figure 93D and the diameter is 15-20 nm. The particle is 12 nm (shown in Figure 93D), indicating the sintering of the adjacent Pd NPs on the tube at high temperature but not aggregating to larger due to the tube immobility. In addition, the growth efficiency was higher than the Pd NPs (~2 nm in diameter as seen in Figure 94) performed without support, as shown in Figure 93E. The high growth efficiency is probably due to the strong Pd-C bond, which immobilizes the Pd NPs on SWNTs to limit the aggregation. By changing the growth condition or decorated metal type, SWNT or MWNT could be obtained.
Figure 93. CNFs were grown by the Pd NPs supported on SWNTs. (A) SEM image of CNFs grown after 3 seconds. The scale bar is 2 μm. The inset is higher resolution image, showing CNFs are grown from or wrapping on the SWNTs. The scale bar is 300 nm. (B) SEM image of CNFs grown after 10 minutes. The scale bar is 20 μm. The inset is higher resolution image, showing CNFs are grown from or wrapping on the SWNTs. The scale bar is 500 nm. (C) TEM image of CNFs after growth. The scale bar is 200 nm. (D) High resolution SEM image of CNFs after growth. The scale bar is 20 nm. The particles are around 12 nm. The inset shows the fishbone structure and diameter (18 nm) of the CNF. The scale bar is 10 nm. (E) Raman spectrum confirms the formation of CNFs. (F) SEM image of CNF grown from unsupported Pd NPs. The scale bar is 10 μm. The inset is the AFM image of preformed Pd NPs. (The size is similar as the supported Pd NPs.) The scale bar is 500 nm.
Figure 94. CNFs grown from Pd NPs supported on CNTs. (A) SEM image of original SWNTs. (B) SEM image of the substrate without Pd decoration under the same growth condition as with Pd. No CNFs were observed without Pd decoration. (C) SEM image of “grass” CNFs grown for 1 hour. (D) Pd NP size distribution formed on substrate without SWNT support for the comparison.

5.5 Summary

A versatile electroless method has been developed for controllable and highly efficient decoration of CNTs by Pd NPs. Chemical modification of CNTs is not a prerequisite in our method. The decoration is selective on CNTs. In addition, the Pd decoration efficiency is higher than Pt and Au. Controllable size NPs can be formed by varying decoration time. Moreover, high density, fine size and uniform PdCl₂ NPs can be formed without ethanol reduction. These NPs can be further reduced to Pd easily.
The decoration mechanism is that Pd NPs are reduced by ethanol not by CNTs, which only serve as nucleation sites rather than reducing agent. PdCl₂ NPs are nucleated and grown on CNTs as activated carbon.

Electronic conductivity can be improved by Pd NPs decorating on the SWNT devices. Doping and contact effects are attributed to this improvement and the contribution weights of each part are varied by the tube density. Conductivity was also improved on CNT buckypaper by pre and post deposition more than 2 fold.

Au NPs and CNFs can be grown with higher efficiency using the Pd as “seed” supported on CNTs.

In summary, a Pd decoration method is proposed with mechanism demonstrated. The properties of the CNTs can be controlled by post treatment (metal decoration). Two promising applications of Pd/CNT hybrid are shown for the first time, with the potential for more. These researches will further the study of CNT/Metal composites.
Chapter 6: Conclusions

This dissertation is mainly focused on the “control” of SWNTs and their devices. After an introduction in chapter 1, it is generally divided into three parts. The first part (chapters 2 and 3) describes the control of the SWNTs by direct growth, the second part (chapter 4) describes the control of their device performance, and the third part (chapter 5) describes the control after growth by metal decoration.

The four major challenges (chirality control, diameter control, location and orientation control, and mechanism) in the SWNT surface production are discussed in chapter 1. In this dissertation, the second and third problems are addressed to a certain degree. The first one is partly achieved. Importantly, our recent results show great potential to realize all the first three together. The last one is and will be gradually improved during the studies of the first three. We can almost see real industrial production of SWNT ICs on the horizon.

Chapter 2 mainly shows the control of SWNT diameters by direct CVD growth. A uniformly distributed small diameter SWNT thin film was produced from Co diblock copolymer micelles. In addition, laser-irradiated CVD provided high quality and highly uniform SWNTs. Moreover, flow pattern was found to be a factor in affecting the SWNT growth for the first time. However, further investigations are needed to elucidate the mechanism.

In chapter 3, we focus on the location and orientation control of SWNT synthesis. Horizontally aligned SWNTs that were millimeters and centimeters long were grown by the high and low gas flow. Such ultra long tubes were used for nanoscale antenna. 3D SWNT structure inside trenches was shown and the proposed alignment is due to the topography effect. In addition, horizontally lattice-aligned SWNTs were formed on ST-cut quartz by various metals. The
hypothesis that the alignment is promoted by the carbon atoms on the outside of the metal nanoparticles is suggested. Mg and Al are first shown to produce SWNTs. A simple pattern method is introduced. Importantly, the selective growth of pure semiconducting SWNT arrays on quartz leads to orientation plus property-controlled SWNTs for numerous applications. The top gate FETs fabricated on such SWNTs support the Raman analysis of the tube type. Moreover, such devices are readily used for real applications.

Chapter 4 describes the variation in device performance by changing the device configuration using experimental data and simulation work. In addition, the metallic SWNT thin film has been demonstrated for the first time even though the mechanism is not understood.

Chapter 5 discusses hybridizing carbon nanotubes including single-walled, double-walled, and few-walled nanotubes with palladium by decorating the nanotube with Pd nanoparticles using a versatile electroless method. The method is easy, cost-effective and easily scaled up. The Pd nanoparticles are controllable in size, uniformity, and oxidation state. A decoration mechanism is demonstrated where carbon nanotubes act as the nucleation sites for Pd nanoparticles which are reduced by ethanol as a reducing agent instead of nanotubes. Pd$^{II}$ (PdCl$_2$) can be adsorbed on carbon nanotubes uniformly, leading to uniform size and high coverage Pd nanoparticles after further reduction. Two attractive applications are illustrated. First, the electronic conductivity of carbon nanotube films was improved by decorating with Pd. Carbon nanotube buckypaper Pd deposition decreased sheet resistance up to 10-fold and increased conductivity up to 5-fold, mainly from the doping effect. A conductivity improvement up to two fold after decorating surface-grown single-walled carbon nanotube device is attributed to both a decrease in electrode-contact resistance and an improvement in the tube network conductance. Second, gold nanoparticles and carbon nanofibers were catalyzed by the Pd nanoparticle “seed”s supported on carbon nanotubes with higher efficiency than without such “seed”s.
These findings are a limited and small achievement in the whole picture of carbon nanotube research history. Hopefully, they can be useful for the investigation and commercialization of carbon nanotubes in the future, pushing forward the Nanotechnology as well as the Science.
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[http://www.hbcpnetbase.com](http://www.hbcpnetbase.com)


Biography

Place and Date of Birth

Dalian, Liaoning Province, People’s Republic of China
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Education

2004-2008 Ph.D. – Chemistry/Nanoscience Program
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2003-2004 M.S. – Computational Engineering
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1999-2003 B.Eng – Electrical Engineering
Tianjin University, Tianjin, China

Publications

1. “Large Area Selective Growth of Aligned Semiconducting Single-Walled Carbon Nanotubes”, Ding, L.; Tselev, A.; Wang, JY.; Yuan, DN.; Chu, HB.; McNicholas, T. P.; Li, Y.; Liu, J.; (Submitted to Nature)


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Yuan, DN.; Feng, YY.; Chu, HB.; Zhang, HB.; Qian, C.; Hou, Y.; McNicholas, T. P.; Woodson, M. E.; Ding, L.; Liu, J.; (Submitted to J Phys Chem C)


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8. “Few-Walled Carbon Nanotube Conducting Film”, Qian, C.; Yuan, DN.; Hou, Y.; Qi, H.; Liu, J.; (Preparing)


Conference Activities


## Honors

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