RICE UNIVERSITY

Wafer-Scale Films and Devices of Spontaneously Aligned Carbon Nanotubes

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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April 2016
ABSTRACT

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One of the grand challenges in nanoscience and nanotechnology is how to create macroscopic devices by assembling nano-objects while preserving their extraordinary properties. For example, individual single-wall carbon nanotubes (SWCNTs) possess unique one-dimensional properties that have stimulated much interest in diverse disciplines, and worldwide efforts are in progress to produce large-scale architectures of aligned SWCNTs. Various methods have been proposed and/or demonstrated, including both direct-growth and post-growth schemes, but the current state of this field is that there is still no method available for producing large-area single-domain films of highly aligned, densely packed and chirality-enriched SWCNTs.

In this thesis, we developed a new process of vacuum filtration to produce a wafer-scale (i.e., inch-size) film of aligned SWCNTs. This method works for SWCNTs synthesized by various methods and can be scaled in all three dimensions (i.e., the lateral size and thickness). We fully characterized the produced large-area films through different microscopy, spectroscopy, and transport methods, demonstrating
perfect global alignment with extraordinary photonic and optoelectronic properties. We created ideal terahertz/infrared polarizers using this approach.

The strikingly high degree of alignment of our films with a nematic order parameter of ~ 1 and a thickness of ~ 100 nm distinguishes our method from both existing two-dimensional and three-dimensional post-growth assembly techniques. We investigated the underlying mechanisms based on a proposed model of 2D confinement induced phase transitions. We identified the factors that affect the degree of alignment, including the filtration speed, the SWCNT concentration, the surfactant concentration, the hydrophilicity of the filter membrane surface, the SWCNT length, and the SWCNT diameter.

Furthermore, combined with well-developed solution-based chirality separation techniques, we produced globally aligned and chirality-enriched films under optimized conditions. These SWCNT films are promising for optoelectronic and electronic device applications. As examples, we demonstrated polarized luminescent devices, polarization-sensitive photodetectors, and thin-film transistors, using aligned semiconducting SWCNT films.

Wafer-scale aligned SWCNT films produced by our vacuum filtration method will open a range of new opportunities not only for fundamental research of physics, chemistry, and materials science but also for applications in electronics, optoelectronics, sensing, imaging, and medicine.
Acknowledgments

After graduating from Shanghai Jiao Tong University as an electrical engineering major with concentration on wireless communications, I decided to take an entirely new challenge in my graduate study at Rice University: photonics, optoelectronics, and material science. I would like to deeply thank all those people who have taught, helped, and guided me through my five-year journey, exploring this fascinating and exciting research area.

Firstly, my greatest gratitude goes to my supervisor, Prof. Junichiro Kono, for affording me the opportunities to learn how to become a scientist. He taught me a lot about every aspect of scientific research: how to define a problem, how to design/debug the experiment, how to analyze the data, how to write a scientific paper, how to give impressive presentations, etc. He showed me how to become a responsible and motivated scholar. His persistent patience, encouragement, and continuing support helped me overcome a number of difficulties. Particularly, I would like to thank Prof. Kono for his generous help during the hard transition period when my previous advisor left.

Secondly, I would like to thank Prof. Pulickel Ajayan and Prof. Jacob Robinson for serving as members on my Ph.D. committee and providing insightful comments and suggestions on my research. I am also grateful to many members of Prof. Ajayan’s group for very fruitful and stimulating collaborations.
I am truly lucky to be able to work in this great group with the fantastic lab mates who have provided me with an ideal place to study and do research. I am grateful that they are always eager to help when I meet difficulties. In particular, I would like to thank Dr. Xiaowei He from the bottom of my heart. Working with Xiaowei will be an unforgettable experience in my whole life.

Finally, I would like to thank my parents Mr. Shan Gao and Mrs. Yuli Jiang in China for their everlasting support and love. It must be hard for them to be apart from their only son for such a long time. They have sacrificed so much for me throughout my life. I also would like to thank my wife, Zhengwei Wu, for her persistent love, devotion, and support for my career. I dedicate this thesis to my beloved family.
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Chapter 1

Introduction

1.1. Scope of the thesis

One of the grand challenges in nanoscience and nanotechnology is how to create macroscopic devices by assembling nano-objects while preserving their extraordinary properties. For example, individual single-wall carbon nanotubes (SWCNTs) possess unique one-dimensional properties that have stimulated much interest in diverse disciplines, and worldwide efforts are in progress to produce large-scale architectures of aligned SWCNTs. However, the current state of this field is that there is still no method available for producing large-area single-domain films of highly aligned, densely packed, and chirality-enriched SWCNTs, despite many years of efforts.

The ultimate goal of this Ph.D. dissertational work is to achieve such SWCNT films. As detailed in this thesis, we have made significant progress toward this goal.
Chapter 2 reviews the crystal and electronic band structure of SWCNTs. It also highlights some of the recent reports on electronic and optoelectronic applications of individual SWCNTs and macroscopic SWCNT ensembles. Furthermore, the challenges in preparing macroscopic SWCNT ensembles using state-of-the-art techniques are summarized. In Chapter 3, we describe the method we developed for fabricating uniform, wafer-scale SWCNT films of an arbitrarily and precisely controllable thickness (from a few nm to ~100 nm) with a high degree of alignment (nematic order parameter $S \sim 1$) and packing ($\sim 10^6$ tubes in a cross-sectional area of 1 $\mu m^2$) in a well-controlled, simple, and reproducible manner, regardless of the synthesis method, metallicity, or chirality of the SWCNTs used. Different characterization methods were used to characterize the films, including microscopy, spectroscopy, and electrical techniques. In addition, we demonstrated the universal applicability and scalability of this method. In Chapter 4, we discuss our investigations on the alignment mechanism. We found several important factors that affect the degree of alignment. Finally, as described in Chapter 5, we combined solution-based chirality enrichment techniques with vacuum filtration to fabricate globally aligned and chirality-enriched SWCNT ensembles for electronic and optoelectronic applications, including polarized luminescent devices, a polarization sensitive photodetector, and field effect transistors with semiconducting SWCNT ensembles.
Chapter 2

Macroscopically Aligned Carbon Nanotube Ensembles for Electronics and Optoelectronics

Carbon is a special but fundamental element in the periodic table, which provides the basis for life and is also promising for replacing silicon in modern electronic and photonic technology [1]. Each carbon atom has six electrons, occupying the 1s, 2s, and 2p atomic orbitals. Two core electrons (1s²) are strongly bound, while four weakly bound electrons (2s²2p²) can form covalent bonds in carbon materials using \( sp^n \) \( (n = 1, 2, 3) \) hybrid orbitals. Other group IV elements like Si and Ge can only exhibit \( sp^3 \) hybridization [1, 2]. The versatile chemical nature of carbon materials results from its different hybridization states, which also determines the properties of the variety of carbon allotropes and organic compounds [3]. Two natural carbon allotropes, diamond and graphite with \( sp^3 \) and \( sp^2 \) hybridization, respectively, show distinct electronic, mechanical, thermal, and
optical properties; they were the only known carbon allotropes for a long time. until
the discovery of C_{60} in 1985 [4], which gave birth to the research field of
nanotechnology. After the advent of C_{60} (a zero-dimensional system), a growing
family of carbon nanomaterials emerged, including carbon nanotubes (CNTs) [5]
one-dimensional) and 2-dimensional graphene [6] (two-dimensional). Still other
members, based on numerous combinations and modifications of carbon atom
hybridization, are yet to be discovered (Figure 2.1) [3].

![Figure 2.1 Synthetic carbon nanomaterials, including fullerenes, carbon nanotubes, graphene, and undiscovered carbon allotropes. Adapted from Ref. [3].](image)

Despite the unique properties of each member of the carbon nanomaterial
family, they have close connections of atomic structure between each other. In a
sense, graphene can be viewed as the most fundamental of these materials because
fullerenes, carbon nanotubes, and graphite can all be derived from graphene (see
Figure 2.2) [7]. In particular, a SWCNT is a rolled-up version of graphene, which possesses unique quasi-one-dimensional electronic, thermal, and optical properties [8-12].

2.1. Crystal and band structure

The crystal and band structure of SWCNTs is highly related to that of graphene. However, the strong confinement of electronic states along the tube
circumference makes a SWCNT look a completely different material. Furthermore, the band structure of SWCNT sensitively depends on the manner how the graphene sheet is rolled up, showing either metallic or semiconducting characteristics.

2.1.1. Graphene crystal and band structure

Graphene consists of a hexagonal lattice of $sp^2$-bonded carbon atoms, as shown in Figure 2.3 [10]. The carbon-carbon bond length $a_{C-C}$ is $\sim 1.42$ Å. The primitive unit cell contains two carbon atoms, A and B, as shown in Figure 2.3(a), which contribute two $\pi$ electrons that play fundamental roles in electrical and optical phenomena [10, 13]. The primitive unit vectors are defined as

$$a_1 = \left(\frac{\sqrt{3}a}{2}, \frac{a}{2}\right)$$

(2.1)

$$a_2 = \left(\frac{\sqrt{3}a}{2}, -\frac{a}{2}\right)$$

(2.2)

where $a = |a_1| = |a_2| = \sqrt{3}a_{C-C}$. Each carbon atom A (B) is bonded to three nearest carbon atoms B (A). The translation vectors $\rho_1, \rho_2, \rho_3$ can be described as follows:

$$\rho_1 = (0, -a)$$

(2.3)

$$\rho_2 = \left(\frac{a}{2}, \frac{\sqrt{3}a}{2}\right)$$

(2.4)

$$\rho_3 = \left(\frac{a}{2}, -\frac{\sqrt{3}a}{2}\right)$$

(2.5)
Figure 2.3 (a) Real space and (b) reciprocal space representation of the hexagonal lattice of 2D graphene. The $\mathbf{a}_{1,2}$ and $\mathbf{b}_{1,2}$ are the primitive unit vectors in real and reciprocal space, respectively. The dashed line parallelogram defines the unit cell of graphene with two different carbon atoms A and B. High-symmetry points, $\Gamma$, $M$ and $K$ are labeled in the 1st Brillouin zone. Adapted from Ref. [10].

The reciprocal lattice of graphene is a hexagonal lattice as well, where the primitive unit vectors are

$$\mathbf{b}_1 = \left( \frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a} \right)$$  \hspace{1cm} (2.6)$$

$$\mathbf{b}_2 = \left( \frac{2\pi}{\sqrt{3}a}, \frac{-2\pi}{a} \right)$$  \hspace{1cm} (2.7)$$

with a norm of $4\pi/\sqrt{3}a$. In the Brillouin zone, there are three important high-symmetry points: $\Gamma$-point (the center of the Brillouin zone), $M$-point, and $K$-point.
The position vectors connecting the \( \Gamma \) and \( M \) points and the \( \Gamma \) and \( K \) points are given, respectively, by

\[
\Gamma M = \left( \frac{2\pi}{\sqrt{3}a}, 0 \right)
\]

(2.8)

\[
\Gamma K = \left( \frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{3a} \right)
\]

(2.9)

The band structure of graphene can be obtained by using the tight-binding approximation \([10, 14]\). In order to obtain the band structure, one solves the Schrödinger equation

\[
H \Psi = E \Psi
\]

(2.10)

where \( H \) is the Hamiltonian, \( \Psi \) is the wave function and \( E \) is the electron energy. In a tight-binding approximation, the Bloch wave function is expressed as a linear combination of atomic orbitals. In a primitive cell of graphene, there are two types of carbon atoms, \( A \) and \( B \), whose respective Bloch functions are given by \([10]\)

\[
u_{A(B)} = \frac{1}{\sqrt{N}} \sum_{A(B)} e^{ik \cdot \mathbf{r}_{A(B)}} X(\mathbf{r} - \mathbf{r}_{A(B)})
\]

(2.11)

where \( X \) is the \( 2p_z \) orbital wave function of an isolated carbon atom. Then the total wave function can be expressed as a linear combination of \( u_A \) and \( u_B \):

\[
\Psi = C_A u_A + C_B u_B
\]

(2.12)
By inserting Eq. (2.12) into Eq. (2.10), we obtain coupled equations for $C_A$ and $C_B$ written in matrix form

$$
\begin{pmatrix}
H_{AA} & H_{AB} \\
H_{BA} & H_{BB}
\end{pmatrix}
\begin{pmatrix}
C_A \\
C_B
\end{pmatrix}
= E
\begin{pmatrix}
C_A \\
C_B
\end{pmatrix}
$$

(2.13)

where $H_{ij} = \langle u_i | H | u_j \rangle$. By symmetry of the graphene crystal structure, we can see that $H_{AA} = H_{BB}$ and $H_{AB} = H_{BA}^*$. Equation (2.13) has a non-trivial solution only when

$$
\begin{vmatrix}
H_{AA} - E & H_{AB} \\
H_{AB}^* & H_{AA}
\end{vmatrix} = 0
$$

(2.14)

which leads to

$$
E = H_{AA} \mp |H_{AB}|
$$

(2.15)

As defined above, $H_{AA}$ and $H_{AB}$ can be expressed as

$$
H_{AA} = \frac{1}{N} \sum_{A} \sum_{A'} e^{ik(r_A - r_{A'})} \int X^*(r - r_A) H X(r - r_{A'}) dr
$$

(2.16)

$$
H_{AB} = \frac{1}{N} \sum_{A} \sum_{B} e^{ik(r_A - r_{B})} \int X^*(r - r_A) H X(r - r_{B}) dr
$$

(2.17)

Let us use the simplest tight-binding approximation, in which only the effects from the nearest-neighbor atoms are considered. As a result, the Eqs. (2.16) and (2.17) can be further approximated as

$$
H_{AA} = \int X^*(r - r_A) H X(r - r_A) dr = E_0
$$

(2.18)
\[
H_{AB} = (e^{i\mathbf{\rho}} + e^{i(\mathbf{\rho} \cdot \mathbf{\rho})} + e^{i(\mathbf{\rho} \cdot \mathbf{\rho})}) \int X^*(r) H X (r - \mathbf{\rho}) dr
\]

\[
= \gamma_0 (e^{-i,\mathbf{\rho} \cdot \mathbf{\rho}} + 2e^{i,\mathbf{\rho} \cdot \mathbf{\rho}} \cos(\frac{k,\mathbf{\rho}}{2}))
\]  

(2.19)

where \(\gamma_0\) is referred to as the transfer integral. Finally, by substituting Eqs. (2.18) and (2.19) into Eq. (2.15), we get the following energy dispersions:

\[
E = E_0 \pm \gamma_0 \sqrt{1 + 4 \cos(\frac{\sqrt{3}k,\mathbf{\rho}}{2}) \cos(\frac{k,\mathbf{\rho}}{2}) + 4 \cos^2(\frac{k,\mathbf{\rho}}{2})}
\]  

(2.20)

The negative sign in Eq. (2.20) represents the valence band of graphene while the positive sign represents the conduction band. Equation (2.20) is shown in Figure 2.4. At the six corners of the first Brillouin zone (i.e., the K points), the conduction band and valence band meet together to close the band gap. Furthermore, near the K points, both the conduction and valence bands exhibit a linear energy relationship, possessing the so-called “Dirac cone”. The slope of the linear dispersion is calculated as

\[
\left. \frac{dE}{dk} \right|_k = \frac{\sqrt{3}a\gamma_0}{2} = \hbar v_F
\]  

(2.21)

where \(v_F (~ 8 \times 10^5 \text{ m/s})\) is the Fermi velocity.
2.1.2. SWCNT crystal and band structure

As mentioned before, a SWCNT can be viewed as a hollow tube made by rolling up a graphene sheet. The way in which the sheet is rolled up can be uniquely specified by defining the chiral vector $C = na_1 + ma_2$, where $n$ and $m$ are positive integers and $n \geq m$; see Figure 2.5. The SWCNT is formed by wrapping the graphene sheet in such a way that the two points connected by $C$ meet. As a result, the SWCNT diameter $d_t$ and the chiral angle $\theta$, which is the angle between the chiral vector and the primitive vector $a_1$, can be obtained as

$$d_t = a\sqrt{n^2 + nm + m^2}$$ (2.22)

$$\theta = \cos^{-1}\left(\frac{2n + m}{2\sqrt{n^2 + nm + m^2}}\right)$$ (2.23)
The chiral vector of a (7,1) SWCNT, defined on the graphene sheet. \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) are the unit vectors of the graphene lattice. Adapted from [10].

The chiral indices \((n,m)\) fully define the crystal structure of the SWCNT and determine many of the properties of the SWCNT. High-symmetry SWCNTs with \((n,n)\) and \((n,0)\) are respectively called armchair nanotubes and zigzag nanotubes. The band structure of a SWCNT can be derived from the band structure of graphene by imposing proper boundary conditions along the nanotube circumference. Considering an infinitely long nanotube, there are two wave vectors associated with it. One is along the tube axis, \( k_// \), and the other is along the circumference of the tube, \( k_L \). \( k_// \) is continuous since the tube is infinitely long, while \( k_L \) is quantized due to the finiteness of the circumference through the boundary condition

\[
k_\perp \cdot C = \pi d \, k_\perp = 2\pi j
\] (2.24)
where \( j \) is an integer. The boundary condition leads to the quantization of \( k_\perp \) and thus, the band structure of the SWCNT can be obtained by “slicing” the graphene energy dispersions in Figure 2.4(b). Different slicing yields different band structure (Figure 2.6). When \( k_\perp \) passes through the K point in the 1st Brillouin zone of graphene, the SWCNT is metallic; otherwise, the nanotube is semiconducting.

![Diagram of 1D band structure of a SWCNT](image)

Figure 2.6 1D band structure of a SWCNT by slicing the 2D band structure of graphene. (a) The 1st Brillouin zone of graphene. The red and cyan lines represent the allowed \( k_\perp \) states in armchair and zigzag carbon nanotubes. In the case of zigzag tubes, different index combinations result in either (b) a semiconducting SWCNT or (c) a metallic SWCNT. However, an armchair tube is always metallic.

For an armchair nanotube with chirality indices \((n, n)\), the allowed \( k_\perp \) states are
where $j$ and $n$ are both integers. Thus, there is always an allowed subband that passes through the $KM$ when $m = n$, and so armchair nanotubes are always metallic, as shown in Figure 2.6 (c). However, a zigzag nanotube with chirality $(n, 0)$ can be either metallic or semiconducting. Since the circumference of the zigzag tube is $na$, the boundary condition, Equation (2.24) becomes

$$k_\perp = \frac{2\pi j}{na}$$

(2.26)

$IK$ is a vector with a magnitude of $4\pi/\sqrt{3}a$, lying in the same direction as $k_\perp$. So, Equation (2.26) becomes

$$k_\perp = \frac{2\pi j}{na} = \frac{3j}{2n}K$$

(2.27)

When $n$ is an integer multiple of 3 (i.e. $n = 3p$, where $p$ is an integer), there is always a $k_\perp$ cutting through the $K$ point, which makes the SWCNT metallic. However, when $n$ is not an integer multiple of 3, there are two possibilities: $n = 3p + 1$ and $n = 3p - 1$. Substituting these equations into Eq. (2.27), we can find the $k_\perp$ that is closest to the $K$ point to be [10]

$$k_\perp = \frac{3K(2q+1)}{2(3q+1)} = K + K \frac{1}{6q+2}$$

(2.28)

$$k_\perp = \frac{3K(2q-1)}{2(3q-1)} = K-K \frac{1}{6q-2}$$

(2.29)
respectively. In both cases, the missed wave vector around the $K$ points is

$$\Delta k = \frac{K}{2} \frac{1}{3q \pm 1} = \frac{2\pi}{3na} = \frac{2\pi}{3\pi d_t} = \frac{2}{3d_t}$$

(2.30)

As a result, the mismatch between allowed $k_\perp$ and the $K$ point is inversely proportional to the diameter, and the corresponding band gap can be calculated to be

$$E_g = 2\hbar v_F \left( \frac{2}{3d_t} \right) \sim 0.7\text{eV} / d_t (\text{nm})$$

(2.31)

The zigzag results shown above can be extended to an arbitrary SWCNT with indices $(n,m)$ [15, 16], and the character of the band structure depends on the value $\nu = (n - m) \mod 3$:

1. If $\nu = (n - m) \mod 3 = 0$, the SWCNT is metallic.

2. If $\nu = (n - m) \mod 3 = 1$ or 2, the SWCNT is semiconducting with a band gap $0.7\text{eV}/d_t (\text{nm})$.

However, due to the nanotube curvature effect [1], only arm-chair tubes are truly metallic. For other tubes with $\nu = (n - m) \mod 3$, there is a small band gap scaling with $1/d_t^2$. 
2.2. Electronic and optoelectronic properties and applications

The rich variety of band structures discussed in Section 2.1 makes SWCNT attract ever-lasting interest from many disciplines including chemistry, material science, physics and nanotechnology. The metallic and semiconducting nature of different chirality SWCNTs possesses unusual electronic and optoelectronic properties valuable for a wide range applications [8, 17].

For electronic properties, the first transport measurements of an individual metallic SWCNT (m-SWCNT) and semiconducting SWCNT (s-SWCNT) were reported in the late 1990s [18-21]. The typical $I_{DS} - V_{GS}$ characteristics of field effect transistors (FETs) built from different SWCNTs are summarized in Figure 2.7. The gate voltage shifts the Fermi level of the SWCNTs to modulate the channel conductivity between drain and source [Figure 2.7(a)]. For a transistor made from an individual s-SWCNT, the drain-source current can be suppressed dramatically down to nearly zero [Figure 2.7(b)], while for a transistor made from an individual m-SWCNT, the current is maintained as a constant value since there is no band gap [Figure 2.7(c)]. Interestingly, for a transistor made from a narrow band gap SWCNT, the current cannot reach to zero [Figure 2.7(d)], unlike the transistors made from s-SWCNTs.
Figure 2.7 (a) Schematic diagram of a typical field-effect transistor built from individual carbon nanotube [22]. The typical $I_{DS} - V_{GS}$ characteristic of transistors made from an individual (b) s-SWCNT, (c) m-SWCNT, and (d) narrow band s-SWCNT. Adapted from [10].

1D nature of SWCNTs limits the direction of carrier scattering to either forward or backward while in a higher dimension material system, scattering directions can be arbitrary. Besides, m-SWCNTs have a limited momentum space, resulting in a suppression of back scattering and a very long mean free path, which is ideal for quantum wire interconnections [20]. Furthermore, field effect transistors built from s-SWCNTs have a strong electric field effect, and show an extremely high room temperature mobility $> 10^5$ cm$^2$/Vs [23, 24].
The density of states (DOS) of SWCNTs shows divergent van Hove singularities \[25\], which produces strong optical absorption and emission from the excitation and recombination of electron-hole pairs (see Figure 2.8) \[26\]. Excitons can be excited either optically or electrically and their radiative recombination results in photoluminescence (PL) or electroluminescence (EL) respectively. In addition, the optical absorption of SWCNTs can be electrically modulated. As a result, SWCNTs are promising for future optoelectronic device applications such as photodetectors \[27, 28\], light-emitting diodes (LEDs) \[29\], solar cells \[30-32\] and electro-optic modulators \[33\], as shown in Figure 2.9.
Figure 2.9 Representative optoelectronic device applications using SWCNTs. (a) A photodiode made from an individual s-SWCNT [27]. (b) A terahertz detector made from a SWCNT film [28]. (c) A light-emitting diode made from an individual s-SWCNT [29]. (d) A solar cell made from carbon nanotube/P3HT [31]. (e) A solar cell made from carbon nanotube/C60 [30, 32]. (f) An electrical reconfigurable optical medium made from a s-SWCNT film [33].

Although individual SWCNTs provide an ideal platform for investigating fundamental properties of SWCNTs and demonstrating proof-of-concept device applications, individual SWCNT devices are still problematic from a practical application point of view because of complicated fabrication process, low efficiency...
and incapability of scaling up [8, 22]. Individual SWCNT FETs are considered to be impractical due to the difficulty in positioning CNTs precisely, which applies to individual SWCNT optoelectronic devices as well. In addition, especially for optoelectronic devices, the light-matter interaction of an individual SWCNT is too weak to be efficiently harvested, prohibiting practical applications. Taking photodetection for example, the generated photo-current from an individual SWCNT photodetector is \( \sim 100 \) pA with incident light power density of \( \sim 1 \) kW/cm\(^2\) [27].

In order to facilitate practical applications, macroscopic assembly of individual SWCNTs is one promising route, in forms of random networks or aligned arrays as also shown in Figure 2.9. An ensemble helps to avoid many challenges in the individual CNT devices: (1) it minimizes device variations; (2) it provides a large active area; (3) it does not require precise individual tube positioning. There is a variety of ways to prepare an ensemble of individual SWCNTs such as the chemical vapor deposition (CVD) method [34, 35] and the solution deposition method [36, 37]. Furthermore, an ensemble can be compatible with large-area, low-cost device fabrication techniques such as transfer [38] and ink-jet printing [39]. This ensemble is more attractive than other materials due to extraordinary electrical, optical and mechanical properties of individual SWCNTs. For example, it can exhibit either a semiconducting or metallic material behavior for different electronic and optoelectronic devices [37, 40-43]. SWCNTs are thermally and chemically stable [44, 45], making them compatible with high-\( \kappa \) material depositions [46-48]. A large ratio of the surface area to the volume of SWCNTs enables an efficient charge transfer doping from surrounding chemicals [49-51]. Excellent mechanical strength of
SWCNTs is ideal for large area flexible electronic/optoelectronic applications [42, 52, 53]. Large active areas possess the potential for an efficient broadband detector [54-57] and solar cells [58-60]. Furthermore, a highly conductive m-SWCNT thin film of a small optical absorption cross-section with strong mechanical properties can serve as a stretchable transparent electrode, which is important for certain security applications and backlit displays [40, 61].

To best preserve extraordinary properties of individual SWCNTs, macroscopic ensembles with a high level of structure perfection of a single domain is highly preferred. Taking SWCNT based FETs for example, the composition and the morphology of the conducting channel, which is constructed from SWCNT ensembles, will strongly affect the device performance. As shown in Figure 2.10, the degree of SWCNT alignment and the purification of s-SWCNTs affect two important FET parameters: the carrier mobility and the on-off ratio [62]. With a perfect aligned s-SWCNT ensemble, the mobility and the on-off ratio of a large scale FET can catch up with the performance of an individual SWCNT FET. However, when the ensemble is a random network, the mobility drops due to enhanced scattering from intertube junctions [22]. Furthermore, metallic tubes dramatically degrade the device performance with a worse on-off ratio because of the metallic percolation path. For example, 1% m-SWCNTs can decrease the on/off ratio by three orders in a short-channel FET made by an aligned SWCNT film [63]. Therefore, it is crucial to separate nanotubes by electronic types and assemble nanotubes in an ordered manner to extend the excellent properties of individual SWCNTs to SWCNT macroscopic ensembles.
Figure 2.10 Mobility and on-off ratio of FETs made from a SWCNTs ensemble with different morphology and composition. From top to bottom: an individual s-SWCNT, an aligned s-SWCNT ensembles, a random network of s-SWCNTs, a random network of SWCNTs with mixture electronic types. Adapted from [62].

2.3. Challenges in sample fabrications

However to date, to have a macroscopic single-domain, highly-aligned, densely-packed, and chirality-enriched SWCNT film is still challenging. So far, many assembling techniques have been developed, which can be classified as two categories: (1) in-situ direct-growth assembly methods and (2) ex-situ post-growth
assembly methods [64]. But both of them have some inherent limitations as stated below.

2.3.1. Direct-growth assembly methods

Direct-growth assembly methods mainly consist of the CVD growth method for either vertical alignment [34, 65] or horizontal alignment [66] to growth substrates. When the site density of the growth catalyst is high enough, due to the crowding effect SWCNTs can be vertically grown with alignment height of ~ mm, as shown in Figure 2.11(a). To in-situ organize SWCNTs into horizontally aligned arrays, electric field directed CVD growth [67, 68], gas flow directed CVD growth [69-71] and epitaxial CVD growth [66, 72, 73] can be utilized. Electric fields can orient SWCNTs due to the large and highly anisotropic polarizability of SWCNTs [Figure 2.11(b)]; a feeding gas flow can produce a flow field that can carry SWCNTs to overcome the gravity to grow along the flow direction [Figure 2.11(c)]; the oriented van der Waals force along the substrate surface can produce horizontally aligned SWCNTs [Figure 2.11(d)].

However, there is a common issue for direct-growth methods: there are few ways to control the chirality during the growth nowadays, which means that obtained aligned arrays have mixed electronic types and it is not desirable in most applications as mentioned before. Furthermore, the packing density of aligned arrays is relatively low. Although the density has been improved up to ~ 50 SWCNTs/µm [73], it is still quite dilute for certain practical applications such as solar cells and photodetectors.
2.3.2. Post-growth assembly methods

Post-growth assembly method mainly consists of solution-based methods for SWCNT alignment [74]. SWCNTs can be synthesized by the arc-discharge method, the high-pressure carbon monoxide (HiPco) method, the CoMoCAT method, etc. More importantly, it can take an advantage of solution-based SWCNT separation
techniques that will be detailed in Section 5.1 such as DNA-wrapping method [75, 76], density gradient centrifugation (DGU) [77, 78], gel chromatography [79-81], aqueous two phase extraction (ATPE)[82, 83], which shows a great potential for practical applications. Common post-growth assembly methods consist of the methods using external force, self-assembly and a liquid crystal (LC) phase transition.

External force used in SWCNT alignment can be mechanical force, magnetic force, and electric force. The simplest method is based on mechanical force by dry-spinning CNTs from a CVD grown CNT forest [43, 84], as shown in Figure 2.12(a). The disadvantage of this method is obvious since it is hard to have a chirality control during CVD growth, as described before. Another method is to use external magnetic field depending on CNT magnetic dipoles. However, the required magnetic field to achieve meaningful alignment [Figure 2.12(b)] is >10 T [85, 86], which makes it impractical in any real application scenario. The relatively affordable and practical method is to align SWCNTs in liquid by an AC electric field, i.e., dielectrophoresis (DEP) [87-89], as shown in Figure 2.12(c). DEP was originally developed to facilitate SWCNT FET fabrications since the SWCNT position was predefined between drain-source electrodes. Recent improvements have significantly increased the packing density to 30~50 SWCNTs/µm [89] but it is still not high enough for certain applications. Furthermore, the alignment quality is relatively poor and a high surface coverage is almost impossible.
Instead, self-assembly methods including evaporation-driven self-assembly (EDSA)\cite{90, 91}, Langmuir-Blodgett (LB) and Langmuir-Shaefer (LS) assembly can produce a large size full surface coverage aligned film. EDSA is based on “coffee ring” phenomena. When a substrate is immersed inside a CNT suspension, the interplay between surface friction force, liquid surface tension, and capillary force can align CNTs at the solid-liquid-air interface [Figure 2.12(d)] \cite{90}. Similarly, when the immersed substrate is pulled out of the CNT suspension vertically (LB) \cite{92} or horizontally (LS) \cite{93}, the 2D confinement at the air-water interface pushes CNTs to orient along certain directions [Figure 2.12(e)]. A s-SWCNT aligned monolayer film of an impressively high packing density $\sim$ 500 SWCNTs/$\mu$m with a full surface coverage has been demonstrated to have significantly improved FET device performance \cite{93}. However, no matter EDSA or LB (LS) method, the obtained film thickness is limited to monolayer or several layers ($\sim$ a few nm) due to the 2D manner of the assembly methods and the degree of alignment is not very high.

In contrast, a liquid crystal phase transition can align CNTs in a 3D manner. One strategy is to mix CNTs with LC polymer matrix \cite{94-96}. Under certain conditions, the LC polymer can go through a liquid crystal phase transition spontaneously with macroscopic ordered structures, where the hosted CNTs follow the same transition. The degree of alignment can be very high but the challenge is to remove the LC polymers completely without destroying the alignment of CNTs. As a consequence, it motivated another strategy to use the liquid phase transition of CNTs based on the Onsager’s theory that will be detailed in Section 4.1. Different aqueous dispersion systems have been investigated to achieve a nematic ordering of
CNTs [97-101] in a short range but macroscopically single-domain aligned SWCNT films through LC phase transitions still remain a challenge [Figure 2.12(f)].

Figure 2.12 Ex-situ post-growth assembly methods of SWCNTs. (a) Dry-spinning after water-assisted CVD growth[84]. (b) Magnetic field induced alignment[85]. (c) DEP[89]. (d) EDSA[90]. (e) LB[92]. (f) The liquid crystal phase transition of CNTs [98].
Chapter 3

Sample Fabrication and Characterization

Post-growth assembly methods are advantageous over direct-growth assembly methods in fabricating 3D macroscopic aligned SWCNT architectures because of the availability of a variety of solution-based chirality separation techniques. However, as mentioned in Section 2.3, there are no existing methods for fabricating large-area single-domain films of highly aligned, densely packed, and chirality-enriched SWCNT ensembles. In this chapter, we present a new way based on vacuum filtration, which can provide a uniform, wafer-scale SWCNT film of an arbitrarily and precisely controllable thickness (from a few nm to ~100 nm) with a high degree of alignment (nematic order parameter $S \sim 1$) and packing ($\sim 10^6$ tubes in a cross-sectional area of $1 \mu m^2$) in a well-controlled, simple, and reproducible manner, regardless of the synthesis method, type, or chirality of the SWCNTs used.
This chapter is organized as follows. In Section 3.1, we describe how to disperse different SWCNTs in water by various surfactants. In Section 3.2, we describe the experiment setup and procedures for preparing aligned SWCNT films using vacuum filtration. Section 3.3 presents the film transfer and micro-fabrication techniques for further characterization and device applications. From Sections 3.4 through Section 3.6, we describe the different characterization techniques we used to demonstrate the excellent properties of our films. Finally in Section 3.7, we show the universal applicability and scalability of the vacuum filtration method for fabricating aligned CNT films.

3.1. Carbon nanotube suspension preparation

Commercial SWCNTs synthesized by different methods are typically supplied in a form of heavily entangled bundles. To utilize the available solution-based chirality-separation techniques (and the vacuum filtration method for alignment), we first need to break the bundles and suspend individual SWCNTs in water by surfactant. Surfactants that are known to work well for suspending SWCNTs are amphiphilic organic molecules with hydrophobic tail and hydrophilic head for functionalization of SWCNTs [102-104]. Ultrasonication is a frequently used method for nanoparticle dispersion [102], agitating molecules either in the form of a ‘bath’ sonicator [Figure 3.1(a)] or a ‘probe’ (or ‘horn’) sonicator [Figure 3.1(b)]. When the generated ultrasound wave interacts with a SWCNT bundle in the surfactant solution, individual SWCNTs are peeled off from the outer part of the SWCNT bundle and immediately wrapped by surfactant molecules, which prevents rebundling.
We used different types of SWCNTs in this thesis work. Two batches of arc-discharge SWCNTs (P2-SWCNT and P8-SWCNT) with an average diameter of 1.4 nm were purchased from Carbon Solutions, Inc. Two types of CoMoCAT SWCNTs (CG 200 and SG 65i) were purchased from Sigma-Aldrich; the former had a wide diameter distribution (0.7-1.4 nm) whereas the latter was enriched in (6, 5) SWCNTs with ~90% purity. CVD-grown TUBALL™-CNTs, which were 75% SWCNTs, were obtained from OCSiAl and had an average diameter of ~1.8 nm. HiPco SWCNTs (batch # 195.5), with a diameter range of 0.9-1 nm, were used after purification and diameter sorting. As surfactants for CNT dispersion, we used sodium deoxycholate (DOC, Sigma-Aldrich) and sodium dodecylbenzenesulfonate (SDBS, Sigma-Aldrich). All CNTs (except for P8-SWCNT) were initially dispersed in either 1% (wt./vol.) DOC or 0.4% (wt./vol.) SDBS by bath sonication (Cole-Parmer 60-W ultrasonic
cleaner, model #08849-00) for 5-10 minutes at a starting concentration of 0.2-0.8 mg/mL.

The obtained suspension was then further sonicated with a tip sonicator (XL-2000 Sonicator, Qsonica, LLC. 1/4” probe, ~30 watts) for certain durations. The suspension was cooled in a frigorific mixture of ice and water bath during the sonication to prevent any side effect from heating. Next, the suspension was ultracentrifuged for 1 hour to 2 hours at 38000 rpm (Sorvall Discovery 100SE Ultracentrifuge using a Beckman SW-41 Ti swing bucket rotor) to remove large bundles of CNTs. After ultra-centrifugation, the upper 60% of the supernatant was collected and then diluted with Nanopure water (Mill-Q, Resistivity 18.2 MΩ•cm). The concentration of surfactant was diluted below its critical micelle concentration (CMC). Depending on the type of CNTs used, the final concentration of DOC before film making varied from 0.02% to 0.1%, and the final concentration of SDBS was ~0.02%.

Arc-discharge P8-SWCNTs were water-soluble because of functionalization by m-polyaminobenzene sulfonic (PABS) acid [105]. The SWCNT powder was directly dissolved into Nanopure water with an initial concentration of ~0.5 mg/mL. In order to get better dispersion, the suspension was tip-sonicated for 45 minutes and then ultracentrifuged, as described before; the upper ~60% of the supernatant was collected for fabricating films.
3.2. Fabrication of aligned carbon nanotube films by vacuum filtration

3.2.1. Filtration setup

Vacuum filtration is a technique for separating a solid product from a solvent. As shown in a diagram in Figure 3.2 (a), the key components of a typical glass microfiltration setup are: 1) a glass funnel, 2) a piece of filter membrane with a certain pore size and density, 3) a clamp, 4) a fritted glass base, and 5) a rubber stopper. The whole setup was mounted on a side-arm flask that was connected to a vacuum pump. We purchased the filtration system shown in Figure 3.2(b) (Millipore® XX1002500 glass microanalysis 25 mm vacuum filter holder) from Fisher Scientific Company, LLC, which included a 15 mL glass funnel, a fritted glass filter support, and a silicone stopper for the attachment to a vacuum filtering flask. We purchased the vacuum pump (Fisher Scientific™ Maimadry™ Oil-Free Vacuum Pump) also from Fisher Scientific Company, LLC.

We placed a piece of filter membrane with a proper pore size on the surface of the glass support. We then poured the CNT suspension as described in Section 3.1 into the filtration funnel. The differential pressure across the filter membrane then pushed the solvent slowly through the pores, leaving CNTs on the filter membrane. To have accurate control of the applied differential pressure across the filter membrane, we used three pressure gauges (Magnehelic Differential Pressure Gauge) with different measurement ranges (0.5, 6, 20 inch of water) from Dwyer
Instruments, Inc. [Figure 3.2(c)]. We used Nuclepore track-etched polycarbonate (hydrophilic, PVP-coated) filter membranes from GE Healthcare Life Sciences. The pore sizes we used were 80 nm, 100 nm, and 200 nm. A typical scanning electron microscopy (SEM) image of a filter membrane is shown in Figure 3.2(d).

Figure 3.2 (a) Diagram of a generic microfiltration system, consisting of a glass funnel, a filter membrane, a clamp, a fritted glass base, and a rubber stopper (http://www.emdmillipore.com/). (b) Photograph of our experimental setup with a CNT suspension contained inside the funnel. (c) Pressure gauges with three different measurement ranges. (d) A typical SEM image of the polycarbonate filter membrane with 100 nm pore size.
3.2.2. Filtration procedure

Vacuum filtration was introduced to the CNT community by Wu et al. when they reported the fabrication of ultrathin, transparent, optically homogeneous, electrically conducting films of SWCNTs and the transfer of those films to various substrates [37]. The filtration method has several advantages over other film fabrication techniques: 1) the film thickness is readily controllable with nanoscale precision by adjusting the concentration of the SWCNT suspension and/or filtrated volume of suspension [Figure 3.3(a)]; 2) the produced film is homogenous over a large-area [Figure 3.3(b)]; 3) it is a universal method regardless of the synthesis method, type, or chirality of the SWCNTs used; and 4) the obtained film has strong mechanical strength for flexible electronic and optoelectronic devices [Figure 3.3(c)]. However, usually, the method can only produce films that are random networks of CNTs, as shown in the atomic force microscopy image in Figure 3.3(d), which severely limits the performance in many applications.

As a promising route to assembling individual SWCNTs into a macroscopic aligned film, 3D liquid crystal phase transitions of SWCNTs have been observed in several systems [97-99]. The mechanism behind this is Onsager’s theory, which will be detailed in Section 4.1. Rod-like molecules, such as SWCNTs, can transform from an isotropic phase to a nematic phase above a certain concentration threshold [106, 107]. It has been observed that vacuum filtration can not only produce a random network of SWCNTs [37] but also induce nematic ordering under certain conditions [98, 99]. The SEM image in Figure 3.3 reveals multiple small domains with a typical
size of hundreds of nanometers and there is no long-range order due to misalignment of different domains. An interesting observation made in Ref. [98] was that a slow filtration speed (~2 mL/hour) is crucial for achieving such nematic ordering. As the concentration accumulates near the membrane surface during slow filtration, a liquid crystal phase transition can occur, driving the system from the isotropic phase to the nematic phase.

Figure 3.3 SWCNT films made using the vacuum filtration method. (a), (b) Large-area homogenous film with controlled thickness on a transparent substrate. (c) Flexible film on a plastic substrate. (d) Atomic force microscopy image of a random
network film. (e) Scanning electron microscopy image of a film with nematic ordering. Adapted from [37, 98]

We demonstrated that, for global ordering in a large area to occur, several critical conditions besides slow filtration have to be satisfied: 1) the surfactant concentration must be below the CMC; 2) the CNT concentration must be below a threshold value; 3) the filtration speed needs to be slow, and 4) the filter membrane needs proper hydrophilicity. Furthermore, the structure parameters (i.e., diameters and lengths) of the SWCNTs used critically affect the above conditions in a quantitative manner. All these conditions will be discussed in more detail in Section 4.3.

We filtered a well-dispersed CNT suspension containing dilute CNTs (~1-15 μg/mL) and dilute surfactant (below CMC) through the above-described vacuum filtration system in a well-controlled manner. We used polycarbonate filter membranes (Nuclepore Track-Etched Polycarbonate Hydrophilic Membranes with PVP-coating) with different pore sizes from 50 to 200 nm. We kept the filtration speed low, i.e., in a range of 1-2 mL/hour. The detailed filtration procedure generally included the following three steps for the purpose of controlling the filtration speed at a slow and steady rate, which was facilitated by the installed three sensitive pressure gauges:

**Step I:** Put a gentle or zero pressure on the filtration system at the beginning so that the filtration speed of the CNT suspension is as slow as 1-2.5 mL/hour. This
can be achieved by controlling multiple valves in the vacuum line to adjust the vacuum pumping rate and choosing filter membranes with different pore sizes.

**Step II:** Monitor the filtration speed during the filtration process. As CNTs are gradually deposited on the filter membrane, the flow rate slows down. Try to keep the speed above 0.5 mL/hour in order to avoid inhomogeneous deposition of CNTs.

**Step III:** Increase the filtration rate at the end of the filtration process. The CNT layer deposited on the filter membrane can be disturbed by the residual solution at the end of the filtration if the speed is slow (~1-2.5 mL/hour). The increase in filtration rate at the end is important to achieve a uniform CNT layer and protect the alignment structures from being destroyed by the residual solution. Usually, the increase begins when there is still a certain distance (~3-5 millimeters) between the upper surface of the filtering suspension and the surface of the filter membrane. Before the two surfaces touch each other, a final steady speed is reached around 1 drop/20 seconds, which corresponds to ~10 mL/hour.

Before transferring the film onto another substrate, the film is pumped on for an additional 15-30 minutes to dry the film completely. The obtained film is shown in Figure 3.4.
3.3. Film transfer and micro-fabrication

For characterization and device fabrication purposes, we transferred the prepared aligned CNT films onto different solid substrates (e.g., SiO$_2$/Si, intrinsic Si, quartz, etc.) using a wet transfer process. This process consisted of the following steps: 1) wet the substrate surface with Nanopure water; 2) put the sample on the substrate with the side of the SWCNT surface touching the substrate surface; 3) dry the sample with nitrogen gas flow so that the SWCNT film can stick to the substrate surface firmly after removing the water in between due to van der Waals interaction; 4) immerse the sample in an organic solvent (N-methyl-2-pyrrolidone (NMP) or chloroform) to remove the filter membrane; 5) after fifteen minutes, take out the sample and rinse it by acetone and then by Nanopure water; and 6) dry the sample by nitrogen gas flow. An optical image of the produced film after being transferred to a transparent substrate is shown in Figure 3.5(a).
Another great application advantage of obtained aligned films using our methods is their compatibility with modern micro-fabrication techniques such as spin-coating, lithography, electron-beam evaporation, lift-off, etc., because of their high packing density and chemical stability, which enable us to fabricate various electronic, photonic, and optoelectronic devices.

3.4. Microscopy characterization

In this section, we demonstrate the excellent properties of arc-discharge P2-SWCNT aligned films prepared by our vacuum filtration method by the following microscopy characterization methods: scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and polarized light microscopy (PLM).

3.4.1. Scanning electron microscopy (SEM)

We transferred an aligned CNT film onto a quartz wafer or a SiO$_2$/Si substrate with a SiO$_2$ thickness of ~285 nm. The alignment structure in the film on a micrometer scale can be examined through scanning electron microscopy (SEM). SEM produces images of a sample by scanning it with a focused beam of electrons, which interact with atoms in the sample producing various signals that can be detected and that contain information about the sample's surface topography. We used a JEOL 6500F Scanning Electron Microscope in our study to characterize the film. SEM and high-resolution SEM images of a highly aligned, densely packed SWCNT (Arc-discharge P2-SWCNT) film are shown in Figure 3.5 (b) and (c), which
demonstrate that individual SWCNTs within the film are all aligned with each other in the same direction.

Figure 3.5 (a) An optical image of the produced film after being transferred to a transparent substrate by dissolving the filter membrane. (b) A scanning electron microscopy image. (c) A high-resolution scanning electron microscopy image.

Furthermore, we showed that alignment occurs globally by examining the film at different positions within a ~ cm² area. Four typical SEM images at four corners [Figure 3.6(a)] indicate perfect alignment with single-domain structure over a large area. Through further systematic analysis of the SEM images at hundreds of
positions within $\sim \text{cm}^2$ area, we confirmed a global ordered structure with an angle standard deviation of $\sim 1.5^\circ$ across the entire film [Figure 3.6(b)].

![Figure 3.6 SEM characterization of global spontaneous alignment of carbon nanotubes. (a) Typical SEM images of aligned film morphology and global alignment in a large area $\sim \text{cm}^2$. (b) Angular distribution of CNTs within $\sim \text{cm}^2$ area of the film, with a standard deviation of $\sim 1.5^\circ$, determined by SEM image analysis.

It should be noted that there was a very thin layer of misaligned CNTs (a few nm) at the top of the film [Figure 3.7(a)], which can be easily etched away through oxygen plasma etching, as demonstrated in Figure 3.7(b).
Figure 3.7 SEM images of the top surface of an aligned CNT film. (a) SEM image of the top surface of a CNT film with a thin misaligned layer. (b) SEM image of the top surface of the CNT film after the removal of the misaligned layer through oxygen plasma.

3.4.2. Transmission electron microscopy (TEM)

The obtained aligned film can also be transferred onto a TEM grid, and the alignment structure on a nanometer scale can be examined. TEM is a microscopy technique in which a beam of electrons is transmitted through an ultrathin specimen, interacting with the specimen as it passes through it. We thinned down an aligned film through oxygen plasma etching and then transferred it onto a TEM grid [Figure 3.8(a)]. A top view TEM image of the film taken by a JEOL 2100 Field Emission Gun Transmission Electron Microscope is demonstrated in Figure 3.8(b), showing strong alignment and high packing density.
Figure 3.8 (a) A schematic of the transferred ultrathin SWCNT aligned film on a TEM grid. (b) A top-view TEM image of the film, showing strong alignment and high density.

We also prepared a cross-sectional CNT sample for further examination of the packing density using the following procedures. We transferred an aligned arc-discharge SWCNT film onto a SiO$_2$/Si substrate and then cut it in a direction perpendicular to the overall alignment direction using a focused ion beam (FIB, FEI Helios 660 SEM/FIB). We used standard procedures [108], including platinum (Pt) deposition for sample protection, bulk-out, U-cut, lift-out, mounting, thinning, and cleaning, in order to prepare lamellae for TEM imaging, as shown in Figure 3.9(a). We reduced the lamellae thickness to ~ 70 nm, as shown in Figure 3.9(b), to expose the circular cross-sections of nanotubes for high-resolution TEM (HRTEM). The FIB sample was loaded onto a double-tilted stage to align the incident electron beam with the CNT alignment direction. The inability to clearly distinguish all the nanotube cross-section in Figure 3.9(c) is highly likely due to slight misalignment.
between the nanotube axis and the incident electron beam. The circular tube cross-section is very sensitive to the tilt angle. A small misalignment (~0.1 degree [109]) can make most of the circular tube cross-section appear out-of-focus since we are looking at the projection of the nanotubes over a ~ 70 nm thickness. Other reasons for blurring include the surface roughness and curvature of the nanotubes along the tube axis.

A high-resolution cross-sectional TEM image in the inset of Figure 3.9(c) shows that, the film is densely packed, with an estimated packing density of ~$10^6$ SWCNTs in a cross-sectional area of 1 μm$^2$. 
Figure 3.9 (a) Side-view SEM image of a FIB-prepared lamella for HRTEM. (b) Top-view SEM image of a FIB-prepared lamella for HRTEM. (c) Cross-sectional TEM image of an aligned carbon nanotube film (inset: A high-resolution cross-sectional TEM image).

3.4.3. Atomic force microscopy (AFM)

We used a Bruker Multimode 8 atomic force microscope to characterize the thicknesses of the prepared CNT films and the average lengths of the CNTs. To accurately measure the thickness of a produced film, we used photolithography to pattern the film with a well-defined edge [see Figure 3.10(a)], which yielded a typical film thickness of ~71 nm across the edge, as shown in Figure 3.10(b).

To characterize the lengths of SWCNTs contained in the film, we prepared samples on a 3-(ethoxydimethylsilyl) propylamine (APDMES) functionalized substrate. For substrate functionalization, we first cleaned the SiO$_2$/Si wafer by an oxygen/argon plasma for 15 minutes, immersed it into 1% APDMES in isopropanol for 20 minutes, and then rinsed it with isopropanol and DI water. Finally, we dried it in an oven at 70 °C for 20 minutes. We diluted a SWCNT suspension by 200 folds into a 0.2% sodium cholate surfactant (SC) / 20 mmol/L sodium thiocyanate (NaSCN) solution. We then titrated the diluted SWCNT suspension on the APDMES-functionalized substrate for 6 minutes, rinsed it with Nanopure water, and dried it with nitrogen gas flow [110]. Figure 3.10(c) shows AFM images of individual arc-discharge P2-SWCNTs on the substrate, which was used in the film fabrication.
Through statistical averaging, we determined the average length in this study [see Figure 3.10(d)] to be \(\sim 226.5\) nm.

![Figure 3.10](image)

Figure 3.10 (a) The AFM image of a P2-SWCNT film on a quartz substrate, and (b) corresponding height profile across the red dashed line in (a). (c) AFM image of arc-discharge P2-SWCNT, and (d) corresponding length distribution.

### 3.4.4. Polarized light microscopy (PLM)

The light absorption properties of CNTs are strongly anisotropic due to their inherently 1D intraband and interband carrier dynamics [111-113]. When the light polarization is parallel to the tube axis, the light is strongly absorbed while when it
is perpendicular to the tube axis, the light transmits. So polarized light microscopy is a powerful method for optically characterizing an aligned CNT film in terms of local and global alignment [98, 99].

We used a Zeiss Axioplan 2 microscope to optically characterize the alignment of CNT films on a large scale. We employed two modes – cross-polarized and co-polarized modes. For the former case, the polarizer and analyzer were placed orthogonally. When the CNT alignment direction was along the polarization direction of the polarizer or analyzer, the film was opaque; when the CNT alignment direction was 45 degrees with respect to the polarization direction, the film was transparent. In the cross-polarized mode, strong optical anisotropy was seen both on a macroscopic (cm) scale [Figure 3.11(a)] and a microscopic (µm) scale [Figure 3.11(b)], reflecting the global and local alignment of CNTs, respectively. Furthermore, the aligned film was robust in water and thus compatible with standard micro-fabrication techniques, which allowed us to easily pattern it using conventional photolithography techniques. Figure 3.11(b) demonstrates a Rice Owl pattern in the aligned CNT film, which was fabricated by standard photolithography. The well-kept global alignment in the patterned film is evidenced by the uniform and strong optical anisotropy.
Figure 3.11 Film is opaque to light polarized parallel to the CNT alignment direction and transparent to light polarized perpendicular to the alignment direction on (a) a macroscopic scale and (b) a microscopic scale. All images were taken with a cross-polarized optical microscope. In (b), the Rice Owl shape was created on the aligned film by standard photolithography.

In the co-polarized mode, the polarizer and analyzer were put parallel. When the light polarization was parallel to the CNT alignment direction, the film was opaque; when the light polarization was perpendicular to the CNT alignment direction, the film was semi-transparent. Shown in Figure 3.12 are optical images taken in the co-polarized mode for an aligned P2-SWCNT film on a quartz substrate. The images in Figure 3.12(a) and Figure 3.12(b) show the same area in the same sample with the polarization direction of incident light parallel and perpendicular to
the CNT alignment direction, respectively. The transmittance of the whole film changed remarkably for the two light polarization directions due to the global alignment of the CNTs in the film. In addition, some cracks can be seen in the film, which, as cleavage of a crystal, indicate the direction of CNT alignment in the film.

Figure 3.12 The co-polarized optical image of an aligned arc-discharge CNT film (P2-SWCNT) when the polarization of incident light is (a) parallel and (b) perpendicular to the CNT alignment direction.

3.5. Spectroscopy characterization

3.5.1. X-ray photoelectron spectroscopy (XPS)

XPS is a surface-sensitive quantitative spectroscopic technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state, and electronic state of the elements that exist within a material. We used XPS to detect surfactant residues in our obtained films of aligned CNTs.
We obtained spectra using an X-ray photoelectron spectrometer (PHI Quantera XPS) to analyze the elemental composition. The monochromatic X-ray source was Al Ka with an energy of 1486.7 eV, a beam spot size of 200 µm, and a power of 50 W. We set the pass energy to 140 eV. Shown in Figure 3.13 is an XPS spectrum from an aligned P2-SWCNT thin film with ~50 nm thickness, transferred onto a SiO₂/Si substrate after thoroughly washing by acetone and Nanopure water. The absence of a sodium 1s (Na1s) peak in the XPS spectrum indicates that the CNT film is clean, free of surfactants.

Figure 3.13 X-ray photoelectron spectrum of aligned SWCNTs on a SiO₂/Si substrate.
3.5.2. Polarized Raman and broadband absorption spectroscopy

Figure 3.14 summarizes results of spectroscopic characterization measurements of aligned CNT films. We used a Renishaw inVia Raman microscope to quantitatively characterize the degree of alignment of CNT films. Figure 3.14(a) shows polarized Raman spectra for a 15-nm-thick aligned film of arc-discharge P2-SWCNTs with an average tube diameter of 1.4 nm, taken with an excitation wavelength of 514 nm in two polarization configurations \((I_{VV}, I_{HH})\). We also performed measurements in another polarization configuration \((I_{VH})\), whose results are not shown here. The \(VV\) configuration is where the polarizations of the incident and scattered beams are parallel to the CNT alignment direction; the \(VH\) configuration is where the incident polarization is parallel to the CNT alignment direction but is perpendicular to the scattering polarization, and the \(HH\) configuration is where the polarizations of the incident and scattered beams are perpendicular to the CNT alignment direction. The dichroic ratio, \(\Delta\), is defined as \(\Delta = A_{//}/A_{\perp}\), where \(A_{//}\) and \(A_{\perp}\) are the parallel and perpendicular absorbance at 514 nm, respectively. We calculated the nematic order parameter, \(S\), based on the polarized Raman spectra taken in three different polarization configurations and the dichroic ratio through the following equation [114]:

\[
S_{\text{Raman}} = \frac{6\Delta I_{VV} + 3(1+\Delta)I_{VH} - 8I_{HH}}{6\Delta I_{VV} + 12(1+\Delta)I_{VH} + 16I_{HH}} \tag{3.1}
\]

The deduced value of \(S\) was 0.96 for this particular film.
Electromagnetic response of this film was strongly polarization dependent in
the whole spectral range, from the terahertz (THz) to the visible, as shown in Figure
3.14(b) with the energy axis on a logarithmic scale. In particular, there is no
detectable attenuation within experimental errors for the perpendicular
polarization in the entire THz/infrared range (< 1 eV), whereas there is a
prominent, broad peak at ~0.02 eV in the parallel case due to the plasmon
resonance [115]. Figure 3.14(c) plots the same spectra with the energy axis on a
linear scale, to more clearly show interband absorption – i.e., the first two interband
transitions for semiconducting nanotubes ($E_{11}^S$ and $E_{22}^S$) and the first interband
transition in metallic nanotubes ($E_{22}^M$). Due to the exceptionally high degree of CNT
alignment, these peaks are completely absent for the perpendicular polarization,
and instead, a broad absorption feature is observed in an intermediate energy
region between the $E_{11}^S$ and $E_{22}^S$ peaks. We attribute this feature to cross-polarized
and depolarization-suppressed $E_{12}^S$/$E_{21}^S$ absorption [116], previously detected in
polarized photoluminescence excitation (PLE) spectroscopy experiments in
individualized CNTs [117, 118].

As noted previously, the exceptionally strong polarization-dependence of
THz transmission through aligned CNT films can be utilized to form an ideal THz
polarizer with an extremely large extinction ratio ($ER$); $ER = T_{//}/ T_{\perp}$, where $T_{//}(T_{\perp})$
is the transmittance for the parallel (perpendicular) polarization. We used THz
time-domain spectroscopy (THz-TDS) to quantitatively characterize the degree of
alignment on a macroscopic scale (~1 mm$^2$). The experimental setup was a
transmission THz-TDS system using an ultrafast Ti:Sapphire laser. Already linearly-
polarized THz radiation went through a wire-grid polarizer before being focused onto the sample. We transferred the SWCNT films onto intrinsic silicon substrates for the transmission measurements. The thickness of the films ranged from 10 to 100 nm, and their areas were on the order of cm$^2$ to fully cover the THz beam size ($\sim$1 mm$^2$). We obtained polarization-dependent THz transmission data by rotating the sample, changing the direction of CNT alignment with respect to the polarization direction of the incident beam. We calculated the reduced linear dichroism ($LD'$) and $S$ based on the THz transmission data using the following equation

$$LD' = 3S_{THz} = 3 \frac{A_H - A_L}{A_H + 2A_L} \quad (3.2)$$

Figure 3.14(d) shows time-domain waveforms of THz radiation transmitted through an aligned arc-discharge SWCNT film on an intrinsic silicon substrate for polarizations parallel and perpendicular to the alignment direction, together with a reference waveform obtained for the substrate alone. The data for the perpendicular case completely coincides with the reference trace, i.e., no attenuation occurs within the SWCNT film. On the other hand, there is significant attenuation for the parallel case. Figure 3.14(e) shows a more detailed polarization-angle dependence of THz attenuation, plotted as a function of the angle between the THz polarization and the nanotube alignment direction. The attenuation anisotropy allowed us to obtain a value of $S\sim1$ in this particular film via a straightforward manner using Eq. (3.2), which agrees well with the value obtained by Raman spectroscopy. The value of $ER$ monotonically increases with the film thickness at $\sim$12 dB/100 nm, while high values of $S$ are maintained even for relatively thick films [Figure 3.14(f)].
Figure 3.14 Characterization of aligned carbon nanotube films through polarization-dependent optical spectroscopy. (a) Raman spectra for an aligned arc-discharge carbon nanotube film for two configurations. In the VV (HH) configuration, both the incident and scattered beams are polarized parallel (perpendicular) to the nanotube alignment direction. (b) Polarization-dependent attenuation spectra in a wide spectral range, from the THz/far-infrared to the visible. (c) Expanded view of (b), showing interband transitions. (d) Time-domain THz waveforms of transmitted THz radiation for parallel and perpendicular polarizations. The data for the perpendicular case completely overlaps with the reference trace, i.e., no attenuation is detectable. The THz beam had a beam size of ~mm² thus probing a macroscopic area. (e) Attenuation as a function of the angle between the THz polarization and the nanotube alignment direction. (f) The nematic
order parameter ($S$), left axis, deduced from the THz attenuation data, and the extinction ratio ($ER$), right axis, as a function of film thickness.

### 3.6. Electrical characterization

In addition to the strongly anisotropic optical properties, the aligned arc-discharge tube films showed a strongly anisotropic electrical properties. To characterize them, we fabricated electronic devices using standard microfabrication techniques and tested their conductivities [Figure 3.15(a)]. An aligned nanotube film was transferred onto a substrate comprised of heavily doped silicon and 285-nm thick layer of thermal silicon oxide. The first photolithography step was to define the electrode area with Shipley Microposit S1813 photoresist. The electrodes were defined and fabricated by lifting off electron-beam-evaporated titanium (1 nm) / palladium (10 nm) / gold (20 nm). The next step was to define a Hall bar structure with one channel parallel and the others perpendicular to the CNT alignment direction, as shown in Figure 3.15(a). We performed electrical transport measurements under ambient conditions via four-terminal sensing using a Keithley 2400 source meter.

We observed strong conductivity anisotropy in Hall-bar devices made of aligned unsorted arc-discharge CNTs at room temperature. The ratio of conductivity between the parallel and perpendicular directions was as high as 60 [Figure 3.15(b)]. The conductivity along the alignment direction was 2500 S/cm; this value is much higher than the typical conductivities reported for aligned films made from
chemical vapor deposition grown CNTs, which are only \( \sim 10 \text{ S/cm} \) along the alignment direction \([119]\) because of their low densities. Furthermore, our films are more conducting than previously reported dense random-network CNT films, whose conductivities are typically on the order of hundreds of \( \text{S/cm} \) without intentional doping\([42, 120]\), while our films are not intentionally doped.

Figure 3.15 (a) Photograph and schematic diagrams of Hall-bar devices with channel length \( \sim 5 \text{ mm} \) and channel width \( \sim 0.5 \text{ mm} \) used to characterize the macroscopic anisotropic transport of charge carriers in an aligned film consisting of unsorted arc-discharge SWCNTs via four-terminal measurements. (b) Voltage-current relationship of the Hall-bar devices when the current flow is parallel and perpendicular to the CNT alignment direction, showing extremely anisotropic conductivities.
3.7. Alignment universality and scalability

Two of the great advantages of the vacuum filtration method to prepare macroscopic ensembles of aligned SWCNTs are its universal applicability and scalability. In other words, there is no limitation on the CNT synthesis method and the produced film can be easily scaled up in all three spatial dimensions.

3.7.1. Universal applicability

Our method of making aligned films is universally applicable to different types of SWCNTs. Table 3-1 lists six representative suspensions used, which contained SWCNTs synthesized by the arc-discharge, CVD, CoMoCAT, and HiPco methods. Here, $d_t$ is the average nanotube diameter, and $l_t$ is the average nanotube length measured by AFM (Figure 3.16 and Figure 3.17). For dispersing CNTs, we used sodium deoxycholate (DOC) for Suspensions #1, #4, #5 and #6 and sodium dodecylbenzenesulfonate (SDBS) for #2, as surfactant. Pre-functionalized, water-soluble SWCNTs were used in Suspension #3; successful formation of aligned films made from this suspension indicates that surfactant is not a crucial element for spontaneous CNT alignment, as long as the CNTs are well dispersed in the suspension. Note, however, that CNTs in all these suspensions were negatively charged, and thus, it is currently not clear whether CNT alignment can be achieved with positively charged or neutral surfactants, which is for future investigations.

Table 3-1: Summary of properties for aligned films made by different types of CNTs.
<table>
<thead>
<tr>
<th>Suspension</th>
<th>Synthesis Method</th>
<th>Surfactant</th>
<th>$d_t$ (nm)</th>
<th>$l_t$ (nm)</th>
<th>$S_{\text{Raman}}$</th>
<th>$S_{\text{Raman}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Arc-Discharge</td>
<td>DOC</td>
<td>1.4</td>
<td>227</td>
<td>~1</td>
<td>0.96</td>
</tr>
<tr>
<td>#2</td>
<td>Arc-Discharge</td>
<td>SDBS</td>
<td>1.4</td>
<td>246</td>
<td>~1</td>
<td>0.94</td>
</tr>
<tr>
<td>#3</td>
<td>Arc-Discharge</td>
<td>N/A</td>
<td>1.4</td>
<td>295</td>
<td>0.77</td>
<td>0.72</td>
</tr>
<tr>
<td>#4</td>
<td>CVD</td>
<td>DOC</td>
<td>1.8</td>
<td>307</td>
<td>0.9</td>
<td>0.85</td>
</tr>
<tr>
<td>#5</td>
<td>CoMoCAT</td>
<td>DOC</td>
<td>~1</td>
<td>166</td>
<td>N/A</td>
<td>0.73</td>
</tr>
<tr>
<td>#6</td>
<td>HiPco</td>
<td>DOC</td>
<td>~0.9</td>
<td>298</td>
<td>N/A</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Figure 3.16 AFM images of #2-#6 SWCNT samples used. (a) Arc-discharge P2-SWCNT dispersed by SDBS. (b) Arc-discharge P8-SWCNT dispersed by Nanopure water. (c) Tuball CNTs dispersed by DOC. (d) CoMoCAT CG200 dispersed by DOC. (e) HiPco SWCNTs (batch #195.5) dispersed by DOC.
Figure 3.17 Length distribution of #2-#6 SWCNT samples used. (a) Arc-discharge P2-SWCNT dispersed by SDBS. (b) Arc-discharge P8-SWCNT dispersed by Nanopure water. (c) Tuball CNTs dispersed by DOC. (d) CoMoCAT CG200 dispersed by DOC. (e) HiPco SWCNTs (batch #195.5) dispersed by DOC.

Also listed in Table 3-1 are nematic order parameters, $S_{THz}$ and $S_{Raman}$ determined through THz (Figure 3.18) and Raman measurements (Figure 3.19), respectively; only $S_{Raman}$ is shown for Suspensions #5 and #6, because the films from these suspensions did not have sufficiently high carrier densities to show strong enough THz attenuation for determining $S_{THz}$. The SEM images in Figure 3.20 show the alignment structures of films made by different types of CNTs.
Figure 3.18 THz transmission spectra of aligned CNT films made by different types of CNTs. (a) P2-SWCNT dispersed in DOC surfactant. (b) P2-SWCNT dispersed in SDBS surfactant. (c) TUBALL CNTs dispersed in DOC surfactant. (d) P8-SWCNT dispersed in Nanopure water.
Figure 3.19 Polarized Raman spectra of aligned films made from different types of CNTs. (a) Arc-discharge SWCNTs (P2-SWCNT) dispersed by SDBS surfactant. (b) PABS functionalized arc-discharge SWCNTs (P8-SWCNT) dispersed in Nanopure water. (c) TUBALL CNTs dispersed by DOC surfactant. (d) CoMoCAT CG200 CNTs dispersed in DOC. (e) HiPco SWCNTs (batch #195.5) dispersed in DOC.
Figure 3.20 SEM images of aligned film made from different types of CNTs. (a) Arcdischarge (P2-SWCNT) dispersed in SDBS surfactant. (b) Tuball CNTs dispersed in DOC surfactant. (c) Arc-discharge (P8-SWCNT) dispersed in Nanopure water. (d) CoMoCAT (CG200) dispersed in DOC surfactant.

Based on the above results, we conclude that our method provides a uniform, wafer-scale (> cm²) CNT film of a controllable thickness (from a few nm to ~100 nm) with a high degree of alignment (S ~ 1) and packing density (~10⁶ nanotubes per µm²) in a well-controlled manner, regardless of the types of the CNTs used.

Furthermore, unlike aligned CNT films grown by CVD, the produced films by this method are compatible with CMOS microfabrication technology to fabricate various electronic and photonic devices.
3.7.2. Scalability

Our method can be also easily scaled up to produce larger area macroscopic aligned films with a 2-inch filtration system [Figure 3.21(a)] instead of a 1-inch filtration system. An SEM image of produced arc-discharge P2-SWCNT aligned film is shown in Figure 3.21(b), and the polarization-dependent absorbance in the visible range (660 nm) in Figure 3.21(c) demonstrates a perfectly aligned 2-inch SWCNT film, which is as good as the film made using the 1-inch system in Figure 3.21(d) with a high $LD'$. 

![Figure 3.21](image-url) Figure 3.21 (a) Photograph of a 2-inch filtration system and a produced CNT film compared to the original 1-inch filtration system. (b) SEM image of aligned P2-SWCNT made using the 2-inch filtration system. (c) and (d) Polarization angle
dependent light absorbance at 660 nm of an aligned P2-SWCNT film made by the 2-inch and 1-inch filtration systems, respectively.

As shown in Figure 3.14(f), we can control the film thickness by using different filtrated volumes. However, our method becomes more difficult to control when the thickness becomes larger than 100 nm, and the produced aligned film quality starts to degrade. Instead, with the 2-inch filtration system, we developed a stacking method to produce a much thicker aligned film. The method is illustrated in Figure 3.22(a). By cutting a large-area globally aligned P2-SWCNT film with a thickness of ~80 nm into several pieces, we can stack them manually to have a much thicker film while maintaining the alignment of CNTs. In the visible range (660 nm), the light absorbance \( A_0 = (A_{/\!/} + 2A_{\perp})/3 \) is linearly increasing with increasing thickness while preserving a good degree of alignment as shown in Figure 3.22(b).
Figure 3.22 (a) Cutting and stacking of an aligned P2-SWCNT film. (b) The light absorbance and $LD^r$ in the visible range with increasing thickness.
Chapter 4

Alignment Mechanism

The surprisingly perfect global alignment of SWCNTs produced by the vacuum filtration method is against the conventional wisdom that vacuum filtration can only produce random networks of SWCNT. In this Chapter, we will investigate the underlying mechanism of this spontaneous alignment phenomenon. At first sight, rod-like SWCNTs of high aspect ratios wrapped by surfactant with repulsive electrostatic forces among them would seem to fit perfectly with the framework of Onsager's theory of liquid crystal isotropic-nematic (IN) transitions. However, the Onsager theory did not provide any insight into how to achieve a phase transition in our system, and the expected time scale. Furthermore, the Onsager theory only provides a steady-state solution at “dialytic” equilibrium, while we believe that understanding molecular dynamics during vacuum filtration is crucial.

In Section 4.1, we first briefly review the Onsager theory of the lyotropic liquid crystal-phase transition. In Section 4.2, we describe the specific IN phase
transition in the vacuum filtration procedure. In Section 4.3, we investigate several factors affecting the degree of alignment obtained in vacuum filtration.

### 4.1. Lyotropic liquid crystal phase transition: the Onsager theory

A liquid crystal is a state of matter, which exists between a crystalline solid and an isotropic liquid. The discovery of a liquid crystal can be traced back to 1900, when scientists Reinitzer and Lehmann heated up and melted cholesteryl nonanoate molecules, two melting points were observed between the solid and liquid phases. The molecules of this property are nowadays referred as thermotropic liquid crystals. In addition, the liquid-crystal phase also appears in certain colloidal solutions such as tobacco mosaic viruses (TMV) in response to the change of solution concentration, which is called a lyotropic liquid crystal. One question needs to be answered is: whether a given type of molecules can lead to an IN phase transition (Figure 4.1) under certain conditions (e.g., solution concentration) [121, 122]. The pioneering theoretical work on rod-like molecules by Onsager provided clues to this question. His theory was based on a simple assumption of “hard-core” interactions among molecules [106] and made far-reaching influence on future theory, leading to a wide range of applications of liquid crystals.
Figure 4.1 Isotropic (I) to nematic (N) phase transition. The nematic phase has a preferential ordering. Adapted from [122].

In the simplest form of Onsager's theory, each molecule is treated as a hard rod, and interactions among them are assumed to be purely *steric*, which means that they cannot penetrate into each other, i.e., there is no possibility of two molecules occupying the same region in space. A key point in any steric approach is to determine the number of arrangements of a given ensemble of molecules at certain concentrations in a given volume, which is directly related to the system entropy [121]

\[ S_e = k_B \ln(Z) \]  \hspace{1cm} (4.1)

Here \( Z \) is the partition function (i.e., the number of arrangements), \( k_B \) is the Boltzmann constant and \( S_e \) is the system entropy, which determines the thermodynamic stability of the system expressed by the free energy \( F = -T S_e = -k_B T \ln(Z) \). In a steric system, both the translational entropy and the orientational entropy contribute to the total system entropy, and the dominance between these two depends on the excluded volume of adjacent rods and the density of rods [121].
The excluded volume is the volume occupied by one molecule where the mass centers of other molecules cannot move (see Figure 4.2). The excluded volume can be calculated for rod-like particles of length $L$ and diameter $D$

$$
V_{\text{excl}}(\Omega, \Omega') \approx 2L^2D|\sin(\gamma)|
$$

(4.2)

where $\gamma$ is the angle between two rods. It is clear that the excluded volume is much larger when two rods are perpendicular (i.e., $\gamma = \pi/2$) to each other than that when they are parallel (i.e., $\gamma = 0$). As a consequence, the translational entropy will favor the parallel alignment to minimize the excluded volume and maximize the free volume for the molecules’ movement, which, however, comes by at the expense of reducing the orientational entropy. Thus, there will be a competition between these two entropies to maximize the total system entropy.

Figure 4.2 Excluded volume occupied by two rod-like molecules of length $L$, diameter $D$. $\gamma$ is the angle between two rods. Adapted from [121].

When the solution is dilute, there is a large free volume. If the molecules are aligned, there is a significant reduction of orientational entropy while there is little increase in translational entropy. Therefore, parallel alignment is not favored, and
the system is in the isotropic phase. However at a higher rod density, parallel alignment will significantly increase the translational entropy although the orientational entropy is reduced. Hence, the nematic liquid-crystal phase will be formed.

The number of arrangements can be found using virial expansions for rod-like particles in a lyotropic liquid crystal [121]. Furthermore, Onsager considered the steric interaction only. The system is athermal and a phase transition is thus expected to occur as a function of concentration, not temperature. Under all these assumptions, and by neglecting high-order virial coefficients, the partition function can be expressed as

$$\frac{\ln(Z)}{N} = -\ln(\eta \lambda^3 \rho) - \int f(\Omega) \ln[4\pi f(\Omega)]d\Omega - \frac{\rho}{2} \int \int f(\Omega) f(\Omega') V_{\text{excl}}(\Omega, \Omega') d\Omega d\Omega' \quad (4.3)$$

where $\rho = N/V$ is the number density as the ratio of the particle number $N$ to the volume $V$, $\lambda = h/(2mE_K)^{1/2}$ is the thermal wavelength where $h$ is the Planck constant, $m$ is the particle mass and $E_K$ is the particle kinetic energy, $\eta$ is a scaling factor consisting of the angle freedom [122], and $f(\Omega)$ is the orientational distribution function. Equation (4.3) provides a method for determining the partition function (free energy) with any rod geometry if $f(\Omega)$ is known. However, in practice, $f(\Omega)$ is unknown and can be determined by minimizing the free energy (i.e., maximizing the partition function) at a certain concentration. Since $f(\Omega)$ is subject to the normalization condition $\int f(\Omega)d\Omega = 1$, one can use the Lagrange method to obtain [121]
\[
\ln(f(\Omega)) + 1 + \nu + \rho \int f(\Omega)V_{\text{exclu}}(\Omega, \Omega')d\Omega = 0
\]  

(4.4)

where \(\nu\) is the Lagrange multiplier. In principle, \(f(\Omega)\) can be found as a function of \(\rho\) and \(\nu\), but, in practice, the general analytical solution for Eq. (4.4) is not available, and approximations are needed.

Onsager chose the following trial orientational distribution function to solve Eq. (4.4) with an adjustable parameter to minimize the free energy

\[
f(\Omega) = \frac{\alpha}{4\pi \sinh(\alpha)} \cosh(\alpha \cos(\Omega))
\]  

(4.5)

where \(\alpha\) is an adjustable parameter and the form of this function with respect to \(\alpha\) is shown in Figure 4.3(a). A higher value of \(\alpha\) indicates better alignment. The nematic order parameter, \(S\), can be calculated using the known orientational distribution as

\[
S = \langle \frac{3}{2} \cos^2(\Omega) - \frac{1}{2} \rangle
\]  

(4.6)
Figure 4.3 (a) Onsager trial orientational distribution function with adjustable parameter \( \alpha \). (b) Computed free energy with respect to the Onsager parameter \( \alpha \) at different concentration \( \rho \). Adapted from [121].

With Eqs. (4.2), (4.3) and (4.5), the computed free energy is shown in Figure 4.3(b). For low densities such that \( \rho < \rho_1^* \), the minimum point of free energy is located at \( \alpha = 0 \), which corresponds to the isotropic phase. For high densities such that \( \rho > \rho_2^* \), the minimum free energy is obtained at finite \( \alpha \), which indicates a stable nematic phase. However, at intermediate densities such as \( \rho_1^* < \rho < \rho_2^* \), two minima are observed, indicating the co-existence of isotropic and nematic phases. In this biphasic region, both the chemical potential and osmotic pressure are in the equilibrium for the isotropic and nematic phases, and under these boundary conditions, the transition densities are determined as

\[
\rho_1^* = \frac{4.252}{L^2D}, \quad \rho_2^* = \frac{5.711}{L^2D}
\]  

(4.7)

or in terms of volume fraction \( \nu_p = \pi D^2 / L \times \rho \)

\[
\nu_{p1} = 3.340 \frac{D}{L}, \quad \nu_{p2} = 4.486 \frac{D}{L}
\]  

(4.8)

The value of \( \alpha \) found in the biphasic region is 18.58, which corresponds to a nematic order parameter \( S \) of \( \sim 0.85 \). The volume fractions are inversely proportional to the aspect ratio of the rod \( (L/D) \) implying that the longer the rods, the lower the volume fraction is at the IN transition.
4.2. 2D confinement induced phase transition

Formation of a nematic liquid-crystal (LC) phase of CNTs has been observed with some local ordering [98, 99, 101]. 3D LC formation would require a high CNT concentration, typically greater than 1 mg/mL in the case of CNTs [99]; this condition was not met in our case, in which the typical concentration was ~ 15 \( \mu \text{g/mL} \). Similarly to previous work [98, 101], we observed some local ordering only when the CNT suspension for vacuum filtration was dilute. This observation suggests that some factors not considered in Onsager’s theory are at work.

A clue for the mechanism comes from our observation that the degree of alignment was sensitive to the hydrophobicity of the filter membrane surface (see Section 4.3.4), similar to a prior report on 2D nematic ordering of DNA-wrapped CNTs [100]. Alignment was achieved only when the filter membrane had a hydrophilic coating layer (PVP).

Based on this observation, we propose that CNT alignment occurs in a 2D manner, as illustrated in Figure 4.4. Hydrophilic PVP coating makes the filter paper surface negatively charged during filtration, and as a result, negatively charged CNTs in the suspension are repelled from the surface. At the same time, CNTs feel van der Waals attraction from uncoated regions of the membrane surface. The competition of these two forces creates a potential minimum near the surface, where CNTs accumulate, interact with each other, and form an ordered 2D phase. A transition from 2D-like to 3D-like ordering occurs as CNTs gradually accumulate on
the surface during the filtration process; once there is an aligned layer, the CNTs that follow tend to align with the already-existing alignment direction.

As a result, in addition to concentration accumulation, the interactions between CNTs and the filter membrane, the interactions among CNTs, and the rotational dynamics of CNTs inside the 2D phase can also play an important role. In the following section, we are going to show several important factors affecting the degree of alignment of produced films using vacuum filtration.

Figure 4.4 Schematic diagram showing a possible alignment mechanism for 2D ordering. CNT alignment appears in a confined region, or a potential “well”, near the surface of the filter membrane.
4.3. Factors affecting the degree of alignment

Before moving forward to discuss the factors affecting the degree of alignment, we first rule out the possibility of alignment induced by some microstructures in the filter membrane surface [90]. The surface morphology of a filter membrane was checked using AFM. Small shallow grooves with depths of 5 to 10 nm, widths of a few μm, and spacing of a few to tens of μm, mostly along one direction on the membrane surface were found [Figure 4.5(a)]. However, after vacuum filtration the alignment direction [red arrow in Figure 4.5(b)] of CNTs did not follow the groove direction (yellow dashed arrow) on the filter membrane, as shown in Figure 4.5(b); there was no relationship between the directions of the grooves and CNT alignment, which further indicates that the alignment of CNTs happens highly likely near the surface but not directly on the surface.

In the following sections, we will discuss the factors truly affecting the degree of alignment of produced films. The figure of merit we used to quickly assess the degree of alignment is $LD' (660 \text{ nm})$ defined by Eq. (3.2).
4.3.1. Filtration speed

The first investigated factor was the filtration speed. This parameter was also a key factor affecting local ordering of CNTs [98]. We prepared two samples with the same CNT (CG200) concentration of ~ 15 µg/mL and the same DOC concentration of ~ 0.045% but at two different filtration speeds (1 mL/hour and 5 mL/hour). Both polarized absorption spectra and SEM images (Figure 4.6) showed that the alignment quality strongly degraded with the increase of the filtration speed. In our proposed 2D ordering mechanism described above, individual CNTs are confined at a certain height above the filter membrane, where they rotate through rotational diffusion while interacting with neighboring tubes. CNTs falling into the confined layer will try to follow those already aligned by rotating themselves. This can happen only when there is enough time for CNTs to rearrange themselves before the
next CNTs arrive. If the delay time between two CNTs sequentially falling onto the confined surface is too short, the formation and growth of aligned layers will be disturbed and eventually terminated.

In order to examine these assumptions, we estimated the average delay time, $\Delta T$, between two CNT arrival times and compared it with the CNT rotational diffusion time within the surface confinement layer. The $\Delta T$ at a given site can be estimated based on the following expression:

$$
(\Delta T)^{-1} = \frac{V c N_A}{M_{CNT}} \left( \frac{L}{R_{filter}} \right)^2
$$

where $V$ is the filtration speed, $c$ is the CNT concentration, $N_A$ is the Avogadro constant, $M_{CNT}$ is the molar mass of CNTs, $L$ is the length of CNTs and $R_{filter}$ is the radius of the overall filtration area on the filter paper surface. For the CNTs used here (CG200), $L$ was $\sim 166$ nm and the average diameter is $\sim 1$ nm, so $M_{CNT}$ can be estimated to be $\sim 2.4 \times 10^5$ g/mol, based on the total number of carbon atoms in one CNT. With $c \sim 15 \mu g/mL$ and $V \sim 1$ mL/hour (5mL/hour), $\Delta T$ can be estimated to be $\sim 0.19$ s (0.038 s).

Based on a previous report [123], the rotational diffusion coefficient, $D^R$, of a CNT with a diameter of $\sim 1$ nm can be estimated to be $\sim 8$ rad/s when it is confined in a narrow layer. Therefore, a typical rotational diffusion time is around 0.125 s ($\sim 1/D^R$). It can be seen that, when $V$ is too high (5 mL/hour), the delay time $\Delta T$ (0.038 s) becomes much shorter than the CNT rotational diffusion time (0.125 s),
i.e., CNTs on the surface do not have enough time to fully align before the next nanotube arrives. This conclusion is consistent with our experiment observations.

Figure 4.6 The influence of the filtration speed on CNT alignment. (a) The angular dependence of CNT film absorption of a polarized laser beam (660 nm). (b) SEM image of a sample made at a low filtration speed (1mL/hour) and (c) a sample made at a high filtration speed (5mL/hour).

4.3.2. Carbon nanotube suspension concentration

The second factor under investigation was the carbon nanotube suspension concentration. In this study, we prepared SWCNT (CG200) suspensions with
different concentrations in the range from 4 to 30 µg/mL by diluting the parent high-concentration suspension with Nanopure water while keeping the concentration of DOC the same (0.05%). In addition, we adjusted the filtrated volume so as to keep the obtained film thickness comparable.

Experimental results showed that alignment started degrading when the CNT concentration became higher than a certain value. Specifically, for the CG 200 sample, this threshold concentration was ~ 20 µg/mL as shown in Figure 4.7.

![Figure 4.7](image)

**Figure 4.7** The SWCNT (CG200) concentration dependence of CNT alignment. (a) Absorption spectra for CNT suspensions with different concentrations. Inset: SWCNT suspensions with decreasing concentration from 30 µg/mL to 4 µg/mL. (b) The $LD^r$ value of aligned CNT films as a function of CNT concentration.

The trend observed here is totally opposite to the case of 3D liquid-crystal phase transitions, where a much higher concentration of CNTs (~ 5 mg/mL) is
required to drive the system from an isotropic phase into an anisotropic phase [94].

Instead, our observation can be understood in the context of 2D nematic ordering. When an ordered phase occurs in a 2D manner, the bulk concentration does not need to be very high because of the natural accumulation of CNTs in a confined layer. In our experiments, at a steady filtration speed, individual CNTs sequentially fall into a confined layer near the surface, leading to an increase of the surface density of CNTs in the confined region. In addition, as discussed before, the formation of alignment requires rearrangements of CNTs. When the CNT concentration is higher, there will be more CNTs falling onto a given position in a given time interval (i.e., $\Delta T$ in Equation (4.9) decreased), which means that they cannot fully align, leading to a decrease in alignment strength. Furthermore, a higher CNT concentration, especially near the 2D surface, will lead to stronger CNT entanglement and lower rotational diffusivity [98, 101], both of which will decrease $\Delta T$, further disfavoring alignment.

### 4.3.3. Surfactant concentration

Next we studied how the degree of alignment changes as we change the surfactant concentration. In this study, we fixed the concentration of CNTs at $\sim 15 \, \mu g/mL$ and varied the concentration of DOC surfactant from 0.03 to 0.5%. We also kept the filtration speed low, as described in Section 4.3.1. As shown in Figure 4.8, the $LD_T$ value decreased dramatically when the concentration of DOC surfactant became larger than the critical micelle concentration (CMC), which is $\sim 6 \, \text{mM}$ or $\sim 0.24\%$ wt./vol. DOC. This result, together with an SEM image, shows that the
formation of CNT alignment is strongly suppressed when the concentration of DOC is too high. Filtration being performed with a surfactant concentration above its CMC is one of the reasons why vacuum filtration usually resulted in random networks of CNTs instead of aligned CNT films.

As the surfactant concentration becomes higher than the CMC, strong attractive depletion interactions from the micelle of surfactant start to lead to re-aggregation of CNTs [124, 125] and as a consequence, CNT entanglement becomes much stronger reducing the rotational diffusivity in the 2D phase. This entanglement effect will disfavor ordered structure formation and degrade the degree of alignment.

Figure 4.8 (a) The $LD^r$ of CNT films (CG 200) as a function of surfactant (DOC) concentration. (b) SEM image of a film made from a CNT suspension with 0.35% DOC concentration.
4.3.4. Hydrophobicity of the filter membrane surface

Another important factor that affects the degree of alignment of the resultant CNT film is the hydrophobicity of the surface of the filter membrane. For this study, we used two types (Type A and Type B) of polycarbonate filter membranes to fabricated films of arc-discharge SWCNTs (P2-SWCNT). The concentration of P2-SWCNT suspension was fixed at 15 \( \mu g/ml \). In Type A filter membranes, the surfaces were coated with a layer of poly (vinylpyrrolidone) (PVP) and therefore were hydrophilic, while the surface of Type B filter membranes were hydrophobic without PVP coating. We detected the presence of PVP coating through the nitrogen 1s (N1s) peak in XPS spectra. As shown in Figure 4.9(a), the nitrogen peak can be clearly seen for a Type A filter membrane but is absent for a Type B filter membrane. We found that strong, global alignment of CNT can occur only on Type A filter membranes [see Figure 4.9(b)]. For CNT films made using Type B filter membranes, the polarization dependence of absorption was weak, indicating that CNT alignment was poor without a PVP coating.

It is known that PVP molecules are polar and have strong interaction with water molecules through hydrogen bonds. This property makes a PVP-coated surface hydrophilic. When PVP molecules interact with water, hydration shells form around the carbonyl groups of PVP. The outside of the hydration shells is covered by negatively polarized oxygen atoms [126]. In addition, PVP molecules have strong interaction with anionic surfactants; its flexible polymer chain can effectively trap surfactants in a solution [127]. Both the formation of hydration shells and the trap
of anionic surfactants will lead to an accumulation of negative charges in the PVP layer.

When negatively charged CNTs, due to the wrapping of negatively charged surfactants, approach the surface, they will face an energy barrier due to the electrostatic repulsion from the PVP layer. At the same time, they will also feel an attraction from the surface due to the van der Waals interactions. According to a previous report[100], the competition between these two forces can create a potential well near the surface, where CNTs are confined in a narrow layer, and an ordered 2D phase appears, as we mentioned before. Thus we believe that the importance of PVP coating is that it makes the filter membrane surface negatively charged, allowing the formation of a potential well near the surface. When CNTs can rotate in the plane and organize themselves in this confined layer, a 2D nematic phase can occur at an appropriate surface concentration. For a PVP-free membrane, there is no electrostatic force to compete with the van der Waals attraction; the absence of a potential well near the surface will make CNTs directly fall down and thus are nearly “stuck” on the surface. Their in-plane mobility on the surface will be severely limited due to the van der Waals attraction, which then suppresses the formation of an ordered phase.
Figure 4.9 (a) X-ray photoelectron spectroscopy of a PVP-coated and PVP-free filter membrane. (b) Polarization dependent absorption (660 nm) of the CNT films prepared on filter membranes with and without PVP coating.

In addition to a PVP coating, the surface hydrophilicity of filter membrane can be engineered by active argon/oxygen plasma treatment [128]. We performed surface treatment of a PVP-free filter membrane using a plasma cleaner (Model 1020, E.A. Fischione Instruments, Inc.). A mixture gas of 25% oxygen and 75% argon was fed into the reaction chamber and a plasma was generated by an oscillating electromagnetic field (13.56 MHz). Ions in the plasma impinged upon the membrane surface with energies of less than 12 eV, which was below the membrane’s sputtering threshold and thus did not pollute the membrane surface. The membrane was mounted on a glass slide with the shiny filtration surface facing up. Radical sites were created by the argon bombardment and subsequently oxidized due to the
presence of oxygen atoms. Polar groups (-COH, -CO, -COOH) were created by recombination of oxygen atoms and the radical sites obtained after homolytic scissions of the polycarbonate –C-C- and –C-H covalent bonds, as shown in Figure 4.10(a) [128]. The incorporation of the oxygen plasma led to a significant increase of the oxygen atom percentage at the surface of the polycarbonate filter membrane, as confirmed by the XPS spectra shown in Figure 4.10(b).

By varying the plasma treatment time, the hydrophilicity of the filter membrane can be systematically controlled, as demonstrated in Figure 4.10(c). We fixed filtration pressure during the different experiments. We found that the filtration speed became much higher with increasing treatment time, likely due to better water intrusion with increasing hydrophilicity [129]. Initially, with a PVP-free filter membrane, the absence of a potential well near the membrane surface leads to weak alignment, as we described above. With increasing hydrophilicity to balance the van der Waals interaction, the optimal potential well height was achieved to facilitate CNT alignment in the 2D phase [see Figure 4.10(d)]. Further increase of the hydrophilicity of the membrane surface leads to the dominance of the repulsive force, which in turn diminishes the potential well height. In addition, the filtration speed increases, as evidenced by the less time required for CNTs to align, which further degraded the degree of alignment, as shown in Figure 4.10(d).
Figure 4.10 Surface engineering of filter membrane surfaces to control the degree of alignment of arc-discharge P2-SWCNT films produced by vacuum filtration. (a) Schematic of argon/oxygen plasma treatment to engineer the hydrophilicity of filter membrane. (b) XPS spectra of a PVP-free membrane before and after plasma treatment. (c) Filtration speed and (d) $LD^r$ value change as a function of plasma treatment time.

**4.3.5. Carbon nanotube length and diameter**

As shown Table 3-1, we used different types of SWCNTs to demonstrate the universal applicability of our vacuum filtration method for preparing wafer-scale
monodomain films of aligned CNTs. Although there was no obvious relationship observed between the structure parameters of SWCNTs and the achieved values of S, we found that arc-discharge SWCNTs tend to align more strongly than other types of nanotubes. To further investigate the influence of SWCNT structure information, systematic studies using length-sorted and diameter-sorted samples are needed. Such studies are described in this section.

We used arc-discharge P2-SWCNT (d ~ 1.4 nm) suspensions with different tip sonication times in our length-dependent studies. It is known that the sonication process can induce a scission effect on CNTs [130], which decreases the tube length with increasing sonication time. As shown in Figure 4.11, different tube lengths were achieved. We adjusted the CNT concentration in the suspension according to the absorbance spectra obtained after tip sonication and ultracentrifugation to have comparable film thicknesses. As expected from Onsager's theory, we found that higher aspect-ratio nanotubes lead to higher degrees of alignment as demonstrated in Figure 4.12. From the AFM images in Figure 4.11, we can see that individual CNTs look like 'rigid rods'. Hence, the hard-rod model of Onsager theory fits well for arc-discharge tubes.
Figure 4.11 Lengths of arc-discharge P2-SWCNT after tip sonication of different times. (a)-(c) AFM images and (d)-(f) corresponding length distributions.

Figure 4.12 (a) $L_D^r$ value and (b) angle dependent absorbance at 660 nm of aligned films made from different batches of arc-discharge P2-SWCNTs with different average tube lengths.
In addition to arc-discharge nanotubes, we also used CoMoCAT SG65i nanotubes ($d \sim 0.73$ nm) with different tip sonication times, in order to investigate the length dependence of alignment for smaller-diameter tubes, as shown in Figure 4.13. Again, we adjusted the CNT concentration according to absorbance spectra after tip sonication and ultracentrifugation to have comparable film thicknesses. Here, we obtained completely opposite length dependence (Figure 4.14): the degree of alignment decreased with increasing tube length.

A clue to this dramatically different length dependence between the SG65i and P2-SWCNT samples can be obtained by comparing the AFM images in Figure 4.11 and Figure 4.13. Unlike the rigid-rod-like arc-discharge nanotubes, the CoMoCAT nanotubes are bent [130], sometimes even with more kinks and junctions. The bending stiffness of a CNT is proportional to the cube of the CNT diameter [131], CNTs of smaller diameters being much less stiff compared to CNTs of larger diameters. Hence, smaller-diameter nanotubes are expected to be more sensitive to their environment and tend to get bent and entangled more easily in the presence of external disturbances, leading to less-ideal alignment structures. By making the tubes shorter through cutting, we found that the alignment strength of small-diameter tubes can be improved. With less kinks and junctions, as shown in Figure 4.13(c), tubes after cutting behave more like rigid rods, and thus, a better degree of alignment was achieved.
Figure 4.13 Lengths of CoMoCAT SG65i nanotubes after sonication of different durations. (a)-(c) AFM images and (d)-(f) corresponding length distributions.

Figure 4.14 (a) LD$^r$ value and (b) angle dependent absorbance at 660 nm of aligned films made from different batches of CoMoCAT SG65i nanotubes with different lengths.
In order to study how the CNT diameter influences the alignment strength, we used diameter-sorted nanotube suspensions prepared from the same batch of HiPco CNTs (batch #195.5). CNTs with diameters smaller than \(~0.8\) nm were removed from the original sample because of the diameter sorting capability of the ATPE method [Figure 4.15(a)]. Shown in Figure 4.15(b) are polarization-dependent absorption spectra of a diameter-sorted sample and the original sample. Note that the filtration conditions for the two samples were kept the same. The increase of \(LD_r\) from \(~0.4\) to \(~0.6\) indicates an enhancement of the degree of alignment through removal of small-diameter CNTs, which further confirms the diameter (bending stiffness) influence on the degree of alignment.

Figure 4.15  (a) Absorption spectra of HiPco SWCNT suspensions with (red) and without (black) the removal of small diameter tubes. (b) The absorption angular dependence of CNT films made from the original sample (red) and the sorted
sample (black) using a polarized laser beam (660 nm). The increase of $LDr$ indicates an improvement of CNT alignment.
Chapter 5

Chirality-Enriched Aligned Films for Device Applications

Our vacuum filtration method not only works for as-grown SWCNTs of mixed electronic types but also can be combined with solution-based chirality separation techniques to achieve chirality-enriched aligned films for a wide range of electronic and optoelectronic device applications. This approach possesses great advantages over direct-growth methods to prepare macroscopically aligned CNT films by overcoming the polydispersity of CNT chiralities during growth.

In Section 5.1, we briefly review solution-based chirality separation techniques including the DNA-wrapping technique, density gradient ultracentrifugation (DGU), gel chromatography, and aqueous two-phase extraction (ATPE). In Section 5.2, we successfully fabricated globally aligned chirality-enriched CNT films by filtrating chirality-enriched CNT suspensions prepared using the gel chromatography and ATPE methods. We describe performance characteristics of
fabricated optoelectronic devices such as polarized luminescent devices and polarization-sensitive photodetectors (in Section 5.3) and a field-effect-transistor electronic device (in Section 5.4).

5.1. Solution-based chirality separation techniques

Solution-based separation techniques can be used to separate SWCNTs not only by electronic types but also by diameters, chiralities, and right/left handedness. In this approach, SWCNTs are dispersed in an aqueous solution and selectively wrapped by dispersants, depending on their electronic types, diameters or chiralities. Chirality-specific chemical processes/properties have to be enhanced for an effective separation [132, 133], and different techniques have been developed, such as the DNA-wrapping technique [75, 76], DGU [77, 78], gel chromatography [79], and ATPE [82, 83].

**DNA Wrapping** DNA molecules have been proven to form ordered structures on SWCNTs through helical wrapping around SWCNT sidewalls. A specific type of DNA likes to pick up SWCNTs of a particular chirality based on its sequence. DNA-wrapped SWCNTs carry negative charges due to a phosphate group of a DNA molecule, and different chirality SWCNTs have different surface charge densities when wrapped by DNA molecules. This subtle selectivity can be enhanced through ion-exchange chromatography (IEX) with a positively charged resin. As a consequence, DNA-SWCNTs are sorted out from each other by different interaction strengths with ionic gels [76]. Later, a more systematic study using more than 20
DNA sequences demonstrated separation of particular \((n,m)\) SWCNTs, and up to 12 chiralities of SWCNTs were successfully separated [75]. However, the DNA-wrapping method is not only limited in scalability but also cost inefficient because of the requirements of specific DNA molecules.

![Diagram of DNA-wrapped SWCNT](image)

Figure 5.1 (a) Schematic diagram of a DNA-wrapped SWCNT and (b) absorption spectra for different-chirality SWCNTs separated by IEX. Adapted from [75].

**DGU** DGU is a bio-inspired separation technique to separate SWCNTs through subtle selectivity based on the different buoyant densities of SWCNTs of different chiralities. In this method, the density differences among different-chirality SWCNTs are enhanced by a linear or nonlinear density gradient [77, 78] where SWCNT suspensions are filled inside a centrifuge tube. Different-chirality SWCNTs
will move to different equilibrium points where their respective buoyant densities match the local densities in the gradient under ultracentrifugation, which leads to separation of SWCNTs into different layers in the centrifuge tube, as shown in Figure 5.2.

![Figure 5.2](image)

Figure 5.2 The DGU method for SWCNT separation. (a) Photograph of different-chirality SWCNTs staying in different layers of a centrifuge tube where their buoyant density matches the local density in the gradient and (b) corresponding optical absorption spectra. Adapted from [77].

By engineering surfactant combinations, both electronic type separation and chirality separation can be achieved with a very high degree of purity. However, the DGU method is also limited in terms of scalability due to its long separation time.
(e.g., up to tens of hours for only a few hundreds of microliters volume separated suspensions). In order to facilitate large-scale separation, the gel chromatography method and the ATPE method are more promising.

**Gel Chromatography** Gel chromatography is a widely used separation technique to separate constituents from a mixture based on the different travelling speeds of various components of different molecule sizes, charge densities, etc. Specifically, when SWCNTs are wrapped by sodium dodecyl sulphate (SDS) molecules, the adsorption efficiencies of SDS molecules onto metallic and semiconducting CNT sidewalls are different, and thus the degrees of hydrophilicity of wrapped metallic and semiconducting CNTs are different. As a consequence, the adsorption abilities of wrapped metallic and semiconducting SWCNTs onto hydrogels filled in a long column are different. The long column is used to enhance the selectivity that metallic SWCNTs move much faster with less adsorption than semiconducting SWCNTs for separating different electronic types of SWCNTs [80, 81]. Later, combined with an overloading effect and a cascading multicolumn technique [Figure 5.3(a)], large-scale separation of single-chirality SWCNTs was achieved [79] [see Figure 5.3(b)]. Gel chromatography is a time-efficient and cost-efficient method with potential scalability.
Figure 5.3 (a) Schematic diagram of a single-surfactant multicolumn gel chromatography method to separate different-chirality SWCNTs and (b) liters of SWCNTs enriched in specific electronic types and chiralities. Adapted from [79].

**ATPE** Another large-scale SWCNT separation technique recently developed is the ATPE method, which has been widely used in biochemistry for non-denaturing and benign separations. One common two-phase system consists of two polymers, dextran and polyethylene glycol (PEG), where the former is more hydrophilic and the latter is more hydrophobic. As in the gel chromatography method, different SWCNTs have subtle hydrophilicity differences when they are wrapped by dispersants. Entropy-driven spontaneous partition happens when dispersant-wrapped SWCNTs mix with two polymers [Figure 5.4(a)] [83]. Careful selection of combinations of dispersants results in sequential, rapid, and high-purity separation of SWCNTs not only in terms of electronic types but also chiralities [Figure 5.4(b)] in an efficient and scalable manner [82].
Figure 5.4 (a) A schematic diagram of the aqueous two phase extraction method to separate different chiralities SWCNTs and (b) separated SWCNT suspensions enriched in specific electronic type and chiralities. Adapted from [82].

5.2. Globally aligned chirality-enriched carbon nanotube film

To fabricate globally aligned chirality-enriched carbon nanotube films, we used the large-scale separation techniques of gel chromatography and ATPE combined with our vacuum filtration method.

We used the gel chromatography method to obtain large-scale suspensions of metallic-enriched SWCNTs and (10,3)-enriched semiconducting SWCNTs from a raw HiPco sample [see Figure 5.5(a)]. Absorption spectra for the obtained suspensions are shown in Figure 5.5(b) and (c). A photoluminescence excitation (PLE) map for
the (10, 3) suspension is shown in Figure 5.5(d), demonstrating high-purity separation with only a trace amount of other semiconducting species.

Figure 5.5 Gel chromatography separated SWCNT suspensions. (a) Photograph of metallic-enriched and (10, 3)-enriched SWCNT suspensions on a large scale and their respective absorption spectra in (b) and (c). (d) PLE map for the (10, 3)-enriched SWCNT suspension.

We also used the ATPE method to enrich SWCNTs of specific chiralities. First, we performed a simple two-step process to achieve SWCNT separation based on diameters. Preferential encapsulation of SWCNTs by various surfactants as well as their particular influence on the hydrophilicity of SWCNTs have been investigated
which showed that sodium cholate (SC) and sodium deoxycholate (DOC) have stronger affinities for smaller diameter tubes, while SDS has a greater affinity toward larger diameter tubes. Furthermore, SC- and DOC-wrapped SWCNTs are more hydrophilic and tend to move towards the bottom dextran phase, while SDS-wrapped SWCNT are more hydrophobic and tend to move towards the top PEG phase, based on which a two-step strategy was developed to achieve diameter-dependent separation. Following that, metal-semiconductor separation was achieved by changing surfactants to SC-SDS and reducing the DOC concentration to a very low value (<0.01% wt./vol.). A certain amount of oxidant was added to enhance the separation fidelity, which was proven to alter the micelle structure on SWCNTs to modify the hydrophilicity [135].

Specifically in our study, we dispersed SG65i SWCNTs (Sigma-Aldrich) using 1% (wt./vol.) DOC of a concentration of 500 µg/mL. We prepared three stock solutions for the two-step diameter separation process (ST$_1$ and ST$_2$) and the subsequent metal-semiconductor separation process (M/S bottom mimic). The components of every stock solution are listed in Table 5-1. For the two-step separation procedures, we first added 2.15 mL SWCNT suspensions with a mixture of 4.25 mL H$_2$O (Nanopure water) and 40.8 mL ST$_1$. After phase separation that occurred during gentle centrifugation (~2000 rad/s), ~ 5 mL ST$_1^B$ of dark pink color was collected while ~ 42 mL ST$_1^T$ of green grey color was discarded (where “B” and “T” stand for the bottom and top phases, respectively). Second, we mixed ~ 5mL ST$_1^B$ with equal volume of ST$_2$ and an addition of ~ 130 µL 4% (wt./vol.) DOC to adjust the DOC concentration for better diameter separation. After the partition, ~
22 mL ST$_2^T$ of pink color in the top phase was enriched in (6, 5) SWCNTs as well as SWCNTs of similar diameters, while ~ 18 mL ST$_2^B$ of light pink color in the bottom phase was enriched in (6, 4) SWCNTs, as shown in Figure 5.6(a). We mixed an equal volume of the M/S bottom mimic solution with the top phase of each separation step for three times to reduce the DOC concentration to a value lower than 0.01%. As the final step, we mixed ~ 16 mL ST$_2^T$M$_T^M$T with 16 mL M/S bottom mimic solution, 0.35 mL 0.1%-0.15% (wt./vol.) sodium hypochlorite (NaClO) solution and 1.4 mL 10% (wt./vol.) SC to remove metallic tubes from the (6,5)-enriched suspension, as shown in Figure 5.6(b). Note that the specific volume of added solution at each step can be scaled up while keeping the same ratio of different components.

Table 5-1 Stock solution components

<table>
<thead>
<tr>
<th>Stock</th>
<th>Dextran(g)</th>
<th>PEG(g)</th>
<th>SDS(g)</th>
<th>SC(g)</th>
<th>DOC(g)</th>
<th>NaCl(g)</th>
<th>H$_2$O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST$_1$</td>
<td>4.9</td>
<td>14.1</td>
<td>1.117</td>
<td>0.49</td>
<td>0</td>
<td>0.142</td>
<td>100</td>
</tr>
<tr>
<td>ST$_2$</td>
<td>2.33</td>
<td>14.5</td>
<td>1.8</td>
<td>0</td>
<td>0.0473</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>M/S Bottom</td>
<td>12.5</td>
<td>2.5</td>
<td>0.7</td>
<td>0.9</td>
<td>0</td>
<td>0</td>
<td>83.4</td>
</tr>
</tbody>
</table>

An absorption spectrum and a PLE map for the collected ST$_2^T$M$_T^M$T$_M$T top phase are shown in Figure 5.6(c) and (d), respectively. Metallic tubes were successfully removed, while the presence of a small amount of semiconductor impurities such as (8,4) and (9,1) tubes can be seen in these spectra.
Figure 5.6 (a) Photograph of a (6,5)-enriched suspension in the top phase after the two-step diameter separation procedure. (b) Photograph of a (6,5)-enriched suspension in the top phase after the metal-semiconductor separation process. (c) Absorption spectrum and (d) PLE map for the prepared (6,5)-enriched suspension.

In addition to semiconducting SWCNTs, we also separated other chirality SWCNTs, such as armchair (6,6) SWCNTs and quasi-metallic (7,4) SWCNTs, using the ATPE method, as summarized in Figure 5.7.
Figure 5.7 ATPE-separated (6,6) and (7,4) SWCNT suspensions. (a) Photographs and absorption spectra of (b) a (6,6) suspension and (c) a (7,4) suspension.

Gel chromatography-separated and ATPE-separated chirality-enriched suspensions are typically mixed with multiple surfactants and/or polymers, which all have detrimental effects on the degree of alignment of produced films using our vacuum filtration method. Therefore, certain cleaning procedures are required to exchange surfactants and remove polymers inside the separated suspensions. To achieve this goal, we used two strategies: 1) precipitation and 2) ultrafiltration.
Precipitation. Depletion-induced interactions and phase separation phenomena in polymer-colloid mixtures are generally studied in cell biology and biochemistry [136]. The presence of polymers creates a crowding environment in a colloid system, where entropic effects result in an attractive force (i.e., depletion force) among colloidal particles, driving them to form large-size clusters (i.e., phase separation). As a result, selective precipitation of colloidal particles can be achieved by controlling the crowding conditions, such as modifying the concentration of polymers. This method has been applied for length-dependent separation of DNA-wrapped CNTs in PEG polymers [137]. Here, we modified this method to selectively precipitate SWCNTs for the purpose of removing PEG molecules. Because surfactant-encapsulated SWCNTs are charged, strong electrostatic repulsive force will compete with the depletion attractive force when two nanotubes are close to each other. As a result, SWCNT aggregation cannot occur simply by increasing the concentration of PEG polymers. This problem can be circumvented by increasing the salt concentration in the system, which leads to strong screening of the electrostatic repulsive force and allows formation of clusters of SWCNTs. Once SWCNTs form clusters under appropriate concentrations of salts and PEG polymers, they can be separated from the PEG phase by gentle centrifugation. The only limitation of this method is that the concentration of SWCNTs needs to be sufficiently high (typically > 20 μg/mL); otherwise, they cannot be precipitated.

Specifically in our study, we adjusted the PEG concentration to a value greater than 10% (typically 12.5%); we adjusted the DOC concentration to 0.1% and increased the NaSCN concentration to 0.25M. We incubated the mixed suspension
for ~10 minutes and then centrifuged it for ~30 minutes. The aggregated SWCNTs formed a pellet near the bottom of the centrifuge tube, and we removed the clear PEG solution from the top by pipetting. In this way, almost all PEG molecules were removed.

**Ultrafiltration** To completely remove polymers, exchange surfactants, and adjust the SWCNT suspension concentration, we found ultrafiltration to be an efficient method. The principle of ultrafiltration is to separate molecules depending on molecular weights (MWs), which is realized using a porous membrane in a sealed cell under strong force. Different ultrafiltration membranes have different values of molecular weight cut-off (MWCO), and molecules of MWs smaller than this value will pass the membrane, while molecules of MWs larger than this value will be blocked. A strong force during ultrafiltration can be implemented by applying a high gas pressure or using a swing centrifuge force. Selecting an ultrafiltration membrane with an appropriate MWCO value is crucial for successful removal of polymers from SWCNT suspensions. The MWs of SWCNTs are normally larger than 300 kDa, while the MWs of PEG and dextran polymers used in the ATPE method are 6 kDa and 70 kDa, respectively. Therefore, we chose to use an ultrafiltration membrane with a 100 kDa MWCO for filtering PEG and dextran molecules while retaining SWCNTs in the suspension. We used Amicon Ultra-15 Centrifugal Filter Unit (Millipore) of a 100 kDa MWCO membrane with a short spin time and a short recovery time for time-efficient ultrafiltration. To remove residual polymers after precipitation procedures, we used 0.5% DOC solution to do ultrafiltration repetitively for tens of times, and then 0.5% DOC solution was exchanged to 0.04%
DOC solution to reduce the concentration of surfactants, which is a necessary
condition to have a good degree of alignment. Note that, with a surfactant
concentration below CMC, SWCNTs strongly aggregate during the ultrafiltration
process. Repetitive pipetting helps remove SWCNTs from the ultrafiltration
membrane. We adjusted the final suspension volume by changing the centrifuge
time to have an appropriate suspension concentration.

After the precipitation and ultrafiltration procedures, we used tip sonication
to cut tubes to an appropriate length, as described in Section 4.3.5. We then
centrifuged the suspension for ~1 hour at 38000 rpm, collected the upper 60% of
the supernatant was collected, and then diluted it with Nanopure water for making
films. We used a PVP-free filter membrane of a 100 nm pore size (Sterlitech), which
was treated by an Ar/O₂ plasma, as described in Section 4.3.4. Under optimized
conditions, obtained films showed good alignment, as confirmed by polarized
absorption spectra (Figure 5.8).
Figure 5.8 Polarized absorption spectra for globally aligned chirality-enriched SWCNT films in the $S_{11}$ ($M_{11}$) range. (a) Metallic-enriched SWCNT film. (b) (10,3)-enriched SWCNT film. (c) (6,5)-enriched SWCNT film.

5.3. Optoelectronic devices

Globally aligned chirality-enriched carbon nanotube films open a new way to fabricating macroscopic CNT optoelectronic devices and electronic devices.
5.3.1. Polarized luminescent devices

The radiative decay of excitons in semiconducting SWCNTs produces narrow-band luminescence, which is promising for making devices with tunable emission energies that are dependent on the SWCNT band gap. When SWCNTs are macroscopically assembled in an ordered manner, emitted light is strongly polarized due to the 1D nature of electronic and excitonic states in SWCNTs. A fabricated (6,5)-enriched macroscopically aligned film showed strongly polarized photoluminescence [see Figure 5.9 (a) and (b)]. This macroscopic manifestation of light emission anisotropy not only provides evidence that the CNTs in the film are highly aligned but also proves that there are very few residual metallic tubes, which are known to be efficient photoluminescence quenchers when in contact with semiconducting nanotubes. A fabricated (10,3)-enriched macroscopically aligned film, which has a larger diameter than (6,5) tubes, also showed strongly polarized photoluminescence at a correspondingly longer wavelength. These results open up new possibilities of developing SWCNT-based light sources for producing polarized monochromatic radiation.
Figure 5.9 (a) Strongly polarized photoluminescence spectra for an aligned and (6,5)-enriched SWCNT film, showing stronger emission polarized parallel to the CNT alignment direction. (b) Polar plot of the intensity of the emitted photoluminescence from the aligned and (6,5)-enriched SWCNT film. (c) Strongly-polarized photoluminescence spectra for an aligned and (10,3)-enriched SWCNT film.

5.3.2. Polarization-sensitive photo-detectors

In addition to luminescent devices, we fabricated a two-terminal photodetector based on macroscopically aligned and (6,5)-enriched SWCNT films
We cut an aligned (6,5) nanotube film into ribbons and then transferred a ribbon onto a glass substrate. We formed two electrodes by sputtering 50-nm gold, using a shadow mask at the two ends of the ribbon. A 660-nm laser beam with a maximum power of ~50 mW was incident near a gold-CNT junction. Due to the Seebeck coefficient difference between the exposed SWCNT film in the channel and the SWCNT film underneath the electrode, a photovoltage was generated through the photothermoelectric (PTE) effect [55-57]. We used a half-wave plate to rotate the polarization of the incident light beam without changing the incident power. The generated photovoltage was amplified by a Stanford Research SR560 voltage preamplifier and then fed into a Stanford Research SR830 lock-in amplifier.

This device exhibited strongly polarization-sensitive photosignal [Figure 5.10(b)], where the polarimetry is intrinsic to the active photodetector material. The polarization ratio of the photosignal magnitude was ~2:1. The responsivity of the photodetector was estimated to be ~0.1 V/W, after taking into account the actual power absorption of ~3.1 mW when the light polarization is parallel to the CNT alignment direction. Compared to previous photodetectors with the same device architecture but consisting of a mixture of metallic and semiconducting SWCNTs [57], the responsivity of the current photodetector was enhanced by at least three times [Figure 5.10(c)], most likely due to the removal of metallic tubes. It should be noted, however, that the device design was not fully optimized. With proper thermal management through selection and adjustment of substrates and other critical
elements [56], the detector performance can be further improved for a better SWCNT polarization-sensitive photodetector.

Figure 5.10 (a) Schematic diagram showing the photodetector device fabricated from an aligned and (6,5)-enriched CNT film. (b) Polarization-dependent photovoltage observed for the device shown in (a), with (c) an improved responsivity ~0.1 V/W compared with a structurally similar device made of unsorted SWCNTs [57].

5.4. Electronic devices

SWCNTs have been used as conducting channel materials in field effect transistors (FETs) as a promising alternative to silicon-based FETs. FET devices
made from macroscopically aligned and chirality-enriched SWCNT films are expected to have extraordinary transistor performance, as discussed in Section 2.2.

Here, we investigated transistor behaviors of a (6,5)-enriched aligned film. The film was transferred onto a substrate comprised of heavily doped silicon (acting as a global back gate) and a 285-nm thick layer of thermal silicon oxide (acting as an insulating layer). The first photolithography step was to define the electrode area with Shipley Microposit S1813 photoresist. The electrodes were defined and fabricated by lifting off electron-beam-evaporated titanium (1 nm) / palladium (10 nm) / gold (20 nm). The next step was to define a Hall bar structure with one channel parallel and the others perpendicular to the CNT alignment direction, as shown in Figure 5.11. We performed field effect transistor measurements under vacuum (~1 × 10⁻⁵ torr), using a Keithley 2634B source meter (for the source-drain voltage) and a Keithley 2400 source meter (for the gate voltage).

Figure 5.11 False-color scanning electron microscopy images of a thin-film transistor with a channel width of ~5 μm and a channel length of ~30 μm made from an aligned and (6,5)-enriched CNT film.
One crucial point to achieve a good FET behavior is complete removal of metallic tubes to avoid the percolation effect [138, 139], which is especially important for an aligned structure. When the metallic tube density is above the percolation threshold, the drain-source current is pinned by the percolation path formed by metallic tubes, and thus, the on/off ratio will severely degrade. We fabricated two structurally identical FET devices using aligned (6,5)-enriched films with different degrees of purity (90% and >98%). As shown in Figure 5.12, the on/off ratio dramatically degrades with the increase of the metallic tube density. In order to achieve a high on/off ratio, metal-semiconductor separation in the ATPE method needs to be well conducted.

Figure 5.12 The influence of the percolation effect due to residual metallic tubes on the on/off ratio of FETs made from (6,5)-enriched aligned films.
As shown in Figure 5.13 the on-current density of a transistor made from a highly purified (6, 5) enriched aligned film in the parallel (perpendicular) direction is ~2 nA/µm (~80 pA/µm), indicating that the on-current density can be improved by aligning CNTs in one direction. Note that these nearly intrinsic semiconducting films are naturally much less conducting than purely metallic films or films with mixed electronic types. As shown previously [140], the on-current density can also be enhanced by using larger-diameter nanotubes, which is also demonstrated by our transistor based on semiconductor-enriched arc-discharge CNTs with an average diameter of 1.4 nm [Figure 5.13(b)]. The device showed an enhancement of on-current density by ~50 times compared to the (6,5) CNT transistor at the same drain-source voltage. The on-off ratios of our transistors are around $10^3$, which are comparable to previous results for transistors made from aligned CNT films. The relatively low on-off ratio is ascribed to the charge screening effect caused by the high packing of CNTs in one direction. It can be potentially overcome by using a high-$\kappa$ dielectric material or using a top-gate architecture [93].
Figure 5.13 (a) The source-drain current versus source-drain voltage of an aligned (6,5)-enriched thin-film transistor at zero gate voltage, showing anisotropic conductivities. (b) The source-drain current at a source-drain voltage of 1 V versus gate voltage of the (6,5)-enriched transistor, showing large and anisotropic transistor action. The on-current density is enhanced by 50 times in a transistor made from larger-diameter semiconductor-enriched arc-discharge SWCNTs.
Conclusions and Future work

6.1. Conclusions

We developed a new process of vacuum filtration to produce a wafer-scale (i.e., inch-size) film of aligned SWCNTs in this thesis work. This method works for SWCNTs synthesized by various methods and can be scaled in all three dimensions (i.e., the lateral size and thickness). We fully characterized the produced large-area films through different microscopy, spectroscopy, and transport methods, demonstrating perfect global alignment with extraordinary photonic and optoelectronic properties. We created ideal terahertz/infrared polarizers using this approach.

The strikingly high degree of alignment of our films with a nematic order parameter of ~ 1 and a thickness of ~ 100 nm distinguishes our method from both existing two-dimensional and three-dimensional post-growth assembly techniques.
We investigated the underlying mechanisms based on a proposed model of 2D confinement induced phase transitions. We identified the factors that affect the degree of alignment, including the filtration speed, the SWCNT concentration, the surfactant concentration, the hydrophilicity of the filter membrane surface, the SWCNT length, and the SWCNT diameter.

Furthermore, combined with well-developed solution-based chirality separation techniques (the gel chromatography and ATPE method), we produced globally aligned and chirality-enriched films under optimized conditions. These SWCNT films are promising for optoelectronic and electronic device applications. As examples, we demonstrated polarized luminescent devices, polarization-sensitive photodetectors, and thin-film transistors, using aligned semiconducting SWCNT films.

Wafer-scale aligned SWCNT films produced by our vacuum filtration method will open a range of new opportunities not only for fundamental research of physics, chemistry, and materials science but also for applications in electronics, optoelectronics, sensing, imaging, and medicine.

6.2. Future work

Chirality-enriched macroscopically aligned SWCNT films prepared using our vacuum filtration method promise a host of new research directions, both fundamental and applied, utilizing low-dimensional carbon materials and their heterostructures. For example, combined with other types of modern low-
dimensional materials, such as graphene, hexagonal boron nitride, and transition metal dichalcogenides, ultimate quantum engineering can be realized via van der Waals heterostructures, as schematically shown in Figure 6.1.

Figure 6.1 Schematic diagram of ultimate quantum engineering via van der Waals heterostructures combining different types of modern low-dimensional materials.
Bibliography


