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Wafer-Scale Films of Aligned Single-Wall Carbon Nanotubes: Preparation, Characterization, and Optoelectronic Applications

by

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ABSTRACT

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Single-wall carbon nanotubes (SWCNTs) are one-dimensional materials defined by a cylindrical and hollow structure with aspect ratios of up to $10^7$:1. Individual SWCNTs have been shown to possess excellent electric, optical, thermal, and mechanical properties that are promising for electronic and optoelectronic device applications. However, when they are assembled into macroscopic objects such as films and fibers, these unique properties tend to vanish, primarily due to disorder. Hence, methods are being sought for fabricating ordered SWCNT assemblies for the development of high-performance devices based on SWCNTs. In this dissertation, we present two methods for preparing highly aligned SWCNT films with excellent optoelectronic properties. The first method is based on vertically aligned SWCNT arrays grown by water-assisted chemical vapor deposition. We transferred these arrays to desired substrates to form horizontally aligned SWCNT films and created p-n junction devices that worked as flexible, room-temperature-operating, and polarization-sensitive infrared and terahertz photodetectors. The second method is based on our discovery of spontaneous global alignment of SWCNTs that occurs
during vacuum filtration of SWCNT suspensions. By carefully controlling critical factors during vacuum filtration, we obtained wafer-scale, monodomain films of strongly aligned SWCNTs. By measuring polarization-dependent terahertz transmittance, we demonstrated ideal polarizer performance with large extinction ratios. The universality of this method was confirmed by applying it to diverse types of SWCNTs, all of which showed exceptionally high degrees of alignment. Furthermore, we successfully fabricated aligned SWCNT films enriched in one specific chirality by combining our new method with an advanced nanotube sorting technique: aqueous two-phase extraction. Transistors fabricated using such films showed very high conductivity anisotropies and excellent on-off ratios.
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<tr>
<td>ATPE</td>
<td>Aqueous two phase extraction</td>
</tr>
<tr>
<td>BFBD</td>
<td>Barrier free bipolar diode</td>
</tr>
<tr>
<td>BV</td>
<td>Benzyl biolgen</td>
</tr>
<tr>
<td>BHJ</td>
<td>Bulk heterojunction</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
</tr>
<tr>
<td>CDPF</td>
<td>Controlled differential pressure filtration</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>D*</td>
<td>Detectivity</td>
</tr>
<tr>
<td>DGU</td>
<td>Density gradient ultracentrifugation</td>
</tr>
<tr>
<td>DEP</td>
<td>Dielectrophoresis</td>
</tr>
<tr>
<td>ER</td>
<td>Extinction ratio</td>
</tr>
<tr>
<td>EL</td>
<td>Electroluminescence</td>
</tr>
<tr>
<td>EDSA</td>
<td>Evaporation driven self assembly</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>FET</td>
<td>Field-effect transistor</td>
</tr>
<tr>
<td>IEX</td>
<td>Ion-exchange chromatography</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
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<tr>
<td>LC</td>
<td>Liquid crystal</td>
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<td>LS</td>
<td>Langmuir-Shafter</td>
</tr>
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<td>LB</td>
<td>Langmuir-Blodgett</td>
</tr>
<tr>
<td>LED</td>
<td>Light emitting diode</td>
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<td>MW</td>
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</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>POM</td>
<td>Polarized optical microscopy</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltage</td>
</tr>
<tr>
<td>PC</td>
<td>Photocurrent</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>DOC</td>
<td>Sodium dexycholate</td>
</tr>
<tr>
<td>SC</td>
<td>Sodium cholate</td>
</tr>
<tr>
<td>SEC</td>
<td>Size exclusion chromatography</td>
</tr>
<tr>
<td>s-SWCNTs</td>
<td>Semiconducting SWCNTs</td>
</tr>
<tr>
<td>TFT</td>
<td>Thin film transistor</td>
</tr>
<tr>
<td>TCR</td>
<td>Temperature coefficient of resistance</td>
</tr>
<tr>
<td>G</td>
<td>Thermal conductance</td>
</tr>
<tr>
<td>THz</td>
<td>Terahertz</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1. Carbon-based electronics and optoelectronics: opportunities and challenges

Carbon nanomaterials, including fullerenes, carbon nanotubes (CNTs), and graphene, have stimulated a great deal of interest from both fundamental and applied points of view.[1-2] They represent prototypical material systems of zero dimension (fullerenes),[3] one dimension (carbon nanotubes),[4] and two dimensions (graphene).[5] While graphene is a two-dimensional (2D) system, consisting of a single layer of $sp^2$-bonded carbon atoms in a honeycomb lattice, CNTs possess a one-dimensional (1D) cylindrical structure that can be considered as a graphene sheet rolled up into a tube with high aspect ratios up to $10^7$.[6] Depending on the number of atomic layers, or concentric walls, they can be categorized into single-wall CNTs (SWCNTs), double-wall CNTs (DWCNTs), and multi-wall CNTs (MWCNTs).[7]
Since their discovery in 1991,[4] CNTs have attracted ever-lasting interest from diverse disciplines including chemistry, physics, materials science, and nanotechnology. These tiny tubes (typical diameter from ~0.5 to 3 nm) possess unusual electronic and optoelectronic properties valuable for a wide range of applications.[8-9] Firstly, SWCNTs are either metallic or semiconducting, determined by their chiral vectors (chirality).[10] The chirality of a SWCNT is characterized by a pair of integers, \((n,m)\), which define the way in which the graphene sheet is rolled. When \(n - m = 3\nu\) (\(\nu\): integer), the SWCNT is metallic; otherwise, it is semiconducting with a direct band gap, the value of which is inversely proportional to its diameter.[10] Secondly, the 1D structure of SWCNTs results only in forward scattering and back scattering of carriers, which leads to extremely high electron mobilities, sometimes exceeding \(10^5\) cm² V⁻¹ s⁻¹ in individual SWCNTs even at room temperature.[9, 11] Therefore, semiconducting SWCNTs (s-SWCNTs) are excellent channel materials in field-effect transistors (FETs). FETs fabricated by individual s-SWCNTs (see Fig.1.1-1a) have shown the highest mobility of \(10^3\) to \(10^5\) cm² V⁻¹ s⁻¹ with on/off ratios of \(10^4\) to \(10^6\).[12] Furthermore, the 1D nature of SWCNTs produces van Hove singularities in the density of states that result in strong optical absorption and emission.[13] Excited electron-hole pairs in SWCNTs are strongly bound with binding energies of a few hundred meV due to enhanced Coulombic interactions characteristic of low-dimensional systems.[14]
Figure 1.1-1. Illustration of SWCNTs’ applications in electronics and optoelectronics. (a) Field effect transistor based on individual s-SWCNT,\cite{12} (b) Photodiode based on individual s-SWCNT,\cite{15} (c) Light emitting diode based on individual s-SWCNT,\cite{16} (d) Flexible thin-film transistor based on s-SWCNT film,\cite{17} (e) Optical micrograph of a flexible integrated circuit made by SWCNT film,\cite{18} (f) SWCNT film based terahertz photodetector,\cite{19} (g) Solar cell based on SWCNTs/P3HT heterojunctions,\cite{20} and (h) Solar cell based on SWCNTs/C_{60} heterojunctions.\cite{21}

Excitons can be created optically and electrically, and their radiative recombination results in photoluminescence (PL)\cite{22} and electroluminescence (EL)\cite{23} respectively. Therefore, SWCNTs are also promising for device applications in optoelectronics, such as photodetectors,\cite{24} light emitting diodes (LEDs),\cite{25} and solar cells.\cite{26} Diodes are the basic building blocks in modern optoelectronic device systems. Thus, how to fabricate diodes with SWCNTs is a very important problem. Existing methods include chemical (polymer) doping,\cite{27-29} electrostatic doping,\cite{15,
Schottky diodes, and barrier free bipolar diodes. In 2004, photodiodes of individual s-SWCNTs were realized by electrostatic doping through a split-gate technique (Fig.1.1-1b), demonstrating almost perfect diode behavior with an ideal factor $\sim 1$. Light emitters based on individual s-SWCNTs have also been successfully realized in various device architectures such as ambipolar FETs, unipolar FETs, and bipolar diodes with asymmetric electrodes (see Fig.1.1-1c).

As far as basic research is concerned, individual SWCNT devices provide ideal platforms to explore and test novel properties of 1D systems, such as ballistic transport of electrons and exciton dynamics. However, from applications’ points of view, individual tube devices are problematic, because of the complication of fabrication processes, the incapability of scaling up, and low efficiency. Individual SWCNT FETs are considered impractical for commercialization due to the difficulty of placing single SWCNT at desired locations. Optoelectronic devices based on individual SWCNTs also have the same problem. Furthermore, signals generated by these nano-devices are too weak for practical applications. For instance, typical values of photocurrent generated in an individual s-SWCNT photodiode are $\sim 100$ pA under incident power densities of $\sim 1$ kW cm$^{-2}$. Such low sensitivity is largely due to the extremely small absorption cross-section of the device ($\sim$ nm$^2$).

A reasonable solution for circumventing the above problems is to use pre-made macroscopic SWCNT films. Depending on the synthesis method, there are a variety of ways to fabricate SWCNT films. For example, SWCNT films can be directly grown by chemical vapor deposition (CVD) and then transferred to other substrates
by dry or wet transfer techniques. SWCNTs synthesized by the arc-discharge, laser ablation, and high-pressure carbon monoxide (HiPco) methods are typically generated in powder form. After certain solution processes for dispersion and purification, they can be deposited on substrates by a number of methods such as vacuum filtration, spin coating, and ink-jet and aerosol printing.\[41-42\] Devices based on SWCNT films offer a practical route to scaling because they are normally easy to fabricate in a top-down process via conventional lithography or printing technology.

SWCNT-based thin-film transistors (TFTs) are transistors where the channel region is composed of numerous SWCNTs assembled into a 2D film,\[17,43\] as shown in Fig. 1.1-1d. TFTs have advantages over individual SWCNT-FETs due to their relatively high device-to-device uniformity and the ease of fabrication.\[12\] In addition, TFTs make full use of strong mechanical strength of individual SWCNTs; they can withstand a high degree of strain and are suitable for applications in flexible electronics, such as flexible logic circuits\[18, 44\] and display.\[45-46\] An integrated circuit was demonstrated by Cao et al. in 2008, which was composed of 88 SWCNT TFTs made by a p-type metal-oxide-semiconductor technique.\[18\] Figure 1.1-1e is an optimal micrograph of the integrated circuit bonded to a curved surface, demonstrating both the scalability and the flexibility of SWCNT TFTs.\[18\] Furthermore, thin films made by MWCNTs or metallic SWCNTs (m-SWCNTs) are highly conductive but optically transparent, so they can serve as stretchable transparent electrodes in various devices, including touch screens\[47-48\] and LEDs.\[49\]
One of the most promising applications of SWCNT films in optoelectronics is photodetection because they show ultrabroadband absorption spanning from the ultraviolet to the terahertz (THz) range. These films can be further combined with organic and inorganic materials, therefore opening up new possibilities for creating various novel device architectures.\cite{9} For example, an infrared photodetector can be constructed from a bilayer consisting of a s-SWCNT thin film and a layer of conjugated polymers.\cite{50-52} In 2011, Bindl et al. built photodiodes based on planar heterojunctions of s-SWCNT thin films and C\textsubscript{60} films, demonstrating a high responsivity of $\sim 0.05$ A/W.\cite{53} Furthermore, photothermoelectric (PTE) detectors (also known as ‘photothermopiles’) constructed from SWCNT networks with asymmetric thermal contacts to substrates (see Fig. 1.1-1f) have successfully detected radiation in the sub-THz region ($\sim 0.14$ THz).\cite{19}

Solar cells based on p-i-n or Schottky diodes can be fabricated by combining p-type SWCNT thin films with n-type silicon.\cite{54-56} Also, SWCNTs have been introduced into organic solar cells (OSCs) to take advantage of their high carrier mobilities and strong absorption in the solar spectrum.\cite{20-21, 26, 57-58} In these devices, the active layer is usually a blend film of SWCNTs and conjugated polymers to form bulk heterojunctions.\cite{26} Depending on the type of polymers used in these devices, SWCNTs play different roles from charge acceptors/donors to charge shuttling enhancers (see Fig. 1.1-1g&h). Additionally, SWCNT film based light sources have been explored, such as SWCNT film based light emitting diodes\cite{25, 59} and SWCNT film saturable absorbers\cite{60} in passive mode-locked solid state lasers.
Although SWCNT film based devices bring about potential scalability and other new possibilities as discussed above, new problems also arise due to the heterogeneous nature of these films. For example, the mobility of single SWCNT-FETs can be up to $\sim 10^5$ cm$^2$ V$^{-1}$s$^{-1}$, but it degrades down to only 1-5 cm$^2$ V$^{-1}$s$^{-1}$ in typical SWCNT TFTs made by solution-processed methods. Even those fabricated by CVD-grown SWCNTs with longer tube lengths and fewer defects have mobilities as low as $\sim 10$ to 20 cm$^2$ V$^{-1}$s$^{-1}$. The performance of a TFT depends on a number of factors such as the device channel length, the gate coupling efficiency, and the average length and defect density of SWCNTs. However, as is shown in Fig. 1.1-2, the degree of SWCNT alignment and the degree of s-SWCNT enrichment affect
most the two critical device parameters: the mobility and on-off ratio. Studies have proved that the mobility decrease is due to enhanced scattering by intertube junctions, and the on-off ratio decrease is a result of electrical shorting by m-SWCNTs.[12] For example, 1% m-SWCNTs can decrease the on/off ratio by three orders in a short-channel TFT made by aligned SWCNTs.[63] Therefore, it is crucial to sort nanotubes by electronic type sorting and assemble nanotubes in an ordered manner to extend the excellent properties of single SWCNTs to SWCNT films.

Table 1-1. Summary of major solar cells based on SWCNT hybrid structures.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Architecture</th>
<th>PCE (%)</th>
<th>( V_{sc} ) (V)</th>
<th>( J_{sc} ) (mA/cm(^2))</th>
<th>Fill factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inorganic</td>
<td>Si p-n junction([64])</td>
<td>25.6</td>
<td>0.74</td>
<td>41.8</td>
<td>82.7</td>
</tr>
<tr>
<td></td>
<td>s-SWCNTs/Si([65])</td>
<td>15</td>
<td>0.6</td>
<td>35</td>
<td>76</td>
</tr>
<tr>
<td>Organic</td>
<td>PTB7-Th:PC(_{71})BM([66])</td>
<td>10.1</td>
<td>0.775</td>
<td>19.47</td>
<td>66.9</td>
</tr>
<tr>
<td>solar cell</td>
<td>P3HT:SWCNTs:PC(_{71})BM([58])</td>
<td>4.39</td>
<td>0.56</td>
<td>14.8</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>SWCNTs:PC(_{71})BM([21])</td>
<td>2.5</td>
<td>0.76</td>
<td>9.31</td>
<td>35.02</td>
</tr>
<tr>
<td></td>
<td>P3HT:SWCNTs([20])</td>
<td>0.72</td>
<td>1.04</td>
<td>1.99</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 1-2. Summary of major SWCNT based photodetectors from the IR to THz range.

<table>
<thead>
<tr>
<th>Classification</th>
<th>Architecture</th>
<th>Responsivity</th>
<th>Response time</th>
<th>Detectivity [cm Hz(^{1/2})/W]</th>
<th>TCR [K]</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR photodiode</td>
<td>InGaAs p-n diode([67])</td>
<td>0.2-1 A/W</td>
<td>10 ns</td>
<td>(10^{12}-10^{13})</td>
<td>N/A</td>
<td>0.9-1.7 (\mu)m</td>
</tr>
<tr>
<td></td>
<td>s-SWCNTs/C(_{60})PHJ([53])</td>
<td>~0.05 A/W</td>
<td>N/A</td>
<td>~10(^{11})</td>
<td>N/A</td>
<td>1-1.4 (\mu)m</td>
</tr>
<tr>
<td>Bolometer</td>
<td>VO(_x) film([68])</td>
<td>(\sim 10^{3}) V/W</td>
<td>N/A</td>
<td>1.09×10(^9)</td>
<td>~3.5%</td>
<td>8-14 (\mu)m</td>
</tr>
<tr>
<td></td>
<td>SWCNTs networks([69])</td>
<td>N/A</td>
<td>10 ms</td>
<td>5.5×10(^6)</td>
<td>~0.1 - 0.2%</td>
<td>0.8-10 (\mu)m</td>
</tr>
<tr>
<td>THz detector</td>
<td>Pyroelectric crystal([70])</td>
<td>(10^{3}) V/W</td>
<td>~0.2 s</td>
<td>(~10^8)</td>
<td>N/A</td>
<td>0.1-30 THz</td>
</tr>
<tr>
<td></td>
<td>SWCNTs aligned Film([19])</td>
<td>2.5 V/W</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.14 THz</td>
</tr>
</tbody>
</table>
These challenges also exist for the application of SWCNT films in optoelectronics. Tables 1-1 and 1-2 list the key parameters of various types of solar cells and photodetectors, respectively, based on SWCNT films in comparison to those commercialized products or prototypical devices in each sub-field. SWCNT/Si solar cells have exhibited power conversion efficiency (PCE) values up to ~ 15%,[65] for which strongly p-doped, (6,5)-enriched SWCNT networks were used; their performance is still far less than that of Si p-n diode solar cells, whose PCE can be as large as 25%.[64] It is expected that the PCE of these SWCNT devices can be further increased by using aligned films, which can increase the junction density and therefore generate more photocurrent.[65] In addition, device reliability needs to be improved by finding an efficient and stable p-doping method for SWCNT films. For SWCNT-based OSCs, the highest PCE of ~4% has been obtained in devices with active layers composed of poly [3-hexylthiophene] (P3HT) : SWCNTs : (6,6)-phenyl-C71-butyric acid methyl ester (PC71BM).[58] However, they are less efficient than the leading OSCs based on fullerenes, which has recently boosted the PCE to 10.1%.[66] Further improvements on SWCNT-based OSCs are needed to better control three factors – SWCNT electronic type, diameter, and the morphology of the active layer.[20-21, 71] Highly enriched s-SWCNTs with a controlled distribution of diameters and strong alignment can potentially optimize the efficiency of carrier dissociation, diffusion, and collection, thereby improving device performance.

The hitherto most efficient IR photodetectors based on SWCNT films are photodiodes with planar heterojunctions formed by enriched s-SWCNTs networks
and conjugated C60 layers.[52-53] The average detectivity ($D^*$) is \( \sim 10^{11} \text{ cm Hz}^{1/2}/\text{W} \), approaching that of commercial InGaAs detectors in the same range.[67] The key problem of this type of device is the short exciton diffusion length (~ 10 nm).[14] In order to make full use of excitons generated in SWCNT films, the exciton diffusion length needs to be increased by using highly aligned and enriched s-SWCNT films.[14]

For bolometers based on SWCNT films,[69, 72] the $D^*$ is lower than that of vanadium oxide bolometers by almost three orders,[68, 73] as is shown in Table 1-2. The major reason is the small temperature coefficient of resistance (TCR) of SWCNT films. Improvement of TCR is expected if one uses highly enriched s-SWCNTs blended in proper polymer matrices.[74]

LEDs based on SWCNT films also suffer many problems from high current thresholds, low illumination intensities to spectral broadening, which are due to multiple reasons such as substrate quenching, the defects on the side walls of SWCNTs, and the polydispersity of the film.[25, 59, 75] Both the control of SWCNT properties (chiralities and qualities) and the optimization of device design are needed for further progress in this field.[25]
1.2. Recent advances in chirality enrichment and sorting

Polydispersity is a critical issue that hinders the progress of the science and technology of SWCNTs, especially in electronic and optoelectronic applications, where reliable and reproducible performance is highly required. Nevertheless, the field of controlled direct synthesis of monodisperse (single-chirality) SWCNTs is still in its infancy due to the lack of deep understanding of growth mechanisms.[12, 76-77] Therefore, post-growth sorting has become the leading strategy to obtain monodisperse SWCNTs at present.[76, 78]

Post-growth sorting methods are generally classified into two categories: solid-based sorting and solution-based sorting. In the former, SWCNTs exist in the form of films during the sorting procedure, and in the latter, SWCNTs need to be suspended in liquid. Solid-based sorting can achieve separation of electronic types;[77] it is usually used for CVD-grown SWCNT films, which are normally incompatible with solution-processing. In this approach, m-SWCNTs are removed from SWCNT thin films by electrical burning,[79-80] plasmas etching,[81] and laser radiation.[82] Electrically burning only metallic tubes selectively requires electrical gating and can also damage semiconducting tubes to a certain degree.[83] In another promising method,[84] metallic tubes are selectively exposed from SWCNT arrays covered by a thin layer of organic material with the help of controlled heating (thermocapillary flows); they were then removed by reactive ion etching. As s-SWCNTs were well-protected, transistors made from such samples achieved mobilities exceeding 1000 cm² V⁻¹s⁻¹ and on/off ratios of ~ 10,000.[84]
Different from solid-based sorting, solution-based sorting can realize SWCNTs separation of all hierarchies, not only electronic types, but also diameters, chiralities, and handedness ("enantiomers"). In this approach, SWCNTs need to be dispersed in liquids at first.\cite{77} Based on the interaction of SWCNTs and dispersants, there are two types of non-covalent dispersion: surfactant encapsulation and polymer wrapping.\cite{78} Once good dispersion is achieved, SWCNTs can then be sorted using a variety of separation techniques such as density gradient ultracentrifugation (DGU),\cite{85} chromatography,\cite{86} and aqueous two-phase extraction (ATPE).\cite{87}

### 1.2.1. Surfactant encapsulation approach

In this approach, SWCNTs are encapsulated by micelle structures of surfactant molecules in water with the assistance of tip sonication.\cite{88} Common surfactants used for suspending SWCNTs include sodium dodecyl sulphate (SDS), sodium dodecyl benzene sulphonate (SDBS), and bile salts such as sodium cholate (SC) and sodium deoxycholate (DOC). The micelle structure covering the sidewalls of SWCNTs is dependent on the affinity between surfactants and SWCNTs,\cite{89,91} which is in turn affected by conformation of the surfactant molecule and intrinsic properties of SWCNTs such as curvatures (diameters), electronic types, and chiralities. For example, SDS has relatively small affinity with SWCNTs, leading to a loose and disordered structure on the sidewalls of SWCNTs that can be easily tuned and reorganized by external factors such as ionic strength, temperature, and oxidation.\cite{92,93} On the contrary, the micelle structures of DOC pack around SWCNTs in a much more compact manner, and therefore, they are less sensitive to the
The modification of micelle structures endow surfactant-SWCNT assemblies with different buoyant densities, hydrophobicities, surface charge densities, and so on, which become the basis for the following sorting methods for SWCNTs.

**Density Gradient Ultracentrifugation (DGU):** DGU is a bio-inspired separation technique that can be used to sort SWCNTs based on the difference of SWCNTs’ buoyant densities. In this method, SWCNT suspensions are loaded into a centrifuge tube filled with a linear density gradient. Under ultracentrifugation, SWCNTs will migrate to a point where their buoyant density matches the density of the gradient, leading to the separation of SWCNTs into different layers in the centrifuge tube. DGU was first introduced to separate SWCNTs by Arnold *et al.* in 2005. With different combinations of surfactants, DGU-sorted s-SWCNTs can have type purities as high as 99%. Also, using co-surfactant (SC+ SDS) to engineer the buoyant densities of SWCNTs, separation of nearly single chiralities can be realized. DGU can also achieve m-s and diameter sorting in a sole surfactant system (SDS) by adjusting the salt concentration of suspensions, which leads to the reorganization of surfactants and thus change the buoyant density of surfactant-CNT assemblies. Another important factor in DGU is the choice of the density gradient. A nonlinear density gradient was utilized in DGU by Ghosh *et al.* in 2010, as shown in Fig.1.2-1. Ten different chiralities of HiPco SWCNTs were sorted by a single step, and separation of mirror-image isomers (enantiomers) of (6,5) SWCNTs was also realized. However, one major drawback of DGU is its long separation times (up to tens of hours for each run) and thus the limited scalability.
Figure 1.2-1. Sorting of SDS dispersed SWCNTs by chirality using nonlinear DGU. (a) Image of a centrifuge tube containing SWCNTs after sorting, (b) Near-infrared absorption spectra of the SWCNT layers with different chirality enrichment, (c) Photoluminescence spectra of 10 species of sorted SWCNTs. Reproduced from [98].

**Gel Column Chromatography:** Chromatography is a sorting technique commonly used in biochemistry for the separation of molecules by their sizes, charges, etc. In chromatography, solutions (mobile phase) move downward through a column filled with gel beads (stationary phase). Due to the differences of sizes, charges, or other properties, different molecules interact with gel beads in the column with different strength; therefore, they travel at different speeds, causing separation. If separation is based on the size (charge) of molecules, it is called size-exclusion chromatography (ion-exchange chromatography). Gel column chromatography was used to sort SDS-suspended SWCNTs by Tanaka et al. (2008) [99] and Moshammer et al. (2009). [100] They showed that m-SWCNTs move much faster than s-SWCNTs through a column filled with agarose or dextran-based
gels, causing the separation between m- and s-SWCNTs. The purity of sorted s-SWCNTs could be as high as 99.9%, as shown in Fig.1.2-2.\textsuperscript{[101]}

Theoretical studies suggest that metal-semiconductor separation in gel column chromatography occurs due to the surfactant-induced selective adsorption of SWCNTs on the hydrogels.\textsuperscript{[102-103]} Metallic SWCNTs are more readily shielded from gels as SDS molecules pack more densely around m-SWCNTs than s-SWCNTs. Although used only for m-s separation initially, this method has since been extended to chirality sorting.\textsuperscript{[86, 104]} By controlling experimental parameters such as SDS concentration,\textsuperscript{[86]} temperature,\textsuperscript{[105]} and pH value\textsuperscript{[104, 106-107]} of the suspension, this method can sort SWCNTs into multiple chiralities with purity in the range of 61-95\%.\textsuperscript{[104]} Very recently, gel column chromatography has also been successfully extended to sorting DWCNTs.\textsuperscript{[108]} However, it is worth noting that only SDS dispersed SWCNTs can be separated by this method, which is likely due to the higher structure tunability of SDS compared to other surfactants.\textsuperscript{[109]} The advantage of gel column chromatography is that it is less time-consuming and more scalable than DGU, and therefore, it is a more promising method for sorting SWCNTs in large quantities.
Aqueous Two-Phase Extraction (ATPE): ATPE is a polymer-extraction technique to sort surfactant-dispersed SWCNTs.\cite{87} Two immiscible phases can be spontaneously formed with the mixture of two water-soluble polymers: polyethylene glycol (PEG) and dextran. The top PEG phase is more hydrophobic, while the bottom dextran phase is more hydrophilic. SWCNTs are sorted by their diameters due to subtle difference of their hydrophilicities. Larger diameter tubes are more hydrophobic, and therefore, go to the top phase, while small diameter tubes are relatively hydrophilic and stay in the bottom phase. The intrinsic hydrophilicity of SWCNTs can be modified by the encapsulation of surfactants.\cite{110} For example, SDS-wrapped SWCNTs are more hydrophobic than DOC-wrapped tubes. By keeping increasing the SDS concentration, SWCNTs can be pushed up to the top phase orderly based on their diameters.\cite{111} In addition, m-s separation can be realized by using co-surfactants (SDS + SC).\cite{111} ATPE separation of SWCNTs was
first achieved by Khripin et al. in 2013, who showed diameter-based separation in a small-diameter region (< 1 nm).\cite{87} It was later extended to a wide diameter range from ~ 0.6 to 1.7 nm by introducing oxidation reaction.\cite{111-112} This method is easy to handle and ready to produce a large quantity in a short time. Another advantage over other sorting techniques is that it does not need any special equipment.

### 1.2.2. Polymer wrapping approach

Polymer wrapping is an alternative approach for SWCNT sorting. Different from surfactants, certain polymers can selectively wrap and disperse SWCNTs of one
electronic type or even a particular chirality. In addition to their affinity for nanotubes, conformations of polymers play an important role in selective wrapping.[78]

One important polymer in this context is DNA. Studies found that DNA can form ordered structures on SWCNTs by helical wrapping around their sidewalls.[114-115] Specifically, depending on its sequence, DNA likes to pick up SWCNTs with a particular chirality. DNA-wrapped SWCNTs are then sorted by ion-exchange chromatography (IEX), in which the stationery phase is ionic, providing Coulomb interactions with SWCNTs.[114] Due to the different surface charge densities of DNA-SWCNTs assemblies, they are sorted out from each other by different interaction strength with ionic gels. This method was first introduced to disperse SWCNTs by Zheng et al. in 2003.[115] Later, size exclusion chromatography (SEC) was introduced to sort SWCNTs by length. By sequentially using SEC and IEX, (6,5) and (9,1) chiralities were firstly separated for DNA-wrapped SWCNTs.[114] In 2009, more than 20 DNA sequences were identified to allow sorting of a particular \((n,m)\) SWCNTs, and up to 12 chiralities of SWCNTs were successfully sorted (see Fig. 1.2-3).[113]

Recently, the ATPE technique was used to sort DNA-wrapped SWCNTs, and 15 chiralities of SWCNTs were separated.[116] Nevertheless, the main problem with this method is the high cost of DNA, which renders the method unaffordable for many laboratories.

Another similar approach is based on wrapping CNTs by designed polymers. In this method, semi-flexible conjugated polymers are used to selectively disperse
SWCNTs in organic solvent. Polymers that have been successfully used include poly(9,9-dioctylfluorene) (common name PFO) and poly[9,9-dicynfluorene]-alt-benzothiadiad-zole (F8BT). These polymers have the ability to selectively wrap and disperse SWCNTs by their diameters or chiralities. The method was first introduced to sort SWCNTs by Nish et al. in 2007. The advantage of this method is its simple sorting procedure, involving only tip sonication and short time ultracentrifugation (~ 1h). After centrifugation, SWCNTs in the supernatant are enriched with certain diameter or chirality, depending on the chosen polymers. A recent report showed that left and right handedness of (6,5) can be sorted by conjugate polymer wrapping. This method relies totally on seeking and designing polymers of desired structures; currently, there are just a few successful sorted species of SWCNTs. One problem with this method is in the difficulty with removal of polymers after sorting, which limits the range of applications.
1.3. Prior work on production of aligned carbon nanotubes

CNTs are promising building blocks for novel electronic and optoelectronic devices because of their uniquely anisotropic electrical, optical, thermal and mechanical properties. However, these properties severely diminish in bulk materials consisting of randomly oriented CNTs. Therefore, an important question is how to organize individual SWCNTs into ordered assemblies for the purpose of preserving their unique properties. So far, many assembling techniques have been developed;\textsuperscript{[121-122]} they can be broadly classified into two categories: 1) direct growth of aligned nanotubes and 2) post-synthetic assembly.

1.3.1. Direct growth of aligned nanotubes

In this approach, CNTs are assembled into aligned structures such as vertically aligned arrays or horizontally aligned films during their growth on substrates.\textsuperscript{[123]} For example, in water-assisted CVD synthesis, CNTs can form a vertically aligned array due to the crowding effect.\textsuperscript{[124]} The height of these vertically aligned arrays can be up to ~ millimeters. Films of horizontally aligned SWCNTs can then be obtained by rolling down the vertical arrays onto substrates along one direction (see Fig. 1.3-1a).\textsuperscript{[125-126]} Aligned CNT films can be also obtained by mechanically stretching DWCNT or MWCNT arrays.\textsuperscript{[127-129]}

A more direct way to get an aligned SWCNT thin film is through epitaxial CVD growth.\textsuperscript{[130]} In this method, CNTs grow horizontally on the substrate (ST-cut quartz) due to the orientated van der Waals forces with the surface of substrates (see Fig.
1.3-1b). The advantage of this method is that it can achieve essentially perfect alignment in a large area; the disadvantage is that the density of CNTs is normally very low. Over the past few years, it has been improved to yield higher densities, with local values up to 60 SWCNTs/µm, but still not high enough for practical applications such as photodetectors.

A common problem with direct growth of aligned CNTs is the polydispersity (heterogeneity) of CNTs. In order to protect the alignment structure, sorting methods available for these films are very limited; they are only capable of sorting electronic types at present.

1.3.2. Post-synthetic assembly

In contrast to direct growth of aligned CNTs, post-synthetic assembly methods assemble CNTs into order structures from solutions, therefore being able to take advantage of high degrees of monodispersity of CNTs provided by solution-based sorting strategies. Post-synthetic assembly methods cover a broad range of techniques, which can be roughly classified into three categories: 1) assembly driven by external forces, 2) self assembly, and 3) liquid crystal (LC) phase transitions.

SWCNTs can be assembled into ordered structures under external forces, such as magnetic field, electrical field, shear forces, and gas flow. Theoretical and experimental studies have shown that the magnetic field strength required to
induce meaningful CNT alignment is as high as 10 T,[134] rendering this method impractical for scalable productions.

An alternatively and more affordable method is to use AC electrical fields to align CNTs between metal electrodes in solution, which is called dielectrophoresis (DEP).[140] It allows for the alignment and placement of CNTs at locations predefined by the electrodes. Recently, this method has been improved largely to get better control over the density and orientation of CNTs. CNTs arrays well aligned (within 10°) between electrodes with a density of ~30-50 SWCNTs/µm have been reported (see Fig. 1.3-1c).[135] However, DEP is a technique rooted in FET fabrication, incapable of providing free-standing aligned CNT assemblies of large sizes.

![Figure 1.3-1. Aligned CNT films made from different assembling techniques. (a) Dry transfer after the water-assisted CVD synthesis,[126] (b) CVD growth on a quartz wafer,[131] (c) dielectrophoresis,[135] (d) evaporation-driven self-assembly,[137] (e) Langmuir-Schaefer method,[141] and (f) liquid crystal phase transition of CNTs.[142]](image)

Compared to DEP, self-assembly is a more flexible and effective route towards the production of large-size and ordered CNT films. There have been a great number of techniques in this category, including blown-bubble assembly,[143] spin
coating,[144] inkjet printing,[145] evaporation-driven self assembly (EDSA),[137-138] and Langmuir-Blodgett[146] and Langmuir-Shaefer (LS) assembly[141]. While each of these methods has its pros and cons, the EDSA[137] and LS[141] methods appear to outperform the rest in terms of the degree of alignment and CNT density. For EDSA, a 1 cm × 1 cm substrate is vertically immersed into a suspension of surfactant-encapsulated CNTs. Under slow evaporation of the solution, CNTs are driven to the substrate-solution interface (i.e., solid-liquid-air interface) by a frictional force, where they aggregate and form into aligned stripes with widths of ∼tens of microns. It can lead to ∼99% of nanotubes lying within 5° of the alignment axis, as reported by Shastry et al. (see Fig. 1.3-1d).[137] Cao et al. were the first to introduce the LS method to align CNTs on a macroscopic scale. In their method, CNTs floating on a water surface (interface between air and water) were driven into a 2D ordered phase by shrinking them into a small area on the interface. The density of CNTs was impressively high (above 500 tubes/µm). However, the degree of local alignment of CNTs was not very high; CNTs were strongly wiggling around the alignment axis (see Fig. 1.3-1e).[141]

The common problem of EDSA and LS is that the assembly process occurs in a 2-D manner, thus only generating a monolayer or a few layers of CNTs (∼ a few nm). On the contrary, LC phase transitions provide a strategy to align CNTs in a 3D manner, possessing the potential of producing bulk ordered assemblies.[139] In this approach, early studies focused on making LCs of CNT-polymer composites. Some polymers can go through a LC phase transition spontaneously, achieving ordered
structures on a macroscopic scale. Using them as hosts, CNTs dispersed in such polymer matrices can be coaxed into aligned structures on a macroscopic scale.[139] The degree of alignment can be very high, with a nematic order parameter ($S$) of up to $\sim 0.7$.[147] Because the majority of applications are incompatible with the host material, the challenging, remaining problem is how to completely remove the polymer matrix without ruining the CNT alignment. Consequently, it motivated an effort to develop LC phases of CNTs themselves.[139] The basis for CNT-LCs is the classical Onsager theory, which predicts that rigid rods in a colloid system can form a LC phase at large enough aspect ratios and high enough concentrations. So far, a nematic CNT-LC phase has been achieved in several dispersion systems, such as the dispersion in superacids[148] and the DNA wrapping.[149] The former method has been successfully applied to the scalable production of highly aligned and conductive MWCNT fibers.[150] Unfortunately, macroscopically aligned SWCNT films through LC phases remain a challenge. According to existing reports,[142, 149, 151] CNT-LCs show nematic ordering without long-range order on a macroscopic scale. Multiple domains can be seen from films made by CNT-LCs with maximal domain sizes on the order of $\sim$ micrometers. Recent experimental studies showed that the morphology of individual nanotubes, such as the length of CNTs and defects on their sidewalls are important factors affecting the formation of long-range order.[152] Relatively short tubes are favorable for high alignment because they seem to be more straight than longer tubes. It has been reported that the nematic order parameter, $S$, was increased from 0.3 to 0.55 by shortening the CNT length.[153]
1.4. Scope of the dissertation

In this dissertation, we present two methods for assembling individual SWCNTs to form macroscopic films composed of densely aligned SWCNTs. Their anisotropic optical properties are characterized and discussed. Devices based on these aligned films are fabricated, demonstrating their potential application in optoelectronics. The dissertation is organized as follows. Chapter 2 presents the assembling of macroscopically aligned films of SWCNTs by a CVD method. Chapter 3 introduces a new method for fabricating highly aligned CNT films based on controlled differential pressure filtration. We describe the detail of the fabrication procedure, present the characteristics of aligned films, and analyze various factors affecting CNT alignment. Chapter 4 presents the fabrication and characterization of IR and THz photodetectors based on aligned films by the CVD method, demonstrating their excellent device performances. In Chapter 5, we first introduce the newly-developed CNT sorting method, ATPE, showing how to obtain (6,5)-enriched SWCNT suspensions through this method. Next, we describe the fabrication of aligned films based on (6,5)-enriched SWCNTs. In the end, we present the characterization of aligned films enriched in (6,5) and their device applications.
Chapter 2

Preparation of aligned carbon nanotube films I: direct growth

SWCNTs can be synthesized by a variety of methods, including the arc-discharge, laser ablation, HiPco, CoMoCAT, and CVD (chemical vapor deposition) methods. Compared to other methods, CVD-grown CNTs tend to have relatively longer lengths and higher mobilities,[12] which are valuable for many applications. More importantly, CNTs can be directly assembled into ordered structures during CVD growth.[123] For example, water-assisted CVD can produce vertically aligned CNT arrays.[124-125] In this chapter, we first present the principle and procedures of growing vertically aligned SWCNTs by CVD and then describe how to prepare horizontally aligned films from vertically aligned SWCNT arrays as well as how to n-dope the aligned films through a chemical doping method.
2.1. Chemical vapor deposition of vertically aligned carbon nanotube arrays

2.1.1. Growth principle

The basic idea of CNT growth by CVD is to choose suitable catalysts and thermally decompose hydrocarbons into carbon atoms on the surfaces of catalyst particles with a controlled temperature.\textsuperscript{[154]} Widely used catalysts for CNT growth are transition metals, such as nickel, cobalt, and iron.\textsuperscript{[155]} Catalyst particles of nanoscale sizes are discretely deposited on the growth substrate. After the decomposition of hydrocarbons at a proper temperature, CNT growth is initiated by the crystallization of carbon atoms on the surface of catalyst particles.\textsuperscript{[154]}

When catalyst particles have strong interactions with the growth substrate, they keep staying on the substrate during the whole growth; on the contrary, carbon atoms crystallize out as a hemispherical dome and then extend upward in the form of seamless graphitic cylinder, as shown in Fig. 2.1-1.\textsuperscript{[154]} This process is called base-growth, which is the case for the growth of vertically aligned CNT arrays. The formation of SWCNTs or MWCNTs is then governed by the size of the catalyst particles as well as the growth temperature.\textsuperscript{[154]}

Generally speaking, the growth of SWCNTs occurs on catalyst particles of small sizes (a few nm) and at a high temperature (~ 750-800 °C).\textsuperscript{[156]} On the other hand, vertical alignment is achieved when the density of growing nanotubes is so high that van der Waals forces between neighboring tubes become strong enough to cause all
tubes to grow upward from the surface of the substrate (the crowding effect). Therefore, the formation of vertically aligned SWCNT arrays requires a dense distribution of catalyst particles on the substrate as well as a high growth yield. Using water-assisted CVD synthesis (“super-growth”), Hata et al. first realized the growth of dense and vertically aligned SWNT arrays with millimeter heights.

Figure 2.1-1. Schematic of the CNT growth mechanism by CVD. Reproduced from [154].

2.1.2. Growth procedure

In this section, we present our growth procedure to grow dense and vertically aligned SWCNTs by water-assisted CVD. The growth recipe used in our experiment was firstly optimized by Pint et al.[156]

Catalyst deposition is the first and also very critical step for the growth of vertically aligned SWCNTs. The size of catalyst particles, their distribution, and stabilization on the substrate strongly affect the growth result. A well-established strategy is to deposit a bilayer structure of catalysts on the substrate, where one
A thin layer of Fe (~0.5 nm - 1 nm) as catalyst particles is on the top, and another thicker layer of alumina Al₂O₃ (~ 10 nm) as the supporting material is at the bottom. Deposition of catalysts and supporting material can be done by electron-beam (e-beam) evaporation, magnetron sputtering, or atomic layer deposition (ALD). Based on a previous study, the former two methods usually generate catalysts layers whose morphology is favorable for high-yield growth.

Shown in Fig. 2.1-2 is a typical TEM image of Fe catalysts on an Al₂O₃ supporting layer deposited by sputtering and e-beam evaporation. The average particle size is on the order of ~ 2-3 nm, suitable for the growth of SWCNTs. In our study, we used e-beam evaporation to deposit Fe as well as Al₂O₃ supporting layer on n-type Si substrates. During the evaporation process, the chamber was kept under high vacuum with a typical pressure of 3 × 10⁻⁶ Torr. The deposition rate was 0.5 Å/sec for Al₂O₃ and 0.1 Å/sec for Fe. The final thickness of Al₂O₃ and Fe after deposition
was \( \sim 10 \) nm and \( \sim 0.8 \) nm, respectively. A slow evaporation rate is essential for the control of the iron particle size and its morphology.

Figure 2.1-3. Schematic of the hot filament chemical vapor deposition reactor. Reproduced from\[156\].

SWCNT arrays of macroscopic sizes are obtained when catalysts and supporting layers are deposited on the entire surface of the substrate. The growth of SWCNT films can also be realized by using catalysts patterned with line shapes on substrates.\[125\] Both strategies were used in our study. For the latter, the line patterns of Fe/Al\(_2\)O\(_3\) were fabricated by photolithography on Si substrates with a line-width of 2 \( \mu \)m or 5 \( \mu \)m. The hot filament CVD apparatus utilized for SWCNT growth is schematically shown in Fig. 2.1-3.\[156\] The reactor consists of a quartz tube furnace in which a 0.25-mm tungsten filament is suspended. The role of the filament is to activate iron catalysts by rapidly reducing the oxidation layers on their surfaces due to the previous exposure in air. Gas control is achieved by a mass flow
controller, which is operated by a LabVIEW program. The turbo molecular pump is to keep the whole system under high vacuum (~1-5 × 10⁻⁶ Torr) when gas flows are off.

The growth process includes the following steps. First, we increase the furnace temperate to 750°C and then turn on gas flows, which consist of 200 standard cubic centimeters (sccm) of H₂, 4 sccm of C₂H₂, and 200 sccm of H₂ with water vapor. Water vapor is introduced in the system by bubbling H₂ through nanopure water at ~207 Kpa upstream from a 200 sccm mass flow controller. Next, we turn on the hot filament by ramping up the current through the tungsten wire to ~9 A while the gas flow is on. When the power applied to the filament is stabilized around 35 W, we open the gate valve and move the sample holder to a point that is approximately 2 mm from the filament. The hot filament rapidly reduces the catalyst from a stable Fe₂O₃ to metallic (and catalytically active) Fe. This occurs due to the high temperature of the filament (typically ~ 2500 °C) that dissociates H₂ into atomic hydrogen. After 30 seconds of atomic hydrogen exposure, we turn off the hot filament, and then growth takes place for an additional 3-30 minutes.

After growth, we move the sample outside the gate valve and into the loading chamber. Finally, we take out the sample after restoring the pressure of the loading chamber by purging N₂ gas. We usually check the sample morphology under a JEOL 6500 scanning electron microscope (SEM). Figure 2.1-4 shows vertically aligned SWCNT arrays and SWCNT films by water-assisted CVD growth. Typically, the height of SWCNT arrays is around ~ 70 µm after growth of 3 minutes. Individual
SWCNTs are touching each other to form ‘bundles’ with typical sizes of ~tens of nm in diameter, and these bundles are vertically aligned inside the SWCNT array.

Figure 2.1-4. SEM images of (a) vertically aligned SWCNT array and (b) SWCNT films grown by water-assisted CVD.

It is worth noting that precise control of water vapor is very important in the growth procedure. Without any water vapor, growth stops very quickly, but the presence of a proper amount of water vapor extends the growth duration, greatly enhancing the growth yield. Studies showed that the growth extension under water vapor is likely due to two reasons. First, excessive carbon atoms on the surface of iron particles will form amorphous carbon and terminate the SWCNT growth quickly; water vapor can etch excessive carbons and therefore increase the catalyst lifetime. Note that too much water will also etch SWCNTs, leading to a decrease of growth yield. Second, the morphology of catalyst particles is affected by the Ostwald ripening at high temperatures, where larger iron particles grow in size while smaller ones shrink in size and gradually disappear via atomic inter-diffusion. The decrease of catalyst density causes termination of growing tubes. Studies showed that water vapor can hydroxyate the substrate surface and enhance the interaction
of iron particles with substrates, therefore impeding the Ostwald ripening to a certain degree.
2.2. Fabrication of horizontally aligned CNT films

Horizontally aligned SWCNT films are desirable for various device applications. Therefore, it is important to convert vertically aligned SWCNT arrays into horizontally aligned films while preserving the original SWCNT alignment as much as possible. The conversion process involves two major steps: substrate etching and film transfer. The water vapor etching and dry transfer techniques used in this dissertation work were originally developed by Pint et al.\textsuperscript{[126]} Aligned SWCNT films made from these methods have been characterized by Ren et al. by polarization-dependent THz spectroscopy, which demonstrated excellent SWCNT alignment.\textsuperscript{[160]} In this section, we present the basic principle and technical details of making aligned films by water vapor etching and dry transfer.

In the CVD process, SWCNTs are grown on a catalyst-coated substrate at a high temperature (\(\sim 750^\circ\text{C}\)). After growth, both the grown SWCNT array and catalyst particles on the substrate will go through a rapid cooling process from the growth temperature to room temperature. As the catalyst particles cool, they form a Fe-C compound, leading to a carbon shell surrounding the catalyst particle. Nanotubes in the vertical arrays are then bonded strongly to the carbon shell through carbon-carbon bonds, making them difficult to be peeled off from the substrate. In order to transfer the grown sample to any other substrate, the Fe-C bonds must be destroyed at first. Fe-C bonds can be broken either by acid etching or water vapor etching, leading to two different transfer techniques: wet transfer and dry transfer. It’s showed that wet transfer based on acid etching cannot keep SWCNT alignment. This
is because during the transfer process in a liquids SWCNTs tend to collapse into random structures under the influence of capillary forces. On the contrary, alignment can be well preserved in a dry transfer process followed by water vapor etching. Water vapor etching has two steps: 1) cooling down the SWCNT sample rapidly after growth, and 2) turning off the flow of C$_2$H$_2$, leaving the sample in the flow of water vapor and H$_2$ at the growth temperature for ~5 minutes. After the process, carbon shells around catalyst particles are etched away, leaving a very weak van der Waals force between SWCNTs and the growth substrate. The etching process is schematically shown in Fig. 2.2-1.

![Figure 2.2-1. Diagram depicting the water etching process for dry transfer after growth. Reproduced from [126].](image)

After water vapor etching, the SWCNT array can be transferred to almost any substrate in a dry environment by the following steps: 1) covering the sample with a smooth and sheared foil on the top, 2) rolling down the SWCNT array along the shearing direction of the foil by a roller with a proper size, in which process the sample is transferred to the foil surface, and 3) peeling off the SWCNT film from the foil and putting it on the target substrate.
Figure 2.2-2 shows the horizontally aligned SWCNT film obtained by dry transfer from vertically aligned SWCNT arrays. The same procedures can be applied to SWCNT films grown by catalysts with line patterns. When the height of SWCNTs is larger than the distance between neighboring catalyst patterns, the rolling down process produces a continuous thin film of SWCNTs as each individual film can overlap with nearby films. When the distance between catalyst patterns is much larger than the height of SWCNT films, a single piece of SWCNT film can be directly peeled off from the growth substrate with fine-tip tweezers. In doing so, the alignment of the original film can be preserved to a large degree, as shown in Fig. 2.2-2b. Note that the thickness of these SWCNT films are determined by the line-width of the catalyst pattern, which can be down to 1 µm using photolithography, thinner than films obtained from SWCNT arrays. Shown in Fig. 2.2-3 is a broadband absorption spectrum of an aligned film. The strong polarization anisotropy of absorption between perpendicular and parallel directions can be observed clearly, indicating good SWCNT alignment.
Figure 2.2-3. Absorbance spectra of dry transferred SWCNT film in the THz and infrared ranges with polarizations parallel and perpendicular to the nanotube alignment direction.
2.3. n-doping SWCNTs by Benzyl Viologen

p-n junctions are inside every semiconductor device in modern electronics and optoelectronics, including diodes, transistors, light-emitting diodes, laser diodes, photovoltaics, and solar cells. Semiconducting SWCNT-based p-n diodes can be realized using various methods such as the split-gate technique, BFBD, and chemical p- and n-doping.[24] Each of these methods has its advantages and disadvantages. For a monolayer of s-SWCNTs with nanometer to micrometer sizes, split-gate technique and BFBD method can make p-n diode with stable and perfect diode behavior, but they hardly work for large-area SWCNT films with finite thicknesses.[24] However, for optoelectronic devices, such as solar cells and IR photodetectors, large-area p-n junctions are often needed. An alternative way is to use chemical doping, which is a relatively simple approach, and applicable for large-size SWCNT films.[29] As SWCNTs easily exhibit p-type behaviors when exposed to air, the establishment of an efficient n-doping method is more pressing. When it comes to chemical n-doping, there are several possible polymers as donors, such as polyethyleneimine (PEI),[161] reduced benzyl viologen (BV),[28, 162] and phosphine derivatives.[29] The essence of these methods is the charge transfer by the redox reaction between the attached polymers and SWCNTs. Compared to n-doping by other polymers, BV n-doping is known to have the best stability.[28] Therefore, in the present study, we used BV to n-dope aligned SWCNT films obtained from water-assisted CVD growth.
The BV used in our experiment was purchased from Sigma Aldrich. The preparation of n-doping solution is as follows. Firstly, a certain amount of BV was dissolved in water, followed by an addition of organic solvent such as toluene with a volume ratio of 1:1. As water and toluene are immiscible, a biphasic solution appears: the bottom is a hydrophilic water phase enriched with BV, and the top is a hydrophobic toluene phase. Secondly, a certain amount of sodium borohydride (NaBH₄) as a reducing agent is added to the biphasic solution. It can reduce the charged state of viologen, \( V_{2+} \), to a neutral state, \( V_0 \). Because \( V_0 \) is hydrophobic, it transfers separately from the water phase to the toluene phase. These reductive BV molecules (\( V_0 \)) enriched in the toluene phase then become dopants n-dope the SWCNT films. Figures 2.3-1 shows the preparation procedure as well as prepared doping solutions with different BV concentrations from 0.1 mM to 100 mM.\(^{[28, 162]}\) The color of the toluene phase is tuned from transparent, yellow to reddish with the increase of BV concentration.

Figure 2.3-1. (a) n-doping solutions with different BV concentrations, (b) Diagram to show the preparation process of doping solution. Reproduced from \([28]\)
n doping was completed by dropping the doping solution (3-5 µL) onto the surface of the SWCNT film. By a spontaneous redox reaction with BV, the originally p-type SWCNTs are converted into n-type. In this process, BV molecules act as reductants; namely, neutral $V_0$ is ionized to $V_{2+}$ and donates electrons to SWCNTs. Under air ambient conditions, the resulted n-type film is stable for a relatively long term (a few months to a year). The relative high stability is due to the hydrophobic nature of $V_0$, which acts as a protecting layer to prevent further oxidation from the air.\textsuperscript{[28]} It is worth noting that the BV concentration for n-doping is usually 70 mM. Generally, the higher the dopant concentration is, the stronger the n-doping will be. However, at high enough concentrations (~100 mM), doping tends to be saturated. In addition, a high concentration leads to an accumulation of a large amount of polymers on the sample surface, likely introducing defects and affecting the original properties of the SWCNT film.
Chapter 3

Preparation of aligned carbon nanotube films II: Vacuum filtration

Post-synthesis assembly, as opposed to direct growth, is a more attractive route for fabricating 3D architectures of aligned CNTs with tailored properties.\textsuperscript{[122]} Post synthesis assembly of aligned CNTs covers a broad range of techniques, such as dielectrophoresis (DEP),\textsuperscript{[135]} inkjet-printing,\textsuperscript{[145]} evaporation-driven self assembly (EDSE),\textsuperscript{[137]} Langmuir–Schaefer (LS) assembly,\textsuperscript{[141]} and liquid crystal (LC) phase transitions.\textsuperscript{[139]} Among these techniques, 2D assembly approaches including EDSE and LS have shown the ability to fabricate aligned CNT films on a macroscopic scale. However, they are limited to single or few layers of aligned CNTs with a low degree of alignment. Another widely explored method is the 3D LC phase transition, which has the potential to align CNTs in a bulk form. The problem with the 3D LC phase transition of CNTs is that there is currently no way to control the director
orientation of multi-domains. Therefore, to date, preparation of highly aligned CNT films on a wafer scale remains elusive.

In this chapter, we present a novel assembly method based on vacuum filtration, which produces monodomain, wafer-scale CNT films with high degrees of alignment. This method is different from both existing 2D and 3D assembly techniques. The strikingly high values of nematic order parameter ($S \sim 1$) that we obtained is far beyond the theoretical limit of the 3D LC phase of rigid rods ($S = 0.79$). Film thicknesses exceeding 100 nm were achieved while maintaining high degrees of alignment, making our method superior to previous 2D self-assembly techniques. CNT alignment in our method likely occurs in a 2D manner, but the aligned structures keep growing in a direction perpendicular to the surface, indicating a transition from 2D-like ordering to 3D-like ordering.

We organize this chapter as follows. In Section 3.1, we introduce the technique of vacuum filtration to produce CNT films, while discussing two studies in particular as examples. In Section 3.2, we describe our novel method – controlled differential pressure filtration (CDPF) – for the assembly of wafer-scale monodomain CNT films. In Section 3.3, we show the excellent properties of these highly aligned films based on results provided by diverse characterization tools. In Section 3.4, we analyze the important factors affecting the degree of CNT alignment during CDPF, mentioning the possible underlying mechanisms.
3.1. Fabrication of carbon nanotube films by vacuum filtration

3.1.1. Vacuum filtration

Figure 3.1-1. (a) Cartoon of a glass filtration setup composed of four parts: (1) glass funnel, (2) clamp, (3) fritted glass base, and (4) rubber stopper. (b) Optical image of a filtration setup mounted on a side-arm flask.

Vacuum filtration is a technique to separate desired solids such as large-size molecules (e.g., bacteria) from a liquid suspension. As shown in Fig. 3.1-1a, the key components of a typical glass microfiltration setup are: 1) glass funnel, 2) clamp, 3) fritted glass support, and 4) rubber adapter. Before starting filtration, the setup is mounted on a side-arm flask that is connected to a vacuum pump. A piece of filter paper with a proper pore size is put on the surface of the glass support; liquid is poured into the glass funnel, which is sealed with the glass support by the clamp. When a reduced pressure in the flask is generated by the vacuum pump, the liquid in the funnel will be sucked into the flask, but solid particles with sizes larger than the pore size of the filter paper will be trapped on its surface.
Vacuum filtration was first introduced to the CNT field by Wu et al. in 2004.\textsuperscript{[163]} Since then, it has become a standard method for fabricating CNT thin films for various studies. It mainly involves four steps: 1) dispersing CNTs in a surfactant solution, 2) vacuum filtering the CNT suspension onto a filtration membrane (forming a homogeneous film on the membrane), 3) dissolving the filtration membrane in a proper solvent, and 4) transferring the CNT film onto a desired substrate. Figure 3.1-2a is a schematic sketch of the procedure of fabricating CNT films through vacuum filtration. This method has the advantages of being able to control the film thickness and achieve a uniform density of CNTs over a large area. As shown in Fig. 3.1-2b, CNT films on a wafer scale can be made by the vacuum filtration method, and their thickness can be as thin as 50 nm (or even thinner) while still keeping a uniform morphology on a macroscopic scale.\textsuperscript{[163]} These films
are flexible and semi-transparent, valuable for applications in flexible electronics and optoelectronics. Nevertheless, the problem with the method is that it produces disordered CNT films (Fig. 3.1-2c), which largely limit the performance of devices made by these films.

3.1.2. Observation of local alignment in CNT films by vacuum filtration

The 3D LC phase transition is a promising way to produce aligned CNT films in a bulk form. The basis of this mechanism is Onsager’s theory, according to which rigid rod-like polymers will go from an isotropic phase into a nematic phase given that they have the large aspect ratio and a high enough concentration. LC phases of CNTs with nematic domain structures have been realized in several suspension systems. However, how to force the director orientations of multiple nematic domains into a uniform direction remains a challenge. Although vacuum filtration has always been recognized as a standard method of making disordered CNT films, there have been a few studies attempting to modify it for the fabrication of aligned films. The basic idea is to realize a CNT LC phase in a vacuum filtration system under certain conditions and convert the CNT LC into an aligned film as the solvent drained away.
In 2013, Dan et al. reported the formation of nematic-like alignment in SWCNT thin films by slow vacuum filtration (~2 mL/h).\[^{151}\] Scanning electron microscopy (SEM) revealed multiple domains in these films with a typical size of ~ hundreds of nm, as shown in Fig. 3.1-3. It can be seen that each domain has its own director orientation; the film has no long-range order due to the random orientation of individual domains. The authors emphasized the importance of slow filtration and suggested that the occurrence of local order was due to a LC phase transition of CNTs. According to the study, slow filtration created a region of high enough SWCNT concentration near the filter membrane, driving the system from an isotropic phase into a nematic LC phase.

In 2014, Oh et al. reported the fabrication of CNT buckypapers with nematic domains by vacuum filtration.\[^{142}\] They found that, only when the concentration of CNTs in the suspension was very large (~1 mg/mL), formation of nematic domains occurred. With the increase of CNT concentration, the domain size grew up to tens
of μm as evidenced by birefringence textures observed under polarized optical microscopy (POM) (see Fig. 3.1-4). The requirement of high CNT concentration seems to be consistent with the picture of 3D LC phase transitions. They also found that the filtration speed affected the formation of netmaic domains. CNT buckypapers made with a high speed (6.3 mL/h) showed much less aligned and loosely packed morphologies compared to the one made with a low speed (3.8 mL/h).

Figure 3.1-4. Self assembled CNT buckypaper by vacuum filtration. (a) SEM image of CNT bucky paper with local aligned structure. (b) Polarized optical microscope image of CNT bucky paper, showing the birefringence textures because of multi-domains in the bucky paper. Reproduced from [142].

Although micro-size domain structures of aligned CNTs were realized in the above studies, there were no suggestions regarding how to achieve large-area monodomain films of aligned CNTs by vacuum filtration. The common assumption in these studies is that the formation of CNT alignment occurs in the suspension, and the filtration process is to convert the domain structures of the liquid into a solid and ordered film. Therefore, the only way to improve CNT alignment appears to be by increasing the CNT concentration and aspect ratio, as suggested by Onsager's theory.
3.2. Assembly of monodomain CNT films by controlled differential pressure filtration

In this section, we present the realization of highly aligned monodomain CNT films using our new technique – controlled differential pressure filtration (CDPF). We start with our discovery of spontaneous alignment of CNTs during vacuum filtration and then describe the preparation of aligned CNT films by CDPF. Finally, at the end of this section, we list detailed filtration procedures for different types of CNTs we used in this study.

In this study, our initial purpose was to make uniform thin films of randomly oriented CNTs by normal vacuum filtration. We followed the thin film making procedures used by previous studies with some small changes. The film making procedure included three major steps: 1) preparation of a CNT suspension, 2) vacuum filtration with a proper filter membrane, and 3) removal of the filter membrane and transfer of the CNT film onto a substrate.

**CNT suspension preparation:** CNT materials we used in the study were arc-discharge SWCNTs (P2-SWCNT) with an average diameter of 1.4 nm, purchased from Carbon Solutions, Inc. The surfactant for CNT dispersion was sodium deoxycholate (DOC), purchased from Sigma-Aldrich. P2-SWCNTs with an initial concentration of 0.4 mg/mL were dispersed in DOC (1% (wt./vol.)) by bath sonication for 15 minutes. The obtained suspension was then further sonicated with a tip sonicator (XL-2000 Sonicator from Qsonica, LLC. ¼” probe, ~30 watt) for 60
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minutes. The suspension was cooled in an ice water bath during the sonication process. Next, the suspension was centrifuged for 1 hour at 40000 rad/minute (Sorvall Discovery 100SE Ultracentrifuge using a Beckman SW-41 Ti swing bucket rotor) to remove large bundles from the suspension. After centrifugation, the upper 60% of the supernatant was collected and then diluted with nanopure water by 10 times; the final concentrations of SWCNTs and DOC were 40 µg/mL and 0.1%, respectively.

**Vacuum filtration:** The filtration setup (Millipore® XX1002500 glass microanalysis) used in the study was purchased from Fisher Scientific Company, LLC, including a 15 mL glass funnel, a fritted glass filter support, and a silicone stopper. Filter membranes with a pore size of 50 nm (Nuclepore Track-Etched Polycarbonate (Hydrophilic) Membranes) were purchased from GE Healthcare Life Sciences. Optical and SEM images of a polycarbonate filter membrane are shown in Fig. 3.2-1.

![Figure 3.2-1](image)

Figure 3.2-1 (a) Optical image of a polycarbonate filter membrane of 1 inch size. (b) SME image of the surface of the filter membrane. The pore sizes are around 50 nm.
The filtration setup was mounted on a side-arm flask, which was connected by a water flow vacuum pump (water aspirator). A 10 mL P2-SWCNT suspension was poured into the glass funnel. After applying a reduced pressure in the vacuum flask by the water aspirator, the liquid was slowly filtered down to the flask with a speed of ~ 2 mL/h. After 5 hours of filtration, a thin film of SWCNTs is formed on the surface of the filter membrane.

**Removal of filter membrane and CNT film transfer:** A wet transfer process was used to remove the filter membrane and transfer the SWCNT film onto a SiO₂/Si substrate. It consists 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 film touching the substrate surface, and dry the substrate by nitrogen gas so that the film stick to the surface of the substrate firmly, 3) rinse the substrate in an organic solvent (N-methyl-2-pyrrolidone (NMP)), 4) after twenty minutes, take out the substrate and clean it by acetone followed by nanopure water, and 5) dry the substrate by nitrogen gas again.

The transferred CNT film on the SiO₂/Si substrate was examined by SEM, as shown in Fig. 3.2-2. Instead of random orientation, CNTs are all aligned in the film with some cracks indicating the alignment direction. Most importantly, CNTs align in one direction over the entire film according to the SEM images. Although the alignment is distorted in some regions, there are no obvious domain boundaries. Note that the density of the film was actually not uniform on a large scale. The film surface was washed away by residual liquid at the end of filtration. Thus, the thin
aligned layer was only at the very bottom of the film. Nevertheless, the film showed monodomain structure, which was surprisingly different from previous reports about CNT films with multi-domains prepared by vacuum filtration. By carefully checking the film making procedure, we found that the major difference between our method and the previous methods was the surfactant concentration. For example, the surfactant concentration was 0.5%-1% in the report of Dan et al. while it was only 0.1% in our case (initially due to an accidental dilution of suspensions by nanopure water). In addition, the slow filtration speed (∼2 mL/h) we used was probably beneficial for the realization of CNT alignment, which was also mentioned by both Dan et al. and Oh et al.

Figure 3.2-2. Images of an aligned CNT film by slow vacuum filtration at a low surfactant concentration. The central panel is an optical image of an aligned CNT film transferred onto a quartz substrate. (a), (b), (c) and (d) are SEM images taken from four randomly-chosen positions on the film. The cracks show the direction of CNT alignment.
Intrigued by this initial discovery, we reproduced and optimized the film making procedure. We first introduced two major changes to the filtration system: 1) adding multiple pressure gauges in the vacuum line and 2) replacing the water aspirator with an oil-free mechanic vacuum pump. These modifications allowed us to adjust the filtration speed in a controlled manner. We then systematically investigated the influence of the filtration speed as well as other possible factors affecting the degree of CNT alignment, which will be discussed in Section 3.4. In order to avoid the washout of the film surface, we added a speed-up step near the end of filtration by quickly increasing the pressure in the vacuum flask to an optimized value. The strong pressure can suck the CNT film firmly on the filter paper, allowing the aligned structure to keep intact during the drying process.

Shown in Fig. 3.2-3 are SEM images of a P2-SWCNT film as well as an optical image of the film on a quartz wafer. It can be seen that the film is very uniform over the entire surface. The four pictures taken from four different positions on the film show that CNTs in the film are all densely aligned towards the same direction. In the direction perpendicular to the film surface, alignment structures grew up to 100 nm, estimated by AFM. There was only a very thin layer of misaligned CNTs (a few nm) on the top of the film, which could be easily etched away by an O² plasma, as shown in Fig. 3.2-4.
Figure 3.2-3. SEM images of bottom surface (the side touch on the filter membrane) of highly aligned CNT film by controlled differential pressure filtration (CDPF). The central panel is an aligned CNT film transferred on Quartz substrate. (a), (b), (c) and (d) are four SEM images taken from four randomly-chosen positions on the film. The uniform aligned directions at different positions show the monodomain structure of aligned CNT film.

Figure 3.2-4. SEM images of top surface (the side away from filter paper) of monomodian and highly aligned CNT film by CDPF. (a) SEM image of the top surface of a CNT film with thin misaligned layer. (b) SEM image of the top surface of the CNT film after the removal of the misaligned layer by oxygen plasma.

In order to test its universality, we also applied the method to other types of CNTs including arc-discharge (P8-SWCNT), CoMoCAT (CG200), HiPco (batch #195.5), and CVD (TUBALL CNTs). With proper adjustments of the filtration speed
and the pore size of the filter membrane, we successfully assembled all these CNTs into aligned films of macroscopic sizes. Shown in Fig. 3.2-5 are SEM images of aligned films made by different types of CNTs. Although the alignment quality varies from sample to sample, all these films are globally aligned, showing that the method is indeed a universal technique of CNT alignment.

Figure 3.2-5. SEM images of aligned films made from different types of CNTs. (a) TUBALL CNTs dispersed in DOC surfactant. (b) Arc-discharge (P8-SWCNT) dispersed in nanopure water. (c) CoMoCAT (CG200) dispersed in DOC surfactant. (d) HiPco (#195.5) dispersed in DOC surfactant.

In the following, we describe the assembling process in detail. The preparation conditions of CNT suspensions, such as the times and strengths of tip sonication and ultracentrifugation, remain the same as before. They are not critical for CNT alignment provided that CNTs are well dispersed. The film transfer is also the same.
as described before. Major changes occur during filtration procedure. The filtration procedure includes four general steps, which are summarized below:

**Step 1:** Putting a gentle or zero pressure on the filtration system at the beginning. The exact value of the initial pressure added to the filtration system depends on the volume of the suspension as well as the pore size of the filter membrane. The purpose of pressure control is to achieve a desired initial speed, which is normally in the range of 1-2.5 mL/hour. The pressure is controlled by adjusting multiple valves in the vacuum line; the value of the pressure is monitored by the pressure gauges in the vacuum line.

**Step 2:** Monitoring the filtration speed during the filtration process. As CNTs are gradually deposited on the filter membrane, the flow rate slows down. The CNT alignment occurs at the certain range of flow speed. It is important to keep the speed above 0.5 mL/hour in order to avoid misalignment of CNTs.

**Step 3:** Speeding up the filtration rate near the end of the filtration process. As discussed before, this step is to stabilize the alignment structures and make the film uniform. The timing of the speedup process is critical. If it occurs too early, the remainder of CNTs in the liquid will form a thick misaligned layer on the top due to the fast speed. If it occurs too late, the process of washing out starts on the film surface, leaving the film thinner at the center and thicker on the periphery. Therefore, the speedup process needs to be started when the majority of CNTs are filtered out and to be completed before the concave meniscus of the remaining suspension touches the surface of the filter membrane.
**Step 4:** Before the transfer process, the film is kept still for 15-30 minutes while the vacuum pump is on. This step is to make sure that the CNT film totally dries out.

Above four steps are applicable for all types of CNTs. However, detailed filtration conditions need to be adjusted for CNTs of different types in order to achieve the best alignment quality. For example, for smaller diameter CNTs, a slower filtration speed is generally required. At the end of this section, we list the filtration details for each type of CNTs used in the study.

**Arc-discharge SWCNTs:** P2-SWCNTs were dispersed by two types of surfactants: sodium deoxycholate (DOC) and sodium dodecyl benzene sulphonate (SDBS). The original P2-SWCNT concentration was 0.4 mg/mL. After 45 minutes of tip sonication followed by 1 hour of ultracentrifugation, a P2-SWCNT suspension of ~0.15 mg/mL in DOC (0.5%) or SDBS (0.4%) was obtained, which was then diluted by nanopure water. The concentration of CNTs after dilution was ~ 15 µg/mL, and the DOC concentration was ~ 0.1% for DOC dispersed samples, while the SDBS concentration was ~ 0.02% for SDBS dispersed samples.

As for P8-SWCNTs, they were water soluble because of functionalization by m-polyaminobenzene sulfonic (PABS) acid. So the CNT 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 also tip-sonicated for 45 minutes and then centrifuged by 1 hour. The concentration of CNTs was then turned into ~ 10 µg/mL. Polycarbonate filter membranes with a pore size of 200 nm were used for the
filtration of arc-discharge CNT suspensions. No pressure was put on the system at the beginning as the pore size of filter membranes was large enough to establish a desired filtration speed. The speeding up process when there was ~15%-20% suspension left. The final speed was stabilized at around 20 seconds per drop. The time for the entire filtration of 4-5 mL sample was 2.5-3 hours. After the filtration process was finished, the film was pumped on for an additional 15-30 minutes, allowing the film to dry completely.

**TUBALL CNTs:** The original CNT concentration was 0.4 mg/mL. A CNT suspension of ~0.14 mg/mL was obtained in DOC surfactant (1%) after the tip sonication and ultracentrifugation processes of the same durations as in the case of arc-discharge CNTs. After dilution with nanopure water, the concentrations of CNTs and DOC surfactant were ~14 µg/mL and 0.1 %, respectively. The filtration procedure was the same as that for the arc-discharge CNTs described above.

**CoMoCAT SWCNTs (CG200):** The original CNT suspension of ~0.4 mg/mL was dispersed in DOC surfactant (1%). After 1h tip sonication and 1h ultracentrifugation, the sample was diluted by nanopure water to make the final concentrations of CNT and DOC surfactant ~5 µg/mL and 0.03%, respectively. Polycarbonate filter membranes with a pore size of 80 nm were used for sample filtration. A weak pressure of 10-30 Pascal was applied to the system at the beginning, which was measured by pressure gauges mounted in the vacuum line. The filtration speed was around 5-6 minutes per drop in the beginning. The final speed was increased up to
20 seconds per drop in order to fix and dry the film fast. For a sample with ~1 mL volume, it took around one hour to finish the entire filtration process.

**HiPco SWCNTs (batch #195.5):** The sample powder was dispersed by DOC (mass concentration 1%) with an initial concentration of ~0.6 mg/mL. After 1 hour centrifugation, the 60% supernatant (~0.3 mg/mL) was collected and further purified and sorted by ATPE. The purified sample was enriched in the chiralities of (10,5), (8,6), and (7,6), and the average diameter was ~0.9 nm. The sample was then diluted by nanopure water, and the concentrations of SWCNTs and DOC surfactant were readjusted to ~12 µg/mL and 0.04%, respectively. Polycarbonate filter membranes with a pore size of 80 nm were used for sample filtration, and the procedure was the same as that for CoMoCAT CG200 described above.
3.3. Characterization of aligned CNT films made by controlled differential pressure filtration

In this section, we present the excellent properties of the films prepared by CDPF revealed by the following characterization methods: polarized optical microscopy (POM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), polarized Raman spectroscopy, terahertz transmission spectroscopy, and atomic force microscopy (AFM). At the end of this section, we list the details of each of these characterization methods.

We used optical, SEM, and TEM images to examine the morphology of aligned CNT films from macro- to nano-meter scales. Figure 3.3-1a shows a uniform and aligned P2-SWCNT film dried out on filter membrane after filtration. Figure 3.3-1b shows an optical image of the same film after being transferred onto a quartz wafer using the wet transfer method described in Section 3-2. SEM and TEM images of the film are shown in Figs. 3.3-1c and d, respectively.

According to these images, the CNT film is densely packed, with a density of \( \sim 10^6 \) CNTs in a cross-sectional area of 1 \( \mu \text{m}^2 \). Individual CNTs within the film are all aligned with each other, forming a globally ordered structure. Furthermore, analysis of the SEM images reveals that the angle standard deviation is around \( \sim 1.5^\circ \) across the entire film (\( \sim 1 \text{ inch}^2 \)), as shown in Fig. 3.3-1e. The film is optically polarized, being opaque to light polarized parallel to the CNT alignment direction and transparent to light polarized perpendicular to the alignment direction.
Figure 3.3-1. Characterization of wafer-scale monodomain films of aligned CNTs. (a) A wafer-scale, uniform CNT film is formed on the filter paper. (b) An optical image of the produced film after being transferred to a quartz substrate by dissolving the filter paper. (c) A scanning electron microscopy image and (d) a transmission electron microscopy image of the film, showing strong alignment and high density. (e) Angular distribution of CNTs within a 1 cm² area of the film, with a standard deviation of 1.5°, determined by SEM image analysis.
Figure 3.3-2. Film is opaque to light polarized parallel to the CNT alignment direction and transparent to light polarized perpendicular to the alignment direction on a macroscopic scale (a) and a microscopic scale (b). All images were taken with a polarized optical microscope. In (b), the Rice Owl shape was created on the aligned film by standard photolithography.

With cross-polarized microscopy, strong optical anisotropy was seen both on a macroscopic (cm) scale (Fig. 3.3-2a) and a microscopic (μm) scale (Fig. 3.3-2b), reflecting the global and local CNT alignment, respectively. Furthermore, the aligned film is very robust in water (unlike the CVD-grown aligned CNT films discussed in Chapter 2) and can be easily patterned using photolithography techniques. Figures 3.3-2b 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 strong optical anisotropy.

Figure 3.3-3 summarizes results of spectroscopic characterization measurements of aligned P2-SWCNT films. Figure 3.3-3a shows polarized Raman
spectra for a 15-nm-thick aligned film with an average tube diameter of 1.4 nm, taken with an excitation wavelength of 514 nm in two polarization configurations. The data was analyzed using standard equations for the angular dependence of SWCNT Raman spectra\cite{167} to deduce the value of the nematic order parameter $S$, which was 0.96 for this particular film. Electromagnetic response of this film was strongly polarization dependent in the whole spectral range, from the THz to the visible, as shown in Fig. 3.3-3b 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) while there is a prominent, broad peak at $\sim 0.02$ eV in the parallel case due to the plasmon resonance.\cite{168} Figure 3.3-3c 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 ($S_{11}$ and $S_{22}$) and the first interband transition in metallic nanotubes ($M_{11}$). These peaks are absent for the perpendicular polarization, and instead, a broad absorption feature is observed in an intermediate energy region between the $S_{11}$ and $S_{22}$ peaks. This weak feature is probably due to the $S_{12}/S_{21}$ absorption, the line-shape of which is similar to the perpendicular polarization spectra calculated by Ajiki and Ando incorporating the depolarization effect.\cite{169}
The exceptionally strong polarization dependence of THz transmission through aligned CNT films can be utilized to form an ideal THz polarizer\textsuperscript{[160]} with extremely large extinction ratios ($ER$); $ER = T_\parallel / T_\perp$, where $T_\parallel$ ($T_\perp$) is the transmittance for the parallel (perpendicular) polarization. Figure 3.3-3d shows time-domain waveforms of THz radiation transmitted through an aligned P8-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. The THz beam had a mm² size, thus probing a macroscopic area. Figure 3.3-3e 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 allows us to calculate the value of $S$ directly,[160] which also agrees with the value obtained by Raman spectroscopy. The value of $E_R$ monotonically increases with the film thickness, as expected, whereas high values of $S$ are maintained even for relatively thick films (Fig. 3.3-3f).

Table 3-1. Summary of properties for aligned films made by different types of CNTs.

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Product name</th>
<th>Surfactant</th>
<th>$d$ (nm)$^a$</th>
<th>$l$ (nm)$^b$</th>
<th>$S_{THz}$</th>
<th>$S_{Raman}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc-Discharge</td>
<td>P2-SWCNT</td>
<td>DOC</td>
<td>1.4</td>
<td>227</td>
<td>~1</td>
<td>0.96</td>
</tr>
<tr>
<td>Arc-Discharge</td>
<td>P2-SWCNT</td>
<td>SDBS</td>
<td>1.4</td>
<td>246</td>
<td>~1</td>
<td>0.94</td>
</tr>
<tr>
<td>Arc-Discharge</td>
<td>P8-SWCNT</td>
<td>N/A</td>
<td>1.4</td>
<td>295</td>
<td>0.77</td>
<td>0.72</td>
</tr>
<tr>
<td>CVD$^c$</td>
<td>TUBALL$^{TM}$</td>
<td>DOC</td>
<td>1.8</td>
<td>307</td>
<td>0.9</td>
<td>0.85</td>
</tr>
<tr>
<td>CoMoCAT</td>
<td>CG 200</td>
<td>DOC</td>
<td>~1</td>
<td>166</td>
<td>N/A</td>
<td>0.73</td>
</tr>
<tr>
<td>HiPco</td>
<td>#195.5</td>
<td>DOC</td>
<td>~0.9</td>
<td>298</td>
<td>N/A</td>
<td>0.72</td>
</tr>
</tbody>
</table>

$^a$Average diameter of CNTs, $^b$Average length of CNTs, $^c$CVD CNTs (TUBALL$^{TM}$) were purchased from OCSiAl.

In addition to aligned films made from P2-SWCNTs, we also characterized aligned films of other types of CNTs. Table 3-1 lists six representative suspensions used in this study. The alignment quality of each CNT film is characterized by the nematic order parameters, $S_{THz}$ and $S_{Raman}$, determined through THz and polarized Raman measurements, respectively. As one can see in the Table, both DOC and SDBS dispersed CNTs can be aligned very well. Even water-soluble P8-SWCNTs (no surfactant) can be aligned, indicating that surfactant is not a crucial element for
spontaneous CNT alignment during CDPF, as long as CNTs are well dispersed in the suspension. For CoMoCAT CG 200 and HiPco, only $S_{\text{Raman}}$ is available because films made by these two types of CNTs do not have sufficiently high carrier densities to show strong enough THz attenuation. Large values of $S (> 0.7)$ show that all these films are highly aligned.

Based on the above results, we conclude that our CDPF method provides a uniform, wafer-scale ($> \text{cm}^2$) CNT film of a controllable thickness (from a few nm to $\sim$100 nm) with a high degree of alignment ($S \sim 1$) and packing density ($\sim 10^6$ nanotubes per $\mu\text{m}^2$) 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 the CDPF method are compatible with CMOS microfabrication technology to fabricate various electronic and photonic devices (see Chapter 5 for more details).

Finally, below, we describe more details of the characterization methods used:

**Polarized optical microscope:** A Zeiss Axioplan 2 microscope was used to optically characterize the alignment of CNT films on a large scale. Two modes (cross-polarized and co-polarized) were used. 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 bright. As for 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.

![Image](image_url)

**Figure 3.3-4.** The polarized optical image of arc-discharge aligned CNT film (P2-SWCNT) when the polarization of incident light is (a) parallel and (b) perpendicular to the CNT alignment.

Shown in Fig. 3.3-4 are optical images taken in the co-polarized mode for an aligned P2-SWCNT film on a quartz substrate. The left and right images 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 perfectly global alignment of the CNT film. In addition, some cracks can be seen in the film, which, as a cleavage of a crystal, indicate the direction of CNT alignment in the film.

**Scanning electron microscopy (SEM) and transmission electron microscopy (TEM):** SEM and TEM were used to characterize the alignment of CNTs on a microscopic scale. All SEM images were taken using a JEOL 6500F scanning electron microscope. TEM images were taken using a JEOL 2100 field emission gun.
transmission electron microscope. The CNT density calculation was based on the average distance between individual CNTs from TEM images and the average diameter of CNTs being used.

**Polarized Raman spectroscopy:** A Renishaw inVia Raman microscope was used to quantitatively characterize the degree of alignment of CNT films. We performed polarized Raman spectra for all films made by CDPF and calculated the nematic order parameter $S$, as shown in Fig. 3.3-5. The spectra were taken under different polarization configurations ($I_{VV}$, $I_{VH}$, and $I_{HH}$) with an excitation laser wavelength of 514 nm. The $VV$ configuration is where the polarization 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 $\Delta = \frac{A_{//}}{A_{\perp}}$, where $A_{//}$ and $A_{\perp}$ are the parallel and perpendicular absorbances at 514 nm, respectively. The nematic order parameter, $S$, was then calculated based on the polarized Raman spectra taken in the three different modes and the dichroic ratio through the following equation:

$$S_{\text{Raman}} = \frac{6\Delta I_{VV} + 3(1+\Delta)I_{VH} - 8I_{HH}}{6\Delta I_{VV} + 12(1+\Delta)I_{VH} + 16I_{HH}}$$  \hspace{1cm} (3-1).
Figure 3.3-5. 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.

**Terahertz transmission spectroscopy (THz-TDS):** THz-TDS was used to quantitatively characterize the degree of CNT alignment on a macroscopic scale (~1 mm²). The experimental setup was a transmission time-domain THz spectroscopy system using an ultrafast Ti:Sapphire laser. Already linearly-polarized THz radiation further went through a wire-grid polarizer before being focused onto the sample.
The CNT films were transferred onto intrinsic silicon substrates for the transmission measurements. The thickness of the films ranged from 10-100 nm, and their areas were on the order of cm\(^2\) to fully cover the THz beam size (\(\sim\) mm\(^2\)). Polarization-dependent THz transmission data (Fig. 3.3-6) were obtained by rotating the sample, changing the direction of CNT alignment with respect to the polarization direction of the incident beam. The reduced linear dichroism (\(LD_r\)) and subsequent \(S\) were calculated based on the THz transmission data using the following equations:
\[ S_{THZ} = \frac{A_{//} - A_{\perp}}{A_{//} + 2A_{\perp}} \] (3-2).

**Atomic force microscopy:** A Bruker Multimode 8 AFM was used to characterize the average length of CNTs and the thicknesses of the CNT films. Figure 3.3-7 shows AFM images of six CNT samples used in this study. The average length of CNTs (see Fig. 3.3-8) was statistically calculated based on the AFM images. Figures 3.3-9a and b show the typical thickness of a P2-SWCNT film to be \( \sim 71 \text{ nm} \).

Figure 3.3-7. AFM images of seven CNT samples used in this work. (a) Arc-discharge P2-SWCNT dispersed by DOC. (b) Arc-discharge P2-SWCNT dispersed by SDBS. (c) Arc-discharge P8-SWCNT dispersed by nanopure water. (d) TUBALL CNTs dispersed by DOC. (e) CoMoCAT CG200 dispersed by DOC. (f) HiPco SWCNTs (batch #195.5) dispersed by DOC.
Figure 3.3-8. Length characterization of six CNT samples used in this work. (a) Arc-discharge P2-SWCNT dispersed by DOC. (b) Arc-discharge P2-SWCNT dispersed by SDBS. (c) Arc-discharge PB-SWCNT dispersed by DI water. (d) TUBALL CNTs dispersed by DOC. (e) CoMoCAT CG200 dispersed by DOC. (f) HiPco SWCNTs (batch #195.5) dispersed by DOC.

Figure 3.3-9. Thickness characterization of CNT films. (a) AFM image of P2-SWCNT film on quartz substrate and (b) corresponding height profile across the red dashed line in (a).
### 3.4. Discussion of factors affecting the degree of CNT alignment

In this section, we discuss the important factors that affect the degree of CNT alignment of films made by the CDPF method. We start with a general discussion about mechanisms of current CNT alignment techniques. We then analyze the functions of three critical factors for CNT alignment in CDPF, which allows us to gain some insight about the alignment mechanism. In the end, we will discuss the discrepancy of the alignment quality for different types of CNTs, emphasizing the influence of CNT stiffness.

Compared to the previous observations of partial CNT alignment in films prepared by vacuum filtration,[142, 151] what is remarkable about our method is the achievement of global (centimeter-size) alignment as well as the exceptionally high degrees of alignment ($S \sim 1$). These differences preclude the possibility that the alignment mechanism is based on the 3D LC phase transition of rigid rods, for which Onsager’s theory predicts an upper limit of $S = 0.79$.[153, 164]

A clue for the mechanism comes from our observation that the degree of alignment was sensitive to the hydrophobicity of the filter paper surface, similar to a prior report on 2D nematic ordering of DNA-wrapped CNTs.[170] When the hydrophilic coating layer was removed from the filter paper, CNT alignment was lost. In fact, many existing alignment techniques have been based on the self-assembly of CNTs on 2D surfaces, such as evaporation-driven self assembly,[137] Langmuir-Blodgett,[146] and Langmuir–Schaefer assembly.[141] What is common in
these techniques is that the ordering phase occurs due to the confinement of CNTs on a 2D surface at a very dilute concentration. We showed that, in our CDPF method, the degree of alignment is strongly dependent on the dilute concentration of CNTs, the dilute surfactant concentration, and the well-controlled flow rate (surface pressure), indicating that spontaneous alignment of CNTs is likely initiated on the surface of the filter membrane.

3.4.1. Three critical factors: CNT concentration, filtration speed, and surfactants concentration

In this section, we discuss the three critical factors that strongly affect the degree of CNT alignment during CDPF. CoMoCAT CG200 CNTs were chosen to study the influence of these factors quantitatively, but experimental phenomena discussed below are applicable to all species of CNTs we used. The polarization-dependent absorption spectra of the fabricated CNT films were measured using a 660 nm diode laser. The $LD_r$ defined as $LD_r = 3(A_{//} - A_{\perp})/(A_{//} + 2A_{\perp})$ at this wavelength was then calculated and used as a measure of the degree of alignment, together with SEM images, to evaluate the alignment quality under different conditions.

**CNT concentration:** In this study, CNT suspensions with different concentrations were prepared in the range from 4 to 30 µg/mL by diluting the parent suspension with nanopure water, while keeping the concentration of DOC surfactant the same (0.05%). Experimental results showed that alignment started degrading when the CNT concentration increases to a certain value. Specifically, for
the CG 200 sample being used here, the transition occurred at the concentration of ~20 µg/mL, as shown in Fig. 3.4-1.

![Absorption spectra and LD value](image)

**Figure 3.4-1.** The alignment dependence on the concentration of CNTs (CG200). (a) Absorption spectra of CNT suspensions with different concentrations. Inset: CNT suspensions with decreasing concentration from 30 µg/mL to 4 µg/mL. (b) The LD value of aligned CNT films as a function of CNT concentration.

The above result clearly shows that CNT alignment is achieved only at low concentrations of CNTs. This fact is fundamentally different from the general 3D LC phase transition, where a high concentration of CNTs, above a certain threshold value, is required to drive the system from an isotropic phase to an anisotropic phase. For example, for CNTs with an average aspect ratio of ~10³, a threshold value of ~5 mg/mL is required for a 3D CNT LC phase transition to occur.[139] This condition was not met in our case (typical CNT concentration ~15 µg/mL, and aspect ratio = 150-550), indicating that a different mechanism is at work. One assumption is that CNTs start forming ordered structures while accumulating on the surface of the filter membrane, but they remain in the isotropic status in the
suspension. Ordering structure on a surface can occur at a very low initial CNT concentration, as shown by previous 2D self-assembly methods.\[141, 170]\)

**Filtration speed:** In this study, two samples were prepared with the same CNT concentration of \(\sim 15 \, \mu\text{g/mL}\) and the same DOC concentration of \(\sim 0.045\%\) but at two different filtration speeds (1 mL/hour and 5 mL/hour). Both SEM images and polarized absorption spectra (see Fig. 3.4-2) showed that the degree of alignment strongly decreases with increasing filtration speed. However, we also found that CNT alignment disappears if the filtration speed is too slow.

![Figure 3.4-2](image.png)

*Figure 3.4-2. The influence of the filtration speed on CNT alignment. (a) SEM image of the sample at a slow filtration speed (1 mL/hour) and (b) the sample at a high filtration speed (5 mL/hour). (c) The angular dependence of CNT film absorption under a polarized laser beam (660 nm).*
Since the filtration speed is related to the pressure that CNTs feel on the surface of the filter paper, our results seem to indicate that alignment can only be achieved when the surface pressure applied to the CNTs is in a proper range. This can be understood in the context of 2D confinement-induced alignment. A slow flow rate means a weak surface pressure. When the surface pressure is too weak, the confinement of CNTs on the filter surface will weaken, leading to a loss of CNT alignment. On the contrary, if the surface pressure is too strong, CNTs will not have the freedom necessary to re-arrange themselves, which again inhibits the development of aligned structures.

**Surfactant concentration:** For this study, the concentration of CNTs was fixed at ~15 µg/mL, and the concentration of DOC surfactant was varied from 0.03 to 0.5%. As shown in Fig. 3.4-3, the \( LDr \) value decreases dramatically when the concentration of DOC surfactant rises above the critical micelle concentration (CMC), which is ~ 6 mM or ~0.24% in mass concentration. 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. Indeed, the use of low surfactant concentration is one of the major differences from previous vacuum filtration methods, where random CNT networks or multiple domains of CNTs were obtained.
Based on Onsager’s theory, 3D nematic ordering is driven by the steric force among rigid rods, which is repulsive and prevents the rods from getting too close to each other.\cite{164,165} During filtration, CNTs will get very close to each other on the filter membrane when the liquid is draining out and many CNTs are being deposited on the surface. Indeed, in our experiments, the density of aligned CNTs is very high; CNTs are present in the form of dense fabric structures in the film. Therefore, we speculate that van der Waals forces among CNTs play an important role in the formation of alignment. In the low concentration of surfactants, CNTs on the surface of filter paper bundle into ordered structures with the assistance of van der Waals attractive interactions. On the other hand, this process could be suppressed by dominated repulsive forces among CNTs in the presence of large amount of surfactants. Furthermore, attractive forces are likely responsible for the accumulation of aligned CNTs along the direction perpendicular to the surface, leading to the transition of 2D ordering to 3D ordering. A reasonable assumption is

Figure 3.4-3. (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 0.3% DOC concentration.
that once there is an aligned layer, CNTs that follow will tend to align along the already-existing alignment direction due to the attractive interaction with CNTs inside the aligned layer.

Based on the above considerations, we suggest that CNT alignment in CDPF occurs due to the confinement of CNTs on the filter paper surface under a proper flow rate. The attractive interactions among CNTs in a low surfactant environment play an important role for the formation and growth of aligned structures. Nevertheless, the mechanism driving the aligned structures to grow into monodomains of macroscopic size is not fully understood at this point.

### 3.4.2. Influence of CNT stiffness

According to our experiments, as long as the three conditions mentioned above are met, global alignment can be achieved for all CNTs independent of the growth methods, species, and surfactant used for dispersion. However, the degree of alignment varies for different species of CNTs as shown in Table 3-1 in Section 3-3. While further studies are needed to establish a detailed relationship between the achievable alignment strength and the geometric properties of CNT species, the existing results show that, generally, large-diameter CNTs (arc-discharge and TUBALL) tend to align better than small-diameter CNTs (CoMoCAT and HiPco).

In order to verify the influence of CNT diameter on alignment strength, we performed a series of tests on the same batch of HiPco CNTs (batch #195.5). CNTs with diameters smaller than ~0.8 nm were removed from the original sample by
using the diameter sorting capability of the ATPE method. Shown in the Fig. 3.4-4 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 $\sim0.4$ to $\sim0.6$ indicates an enhancement of the degree of alignment through removal of small-diameter CNTs.

![Absorption spectra and angular dependence](image)

Figure 3.4-4. (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 by original sample (red) and sorted sample (black) under a polarized laser beam (660 nm). The increasing of $LD_r$ indicates the improvement of alignment in CNT films.

Based on these results, we propose that the stiffness of CNTs with different diameters affect the degree of alignment. Because the in-plane stiffness is proportional to the cube of the CNT diameter,\textsuperscript{171} CNTs of small diameters are much less stiff compared to CNTs of large diameters. Hence, they are expected to be more sensitive to their environment and get bent and entangled more easily in the presence of external disturbances, leading to less-ideal alignment structures. This hypothesis is consistent with the optimized filtration conditions of CNTs of different diameters we presented in Section 3-2. CNTs with smaller diameters need a slower
flow rate and longer time to get aligned because the slower flow rate probably gives a more stable solution environment in which small diameter tubes can be aligned without disturbance. The difference of stiffness for CNTs with different diameters also can be visualized from AFM images in Fig. 3.3-7. One can find that CoMoCAT and HiPco CNTs tend to be wiggled and curved, while arc-discharge and TUBALL CNTs are straighter and less flexible. Therefore, in order to improve the alignment strength of small-diameter tubes, we need to find an effective way to overcome their flexibilities.
Photodetectors based on aligned carbon nanotube films grown by CVD

Photodetectors play key roles in many applications such as remote sensing, night vision, thermal and medical imaging, and chemical detection. Several properties including performance, reliability, ease of integration, cost and weight are all important in determining the attributes of photodetectors for particular applications. While a number of materials have been used over the past several decades to address photodetection needs across the electromagnetic spectrum, the advent of nanomaterials opens new possibilities for photodetectors. In particular, CNTs possess unique properties that have recently been explored for photodetectors.

In this chapter, we first review photodetectors of different types that have been realized with CNTs previously and then present our studies on IR and THz photothermoelectric (PTE) detectors based on macroscopically aligned SWCNT
films grown by CVD. It covers results of device fabrication and characterization, analysis of device mechanisms as well as various factors affecting device performances.
4.1. Review of carbon nanotube photodetectors

CNTs are promising candidates for new-generation photodetectors because of their strong broadband absorption, excellent electric, thermal and optoelectronic characteristics, superb mechanical and chemical stabilities. During the last decades, studies on CNT-based photodetectors have made substantial progress, and a variety of device prototypes have been reported. Based on the operation mechanism, these devices can be classified into the following types: phototransistors, photoconductors, photodiodes, bolometers, and photothermopiles. CNT phototransistors and photoconductors are most immature from the perspective of applications although they are often used to study the basic photophysics of CNTs. Studies relevant to applications focus on using CNT films to make photodiodes, bolometers, and photothermopiles, which are summarized in Fig. 4.1-1. The working spectral ranges of these detectors are from the THz to IR region to the ultraviolet range, and a few of them show performance characteristics approaching those of commercial photodetectors, while the majority of them are still immature, requiring much improvement.
4.1.1. CNT photodiodes

Photodiodes work based on the photovoltaic effect,\textsuperscript{[176]} in which optically excited electron-hole pairs are separated by a built-in electric filed to produce photocurrents. Compared to conventional semiconducting materials, using s-SWCNTs to make IR photodiodes is attractive due to several advantages, including strong absorption of CNT films in the IR region, and their superb mechanical and chemical stabilities. For instance, s-SWCNTs with a suitable diameter distribution have an absorption coefficient of up to $10^4$-$10^5 \text{ cm}^{-1}$ from the near-IR to the middle-IR, which is larger by about one order than those of traditional materials used in IR detection such as mercury-cadmium-telluride (MCT).\textsuperscript{[181]} With the ever-lowering cost of synthesis methods for SWCNTs and the continuous improvement of post-
growth sorting techniques, it is highly possible that compact, light-weight, flexible, low-cost, and high-efficiency IR photodiodes based on s-SWCNT films will be developed in the near future.

So far, CNT-photodiodes have been realized on various structures, including p-n junctions, asymmetrical electrodes, and type-II heterojunctions. The studies of CNT photodiodes have been roughly going through three phases: i) individual s-SWCNT photodiodes, ii) photodiodes based on s-SWCNT arrays or films, and iii) photodiodes based on s-SWCNT film/polymer heterojunctions.

Table 4-1 lists some of the most important results in this field from 2003 to today. The development of CNT photodiodes tackles two key problems: i) how to construct a diode structure to efficiently separate electron-hole pairs into free carriers and ii) how to increase the absorption cross-section of the device. As shown in Table 4-1, in recent years, significant progress has been achieved, with the responsivity increasing from ~ pA/W to ~ A/W. Photodiodes based on aligned s-SWCNT arrays are promising with much improved responsivity compared to individual s-SWCNT diodes. The next challenge is how to increase the low density of SWCNTs arrays in the device channel, which is largely limited by the synthesis method. Up to now, the most successful CNT photodiode is the one based on SWCNT/C_{60} PHJ with the external quantum efficiency (EQE) of 12% and an average detectivity of ~ 10^{11} \text{cm Hz}^{1/2}/\text{W} (see Fig. 4.1-2), approaching commercial InGaAs detectors (10^{12} \text{cm Hz}^{1/2}/\text{W}) in the same working range. Further improvement
relies on the increase of the exciton diffusion length, which probably can be achieved by using aligned s-SWCNT thin films.

Table 4-1. Summary of major CNT-based photovoltaic detectors from 2003 to 2014.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Individual SWCNT[182]</td>
<td>p-i-n diode</td>
<td>N/A</td>
<td>N/A</td>
<td>~0.4 pA/W</td>
<td>N/A</td>
<td>1.5</td>
</tr>
<tr>
<td>SWCNT array[181]</td>
<td>BFBDb)</td>
<td>~10.4%</td>
<td>N/A</td>
<td>~6.58 × 10^{-2} A/W</td>
<td>1.09 × 10^7</td>
<td>0.785</td>
</tr>
<tr>
<td>P3HT:SWCNTs/C_{60}[50]</td>
<td>PHJc)</td>
<td>2.3%(44%)</td>
<td>7.2 ns</td>
<td>0.023 A/W</td>
<td>10^{10}-10^{11}</td>
<td>0.4-1.45</td>
</tr>
<tr>
<td>s-SWCNTs/C_{60}[53]</td>
<td>PHJ</td>
<td>12.9%(91%)</td>
<td>N/A</td>
<td>0.05 A/W</td>
<td>0.6 × 10^{12}</td>
<td>1.2</td>
</tr>
<tr>
<td>s-SWCNT/GO/PC_{71}BM[183]</td>
<td>BHJd)</td>
<td>2.3%</td>
<td>30-50 ms</td>
<td>0.25 A/W</td>
<td>0.9 × 10^{12}</td>
<td>0.86</td>
</tr>
</tbody>
</table>

a)The table only lists the devices where major device parameters are available. The data that are not available are marked as N/A. b)Barrier Free Bipolar Diode, c) Planar Heterojunction, d) Bulk Heterojunction.
4.1.2. CNT bolometers

Bolometers operate via the absorption of electromagnetic radiation and its conversion into heat, which in turn changes the resistance of the material according to its temperature coefficient of resistance (TCR) defined as

\[
TCR = \frac{1}{R} \frac{dR}{dT},
\]

where \( R \) is the resistance of the bolometer material and \( T \) is the temperature. Generally, the efficiency of a bolometer depends on several factors: large optical
absorption, high TCR, low heat capacity, and good thermal isolation to the environment.

CNT films have strong broadband absorption\textsuperscript{[184]} excellent thermal characteristics, such as low specific heat capacity\textsuperscript{[185]} and strong thermal stability\textsuperscript{[186]}, all of which are suitable for bolometer applications. However, the TCR of CNT films is normally $\sim0.1\%/K$ at room temperature\textsuperscript{[187]} far less than that of vanadium oxide (above 3%/K), which is the leading platform for uncooled bolometric detection at present\textsuperscript{[188]} Many efforts in the study of CNT bolometers have been put on improving the TCR of CNT films. In this regard, a variety of methods have been investigated such as variations of CNT film thicknesses\textsuperscript{[72]} sorting electronic types\textsuperscript{[74]} and engineering of the activation energy for carrier transport through inter-tube junctions by using polymer matrices\textsuperscript{[189-191]}

The study of bolometers based on CNT films was initiated by the pioneering work of the Haddon group in 2006\textsuperscript{[72]} in which they demonstrated the IR photoresponse of suspended SWCNTs in vacuum due to the bolometric effect (see Fig. 4.1-3). During the past a few years, CNT-based bolometric detectors have made much progress, and their performances are continuously being improved. Table 4-2 lists some of the most important results from 2006 to 2015, in which all device parameters were measured at room temperature. CNT-based bolometric IR detectors can be classified into three categories: i) SWCNT films, ii) SWCNT-polymer composites, and iii) MWCNT bundles or films. In going from SWCNT films to SWCNT-polymer composites, the TCR has been improved from $\sim0.1\%/K$ to
~6.5%/K. Unfortunately, the increase of TCR also came at the cost of other important properties such as the response time. The typical response time of these devices is in the range of tens of milliseconds, and the typical detectivity is ~10^6-10^7 cm Hz^{1/2}/W with working wavelengths spanning from the near IR (~0.94 µm) to the long-wavelength IR region (~20 µm). Currently, the detectivity of the best CNT bolometers is still 1-2 orders lower than that of commercial bolometers (~ 10^8 cm Hz^{1/2}/W).[188]

Figure 4.1-3. (a) Diagram of a bolometer based on a suspended SWCNT network. (b) 100-nm-thick SWCNT film suspended across a 3.5 mm opening of a sapphire ring. (c) Modulation of the resistance of a SWCNT film at 50 K under square-wave pulse of IR radiation with a power of 0.12 µW. (d) Spectra of near-IR absorption (curve a) and electrical photoresponse of SWCNT film (curve b). Reproduced from [72].
Table 4-2. List of major CNT-based bolometric photodetectors with key device parameters from 2006 to 2015

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>SWCNTs</td>
<td>Suspension (vacuum)</td>
<td>~0.1-0.7%</td>
<td>~50 ms</td>
<td>~10</td>
<td>N/A</td>
<td>0.94</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Suspension (patterned Si)</td>
<td>~0.17%</td>
<td>40-60 ms</td>
<td>~250</td>
<td>4.5X10^6</td>
<td>1.3</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>Pixels suspension (patterned Si)</td>
<td>N/A</td>
<td>10 ms</td>
<td>N/A</td>
<td>5.5X10^6</td>
<td>0.8-10</td>
</tr>
<tr>
<td>Aligned SWCNTs (PVP matrix)</td>
<td>Coating (Si)</td>
<td>~2.94%</td>
<td>~0.94 ms</td>
<td>~230</td>
<td>1.22X10^8</td>
<td>0.3-2</td>
</tr>
<tr>
<td>Aligned SWCNTs (polystyrene matrix)</td>
<td>Suspension (air)</td>
<td>~0.82%</td>
<td>150-200 ms</td>
<td>~500</td>
<td>N/A</td>
<td>2.5-20</td>
</tr>
<tr>
<td>SWCNTs (PNIPAm matrix)</td>
<td>Suspension (air)</td>
<td>~10%</td>
<td>83 ms</td>
<td>48</td>
<td>N/A</td>
<td>1-20</td>
</tr>
<tr>
<td>MWCNTs (pristine)</td>
<td>Suspension (patterned Si)</td>
<td>~0.07%</td>
<td>~1-2 ms</td>
<td>N/A</td>
<td>3.3X10^6</td>
<td>1.3</td>
</tr>
<tr>
<td>MWCNTs (pristine)</td>
<td>Suspension (patterned resist)</td>
<td>~0.08%</td>
<td>60 ms</td>
<td>~110</td>
<td>4 X10^6</td>
<td>0.94</td>
</tr>
<tr>
<td>MWCNTs (pristine)</td>
<td>Suspension (Ag antennas)</td>
<td>0.3%</td>
<td>25 ms</td>
<td>~800</td>
<td>1X10^7</td>
<td>10.6</td>
</tr>
<tr>
<td>Aligned MWCNTs (pristine)</td>
<td>Suspension (air)</td>
<td>0.144%</td>
<td>4.4 ms</td>
<td>~30</td>
<td>N/A</td>
<td>0.98</td>
</tr>
</tbody>
</table>

a) The table only summarizes the devices which have given out major device parameters. The data that are not available are marked as N/A.

4.1.3. CNT PTE detectors

The photothermoelectric (PTE) detector (also known as photothermopile) is another type of widely used thermal detector.[176] CNT-PTE detectors show ultrabroadband response, covering the electromagnetic spectrum from the UV, visible, infrared, to the THz region. They are advantageous in the detection of long-wavelength radiation, and are promising for THz detection at room temperature.[176]
The operation of a PTE detector is based on the Seebeck effect, where the light heats the device and generates a temperature gradient along the device channel, which in turn gives rise to a photovoltage (photocurrent) across the device. The thermovoltage is defined by

\[ \Delta V = -\int S \nabla T \, dx \]  

(4-2)

where \( S \) is the Seebeck coefficient of the active material, and \( \nabla T \) is the temperature gradient in the sample channel. While \( S \) is an intrinsic property of the material itself, large temperature gradients require efficient thermal isolation of a device from the environment. Based on Eq. (4-2), a temperature gradient must be generated in the device, and this leads to three main device designs: in the first design, the device is symmetric, and only one of the two contacts is illuminated, leading to a temperature gradient between the two electrodes. In the second design, the device is asymmetric with two different electrodes made by metals of different work functions, and the device works under global illumination. In the third design, a p-n junction is created in the device channel, and the p-n junction is illuminated, causing a temperature gradient between the p-n junction and the contacts.

In the case of illumination at one contact in a symmetric device,\(^{[197]}\) the thermovoltage is

\[ \Delta V = \Delta T \left( S_{\text{CNT}} - S_{\text{metal}} \right) \]  

(4-3)
where $\Delta T$ is the temperature difference between the two electrodes, and $S_{\text{metal}}$ is the Seebeck coefficient of metal electrodes. This component is usually small compared to that of the active material (the CNT material in this case), and can usually be neglected for a high-performing device. In the case of the p-n junction, we have instead

$$\Delta V = \Delta T \left( S_p - S_n \right) \quad (4-4)$$

where $S_p$ and $S_n$ are the Seebeck coefficients for the p-type and n-type CNT materials, respectively. Since the Seebeck coefficients of p-type and n-type materials have opposite signs, it is immediately clear from these two expressions that a p-n junction geometry is advantageous, provided that a high Seebeck coefficient can be realized for the p-type and n-type doping, and that a similar temperature gradient can be generated. As in the case of the bolometric detector, the device response time is given by:

$$\tau = \frac{C}{G}. \quad (4-5)$$

Given the simplified situation where Johnson noise dominates the detector noise, the detectivity of a CNT-PTE detector depends\[198] on the thermoelectric figure of merit $ZT$ as $D^* \sim (ZT)^{1/2}$, where

$$ZT = \frac{S^2 \sigma}{\kappa} \quad (4-6)$$
with $\kappa$ the thermal conductivity of the CNT film. Thus, improving the performance of
PTE detectors requires improving the full thermoelectric properties of the active
material. CNTs are suitable to make broadband PTE detectors working in the long
wave-IR and the THz because of the following reasons: i) strong optical absorption
due to the free carrier absorption and plasmonic resonances,[199] which can lead to
large temperature increases, ii) relatively large Seebeck coefficient, with values of $\sim
80 \ \mu V/K$ to $\sim 160 \ \mu V/K$ due to enhancement through the incorporation of
polymers[200] or electronic type separation,[201] iii) conversion from p-type to n-type
by diverse doping methods,[29] allowing for the fabrication of CNT-PTE detector
based on p-n junctions,[202-204] and iv) the flexibility and strong mechanic properties,
allowing CNT films to be suspended or deposited on many types of substrates.[203]

CNT-PTE detectors have been made by using large-size CNT films, including CNT
networks,[200, 204-205] aligned CNT films[202-203, 206] and CNT-polymer composites.[207]
The device architectures are diverse, including p-n junctions,[200, 202-204] asymmetric
metal electrodes[206] and asymmetric thermal contacts.[19, 208] For example, recently,
a CNT-PTE detector with asymmetric metal electrodes has been developed in our
laboratory, based on macroscopically aligned SWCNT films grown by the CVD
method.[206] It is broadband and polarization sensitive, and the generated
photocurrent is maximized at the interface between the electrodes and SWCNT
channel, as shown in Fig 4.1-4

Table 4-3 lists the major CNT-based PTE photodetectors with key device
parameters from 2006 to 2015. As can be seen, the response time of a PTE detector
is normally slow, from milliseconds to seconds, due to its reliance on thermal dissipation. Currently, the detectivity of CNT-PTE detectors is also low, less than $10^7$ cm Hz$^{1/2}$/W, which is comparable to that of most CNT bolometers.

Figure 4.1-4. (a) Schematic of a PTE photodetector based on macroscopically aligned SWCNTS film. Inset: SEM image of the aligned SWCNT film. (b) I-V curves in the dark and under global illumination at 660 nm on the photodetector with asymmetric contacts. (c) Linear power dependence of the open-circuit photovoltage at various wavelengths. (d) Photocurrent map showing that the signals are located at the interfaces between electrodes and sample channel. Reproduced from [206].
Table 4-3. List of major CNT-based PTE photodetectors (also known as photothermopiles) with key device parameters from 2006 to 2015.

<table>
<thead>
<tr>
<th>Materials\textsuperscript{a)\textsuperscript{[200]}}</th>
<th>Architecture</th>
<th>Response time</th>
<th>Responsivity [V/W]</th>
<th>Detectivity [\text{cm Hz}^{1/2}/\text{W}]</th>
<th>Wavelength [\mu m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT networks\textsuperscript{[200]}</td>
<td>p-n junction</td>
<td>&gt;10 s</td>
<td>~1.3 V/W</td>
<td>N/A</td>
<td>0.98</td>
</tr>
<tr>
<td>SWCNT networks\textsuperscript{[204]}</td>
<td>p-n junction</td>
<td>0.034 s</td>
<td>~0.9-1.8 V/W</td>
<td>2X10\textsuperscript{6}</td>
<td>0.66-1.8</td>
</tr>
<tr>
<td>Aligned SWCNT film\textsuperscript{[206]}</td>
<td>Asymmetric electrode</td>
<td>~32 us</td>
<td>~0.028 V/W</td>
<td>1.1X10\textsuperscript{5}</td>
<td>0.66-3.3</td>
</tr>
<tr>
<td>SWCNT networks\textsuperscript{[19]}</td>
<td>Asymmetric thermal contact</td>
<td>N/A</td>
<td>~2.5V/W</td>
<td>N/A</td>
<td>140 GHZ</td>
</tr>
<tr>
<td>DWCNT network\textsuperscript{[208]}</td>
<td>Asymmetric thermal contact</td>
<td>~0.2-8 s</td>
<td>~0.022 V/W</td>
<td>N/A</td>
<td>2.52 THZ</td>
</tr>
</tbody>
</table>

\textsuperscript{a)\textsuperscript{[200]}} The table only lists the devices where major device parameters are available. The data that are not available are marked as N/A.
4.2. CNT infrared photodetectors

Light polarization is used in the animal kingdom for communication, navigation, and enhanced scene interpretation,\textsuperscript{[209]} and also plays an important role in astronomy,\textsuperscript{[210]} remote sensing,\textsuperscript{[172]} and military applications.\textsuperscript{[211]} To date, there have been few photodetector materials demonstrated to have direct polarization sensitivity. While in animals polarization detection is intrinsic to their photoreceptors, most technological implementations of polarimeters utilize a non-monolithic approach, where polarizers are positioned in front of photodetectors.\textsuperscript{[212]} Removing this design complexity would be very valuable, and such monolithic approaches have been explored with quantum-well infrared photodetectors.\textsuperscript{[213]} Unfortunately, these systems require the use of a grating to couple the incident light into the quantum wells\textsuperscript{[214]} and are not amenable to flexible or nonplanar applications. One question therefore is whether one can take advantage of carbon-based materials, as nature does, to circumvent some of these issues. There have been many studies exploring the use of carbon nanotubes (CNTs) in photodetection, from individual CNTs\textsuperscript{[30, 179, 215]} to large-size CNT films.\textsuperscript{[176]} Individual CNT devices are limited by their minuscule optical absorption, while most previous studies on large-size CNT-film devices were based on randomly distributed CNT networks and therefore are not polarization sensitive.\textsuperscript{[50, 204, 216]}

In this section, we present the realization of a carbon-based broadband photodetector, where the polarimetry is intrinsic to the active photodetector material. The detector is based on p-n junctions formed between two macroscopic
films of single-wall carbon nanotubes. A responsivity up to \( \sim 1 \text{ V/W} \) was observed in these devices, with a broadband spectral response spanning the visible to the mid-infrared. This responsivity is about 35 times larger than previous devices without p-n junctions. A combination of experiment and theory is used to demonstrate the photothermoelectric origin of the responsivity and to discuss the performance attributes of such devices.

### 4.2.1. Device fabrication

Our p-n junction IR detectors were constructed with horizontally-aligned SWCNT films. The preparation of these SWCNT films involves three steps: 1) water-assisted CVD growth, 2) water vapor etching, and 3) dry transfer. We started from
the growth of vertically aligned SWCNT arrays on 1 cm × 1 cm Si substrates coated with a bilayer of Fe/Al₂O₃. The growth time was 3 minutes followed by 5 minutes of water vapor etching. These samples were checked under a JEOL 6500 scanning electron microscope. The height of vertically aligned SWCNT arrays was typically around 60 µm. They were then rolled down and transferred to Teflon tapes or smooth Al foils. After the transfer, SWCNT arrays became horizontally aligned films with the area of 1 cm× 1 cm and the thickness of a few µm. They were cut into small strips with width of 1 mm and length of 3-5 mm. These SWCNT strips on Al foils were then peeled off, putting on other desired substrates such as glass slides and AlN substrates. Prepared BV solution with a concentration of 70 mM was used to dope SWCNT films from unintentionally p-type into n-type.[28] The fabrication of p-n junctions was achieved by overlaying a p-doped SWCNT film onto an n-doped SWCNT film. Two electrodes were made by daubing silver paste on the two edges of the film. Shown in Fig. 4.2-1 is the diagram of the whole process of our device fabrication.

4.2.2. Photoresponse measurements

The photoresponse of our devices were measured using different light sources to cover the range from 660 to 3300~nm: a 660-nm laser diode; a tunable Ti:sapphire laser to cover the range from 700 to 1100~nm; the signal output of an optical parametric oscillator (OPO) for the range from 1100 to 1600~nm, and the OPO idler output for the range from 1600 to 3300~nm. The measurements were
performed at room temperature in air. Two-probe current-voltage ($I$-$V$) curves were taken using a Keithley 2400 source meter.

$I$-$V$ curves with and without laser illumination of the junction are shown in Figure 4.2-2a. Although there is a p-n junction at the center of the device, the $I$-$V$ curve is linear, indicating the absence of rectification. This is not surprising because CVD-grown samples contain a mixture of semiconducting and metallic SWCNTs, and the presence of metallic SWCNTs in the films gives the device metallic transport characteristic. Upon illumination of the junction, the $I$-$V$ curve shifts upward, producing both a photovoltage (PV) at zero current and a photocurrent (PC) at zero voltage. From this, the open-circuit PV ($V_{oc}$) and short-circuit PC ($I_{sc}$) are determined as ~2 mV and ~25 mA, respectively. The broadband response of the photodetectors is demonstrated in Figure 4.2-2b, where it is seen that the photoresponse is essentially flat from 700 to 3300~nm within the uncertainties of the measurements. Good linearity of the response are also obtained (inset in Fig. 4.2-2b) across the range of measured wavelengths. Most importantly, the photodetector exhibits strong polarization sensitivity due to the horizontal alignment of SWCNTs. Our measurements indicate that the polarization sensitivity of the detector increases from the visible to the infrared region, consistent with previous report regarding polarization-dependent terahertz, infrared and visible absorption measurements of a similar film. As shown in Figure 4.2-2c, the ratio between the parallel and perpendicular polarization PV is around 0.78 and 0.61 at 660~nm and 3300~nm, respectively.
4.2.3. PTE mechanism

In order to understand the origin of the photoresponse, we performed scanning PV microscopy (SPVM) on devices made by pure p-doped film and pure n-doped film and p-n junction film. The measurements were performed using the 660-nm...
diode laser and a home-built scanning photocurrent microscopy system.\cite{206} The laser beam was focused to a diameter of \( \sim 1\mu m\) on the device channel through a long working-distance apochromatic objective lens with a typical CW power of 10 mW.

SPVM measurements were shown in Figure 4.2-3a, one can find that for pure p- and n-doped device, the PV is only observed near the contacts, which is consistent with previous reports of PTE effect in large-area SWCNT films.\cite{197, 206} However, the p-n junction device showed an additional, much larger peak at the junction. In a conventional p-n junction where the response is photovoltaic, the PV is proportional to the junction area. Thus, one question is whether the photoresponse of the devices studied here scales in the same manner. To explore this issue, two different devices, A and B, were made (the inset of Fig. 4.2-3b). In both devices, the n-type SWCNT films were doped with the same BV concentration. For device A, a very narrow p-n junction was made, but for device B, the overlap distance was very long (\( \sim 1mm\)).
Figure 4.2-3. Scanning photovoltage microscopy of CNT devices. (a) Comparison of the photoresponse of p-doped, n-doped, and p-n junction devices on Teflon. (b) Comparison between two devices on Teflon with a short and long overlapping length in p-n junction region. (c) Theoretical predictions of the photovoltage profile when the laser spot is scanned across the device for three different p-n overlap distances ($L = 1, 4,$ and $8$ mm), where the overlap region is between $-L/2$ and $L/2$.

Figure 4.2-3b shows the PV position dependence for the two devices. It can be found that there is only one peak appearing at the junction of device A, but two peaks appear for device B, which are located at the two edges of the p-n junction. In
the overlapping region of device B, the PV becomes much smaller compared to the edges. This means that most of the signal comes from the edges instead of the overlapping region, and that the photoresponse is maximized with smaller area of the p-n junction, in contrast to conventional photovoltaic p-n junction devices.

These unusual results can be explained based on a PTE model where the generated PV originates from the individual contributions of each CNT film. In such a model, the p-type film makes one arm of a thermocouple while the n-type film makes the other arm. Considering a geometry where the p-type film extends from \( x = -L/2 \) to \( x = \infty \) and the n-type film from \( x = -\infty \) to \( x = L/2 \). The total PV generated in the device is given by

\[
\Delta V = \Delta V_p + \Delta V_n = S_p T_p(-L/2) - S_n T_n(L/2)
\]

where \( S_p (S_n) \) is the Seebeck coefficient of the p-type (n-type) film and \( T_p (T_n) \) is the position dependent temperature of the p-type (n-type) film. This equation shows that the photoresponse depends on the temperature at specific positions in each film.

The unusual position dependence of the PV in Figure 4.2-3b can now be understood from this model. The temperature profile under localized optical illumination is given by

\[
T(x-x_0) = T_{\text{max}} e^{-\frac{|x-x_0|}{l/2}}
\]
where \(x_0\) is the position of the laser spot and \(\lambda\) is the thermal decay length of the device. Using this expression, the total PV can be obtained as follows,

\[
\Delta V = T_{\text{max}} \left( S_p e^{j x_0 + t / \sqrt{\lambda}} - S_n e^{j x_0 - t / \sqrt{\lambda}} \right)
\]  

(4-9)

Figure 4.2-3c shows the behavior of this expression for a thermal length scale of 1mm and for three junctions with overlap lengths of 1, 4, and 8mm. The expression reproduces the experimentally observed behavior, with two peaks located at the edges of the films, which come together as the overlap length decreases. The good agreement between the theory and our experiment suggests PTE effect is the origin of the photoresponse in the p-n junction SWCNT photodetectors.

4.2.4. Factors affecting the device performance

**Effect of substrates.** For PTE detectors, it’s expected that thermal management should be strongly affect devices performance,\(^{[197]}\) which we explored by varying the substrate thermal conductivity. Figure 4.2-4a compares experimental SPVM results for p-n junction devices on Teflon tape, glass, and AlN substrates. For the device on Teflon tape, the spatial profile of PV at the p-n junction is broad, and its peak is \(~10\,\text{mV}\), corresponding to a responsivity of \(~1\,\text{V/W}\). When the film is placed on glass or AlN substrates, the PV amplitude decreases, and the spatial profile becomes narrow. These results are consistent with the PTE effect. In fact, the thermal length scale for optical heating is given by

\[
\lambda = \sqrt{\frac{\kappa_{\text{CNT}} h}{G}}
\]  

(4-10)
while the maximum temperature is

$$T_{\text{max}} = \frac{P}{\sqrt{G}} \sqrt{\kappa_{\text{CNT}} W} \tag{4-11}$$

where $\kappa_{\text{CNT}}$ is the thermal conductivity of the SWCNT film, $h$ the film thickness, $W$ its width, $P$ the absorbed optical power, and $G$ the thermal conductance of the SWCNT/substrate interface. It is expected that the thermal conductance $G$ will be proportional to the substrate thermal conductivity $\kappa_{\text{sub}}$, thus implying that $\lambda$ and $T_{\text{max}}$ should scale with $\kappa_{\text{sub}}^{-1/2}$. We find that this is indeed the case: Figure 4.2-4b shows the values of $\lambda$ and $\Delta V_{\text{max}}$ extracted from Figure 4.2-4a plotted as a function of $\kappa_{\text{sub}}^{-1/2}$, where we used the values $\kappa_{\text{AlN}} = 280 \text{ W/m-K}$, $\kappa_{\text{glass}} = 1 \text{ W/m-K}$, and $\kappa_{\text{Teflon}} = 0.25 \text{ W/m-K}$. A linear behavior is obtained as the substrate thermal conductivity varies by three orders of magnitude.

Figure 4.2-4. (a) Comparison of experimental scanning photovoltage microscopy for photodetectors on Teflon, glass, and AlN substrates. (b) Dependence of the signal width ($\lambda$) and strength ($V_{\text{max}}$) on the substrate thermal conductivity.

According to Figure 4.2-4a, the device on Teflon tape shows a responsivity of $1 \sim V/W$, which is the largest responsivity reported to date in a polarization-sensitive, macroscopic CNT device, eclipsing that of previous polarization-sensitive
devices without p-n junctions by a factor of 35.\textsuperscript{[206]} This value is comparable with the responsivity ($\sim 1.6\text{V/W}$) of the polarization-insensitive thermopile using disordered carbon nanotube films,\textsuperscript{[204]} but smaller than the CNT/Si p-n junction solar cell (0.286 A/W or 5.3V/W) based on the photovoltaic effect.\textsuperscript{[55]}

The PTE nature of the photoresponse also has implications for the device temporal response. We studied the PV response time of devices on different substrates. A comparison of the PV response of devices on three substrates is shown in Figure 4.2-5a. One can find that for the device on AlN substrate the PV amplitude is much smaller but its response is faster as compared with the device on the other two substrates. In order to extract the response time more accurately, an oscilloscope and chopper were used. Figure 4.2-5b shows the response time measurement of the device on an AlN substrate. By exponential fitting, we determine the turn-on and turn-off times, respectively, of $\tau_{\text{on}} = 90\text{ s}$ and $\tau_{\text{off}} = 84\text{ s}$ while $\tau_{\text{on}}$ for the devices on Teflon and glass was $\sim 0.6$ and $\sim 0.16\text{ s}$, respectively.

The substantial impact of the substrate on the response time can also be understood from the PTE effect. Indeed, the heat conduction equation gives a time scale

$$\tau = h\rho C_p / G$$  \hspace{1cm} (4-12)

where $\rho$ is the mass density and $C_p$ is the heat capacity. Note that the response time is inversely proportional to $G$, the thermal conductance between the SWCNT film and the substrate. As discussed before, for the device on AlN, $G$ is much larger than
the one on Teflon, thus giving a much faster response time. This behavior is verified in Figure 4.2-5c, where the response time is plotted as a function of $\kappa_{\text{sub}}^{-1}$.

Effect of n-doping level. In order to study the role of n-type doping on the photodetector performance, a series of devices with sharp p-n junctions on Teflon tape were made with varying n-type doping. Different doping levels were achieved
by dropping different concentrations of BV solution onto SWCNT films, ranging from 0 to 400 mM (while keeping the same solution volume around 10 µL). Shown in Figure 4.2-6 is the experimental result, where it can be seen that the dependence of the PV on the doping concentration is nonlinear. It increases rapidly at lower concentrations, reaches a maximum at intermediate concentrations, and then slowly decreases. This result is consistent with the PTE model described above. For a film with a small overlap, the PV for illumination at the junction is $\Delta V = (S_p - S_n) \times T_{\text{max}}$.

Because the n-type film is p-type before doping with BV, its Seebeck coefficient can be written as $S_n = S_p - \Delta S_n$, where $\Delta S_n (> 0)$ is the change in the Seebeck coefficient upon BV doping. The photovoltage is thus $\Delta V = T_{\text{max}} \times \Delta S_n$.

The inset in Figure 4.2-6 shows the doping-level dependence of the semiconducting CNT Seebeck coefficient. If we assume an initial p-doping corresponding to the dashed vertical line in the inset, then increasing the n-type doping through BV evolves the Seebeck coefficient from p-type to intrinsic and then to n-type. $\Delta S_n$ (and thus the PV) follows the behavior of the Seebeck curve as the BV doping is increased, with the initial p-doping corresponding to zero BV concentration and zero signals. At higher concentrations, the PV seems to become independent of BV doping, likely due to the BV doping method having reached its saturation. Nevertheless, the results indicate that intermediate levels of doping are required to optimize the photoresponse of these devices.
Figure 4.2-6. Photovoltage of devices on Teflon tape as a function of the concentration of BV n doping solution. Dashed line is the theoretical prediction based on the Fermi energy dependence of the Seebeck coefficient shown in the inset.
4.3. CNT THz photodetectors

THz technologies including THz generation, detection and manipulation are promising for diverse areas such as medicine, bioengineering, astronomy, environmental monitoring, and communications.[217-218] However, despite decades of world-wide efforts, the THz region of the electromagnetic spectrum still continues to be elusive for solid state technology. For example, current THz detectors are mostly cryogenic, narrow-band, or bulky, and thus, entirely novel approaches or materials systems are being sought for detecting THz radiation. CNTs have strong intraband absorption in THz region due to plasmon resonance processes,[168] relative large Seebeck coefficients of ~ 80 µV/K to ~160 µV/K,[176] all of which are valuable for application of THz thermal detectors. THz detection has been reported by using antenna-coupled, bundled[219] and individual[220] metallic single-wall CNTs at low temperatures. However, so far few uncooled CNT THz detectors have been reported. Furthermore, none of the existing approaches have demonstrated intrinsic polarization sensitivity because of the use of CNT networks.[19, 208] In this study, we present the realization of a compact, flexible, broadband and polarization-sensitive CNT-THz detector, which works at room temperature.

4.3.1. Device fabrication

Our THz detectors were constructed by using highly-aligned and ultralong single-wall CNT thin films, synthesized by water-assisted CVD method, as
described in chapter 2. Using photolithography and electron-beam evaporation, we

![Figure 4.3-1. Terahertz photodetector based on a p-n junction film containing macroscopically aligned, ultralong single-wall carbon nanotubes.](image)

(a) A scanning electron microscopy image of vertically aligned CNTs grown on a silicon substrate. (b) An optical microscope image of horizontally aligned CNTs after transfer to a Teflon substrate. The inset shows a photograph of the CNT film, which is highly bent, to demonstrate its flexibility. (c) An optical image of the fabricated detector with two gold electrodes. The n-type region was made by doping the as-grown, p-type film with benzyl viologen.

firstly formed micro-lines of double-layer catalysts (Fe/Al₂O₃) on a Si substrate with a width of 2 μm and length of 2 mm. Vertically-aligned SWCNT films were grown on these micro-lines of catalysts. The grown samples were checked under
SEM, which showed that these SWCNT films had a typical height of $\sim 150 \, \mu m$, as shown in Figure 4.3-1a. After water etching, they were peeled off from growth substrates and then dry transferred to desired substrates (Teflon tape or AlN) to form horizontally aligned CNT thin films. These films are highly aligned and flexible, as shown in Figure 4.3-1b. BV doping solution was then used to convert the unintentionally p-doped SWCNT films to n-type.[28] A intra film p-n junction was created by n-doping only one half of the p-type film, as shown in Figure 4.3-1c. Two gold electrodes with a thickness of 50 nm were deposited on the two ends of the film by electron-beam evaporation.

### 4.3.2. THz response measurements

In order to measure THz response of our devices, we used a model 295 FIR laser (Edinburgh Instruments, Ltd.) pumped by a model PL5 CO$_2$ laser as the THz source. The PL5 CO$_2$ laser produces 9-11 $\mu m$ wavelength CW infrared radiation with output power more than 50 W. The model 295 FIR laser generates 40 $\mu m$ - 1.2 mm wavelength (0.25-7.5 THz) CW radiation, and the maximum output power is roughly 150 mW. For the present study, we used the 1.39 THz, 2.52 THz, and 3.11 THz laser lines, using difluoromethane (CH$_2$F$_2$) for the 1.39 THz line and methanol (CH$_3$OH) for the 2.52 and 3.11 THz lines as the gain medium pumped by the CO$_2$ laser. The THz beam was measured to be a Gaussian-shaped beam with a typical diameter of $\sim 1 \, mm$. It first went through a linear polarizer and was then reflected and focused by an off-axis parabolic mirror onto the p-n junction region of the device. Figure 4.3-2b shows the $I-V$ characteristic of the device in the absence (black curve) and
presence (red curve) of THz radiation at 2.52 THz. It is observed that the $I-V$ curve rigidly shifts to one side in response to the THz beam, producing a finite $I_{sc}$ and $V_{oc}$, as indicated in the graph. The absence of any change in the slope of the $I-V$ curve excludes bolometric effects as the origin of the THz photosignal observed here.

The THz photo-signal produced by our detector is strongly dependent on the polarization of the incident THz beam with respect to the nanotube alignment direction, as shown in Figure 4.3-2c this behavior arises from the polarization-dependent CNT absorption. Here, the THz-induced $V_{oc}$ is plotted for the three THz frequencies used as a function of the angle between the THz polarization and the CNT alignment direction; the photovoltage is normalized to the value obtained when the THz polarization is parallel to the nanotube alignment direction. In the perpendicular geometry (i.e., 90°), the photovoltage is suppressed by as much as ~82% (or, the parallel-to-perpendicular ratio ~5:1) in the case of 2.52 THz. Finally, Figure 4.3-2d shows the power dependence of $V_{oc}$ for the three frequencies, showing a linear response in a wide range of incident power. We can determine the responsivity of the detector from the slope of the photovoltage versus power curve. The extracted responsivity values are 2.5 V/W, 2.4 V/W, and 1.7 V/W at 3.11 THz, 2.52 THz, and 1.39 THz, respectively.
4.3.3. Thermoelectric and optothermoelectric measurements

PTE effect has been widely considered as a dominated mechanism for the photoresponse in carbon-based devices, such as graphene and CNTs, but to date few measurements have been provided that directly verifies the PTE nature of the signal. In this study, we performed direct thermoelectric and optothermoelectric measurements to verify the PTE nature of our devices.

We obtained the Seebeck coefficients of SWCNT films in our devices by creating
a temperature gradient across the devices using a resistive heater positioned
under one side of the devices while measuring the voltage across the electrodes in
a probe station in ambient. The temperature profile across the devices was
measured using an infrared camera. The temperature gradient was obtained from
the difference in temperature on the SWCNT film near the two contacts. Based on
Eq. (4-3), the Seebeck coefficients of SWCNT films were calculated from the
thermovoltage and temperature measurements taking into account the Au Seebeck
coefficient of $\sim 1.5 \mu V/K$. For p-type and n-type films, obtaining values of $S_p = 75.2$
$\mu V/K$ and $S_n = -71.0 \mu V/K$, respectively, as shown in Figure. 4.3-3a, b. It is clear
that these SWCNT films have a significant Seebeck coefficient, and that the BV
doping is efficient at converting the films to n-type.

Based on PTE, the thermal voltage across a p-n junction device due to heating is
given by\cite{202}

$$\Delta V = S_p \Delta T_p - S_n \Delta T_n$$  \hspace{1cm} (4-13)

where $\Delta V$ is the voltage across the electrodes, $S_p$ is the Seebeck coefficient of the p-
type film, $\Delta T_p$ is the temperature difference across the p-type segment, and similarly
for the n-type film.

We used direct heating of the p-n junction with a localized heater (no
illumination) to demonstrate that heat alone is sufficient to generate a voltage (Fig.
Figure 4.3-3. Thermoelectric measurements of the carbon nanotube THz detector. (a) Top: Representation of device setup for Seebeck coefficient measurements consisting of the p-type CNT film (blue) being contacted by two Au electrodes (gold) atop of Teflon tape (light aqua) supported by a glass slide (aqua), which is being thermally contacted on one side by Cu foil (orange) whilst being heated by the heater (grey). Bottom: Thermovoltage as a function of the temperature difference between the two edges of the film ($\Delta T$) for the p-type CNT film. The temperature is measured using an infrared camera. (b) Top: Representation as in (a), but with the CNT film being n-doped (green). Bottom: same as in Panel (a), but with the n-doped CNT film. (c) Top: Representation as in Panel (a), but with a p-n junction CNT device with glass slide removed and the heater and Cu foil being repositioned to heat the Teflon tape directly below the p-n junction. Bottom: Thermovoltage measurements as a function of the temperature difference between the middle and the n-side edge (blue) and between the middle and the p-side edge (red). (d) Top: Representation of the focused laser illumination setup for determining the temperature profile across the film length using an IR camera. Bottom: IR camera image of a film being heated by a focused laser with the temperature scale as indicated. (e) Temperature profile across the heated portion of the CNT film during laser illumination for different laser power densities. (f) Maximum temperature rise as a function of laser power obtained from the data of Panel (e).

4.3-3c) of the same sign as that obtained from the THz illumination experiments.

Compared to Figure 4.3-3a and c, one can find that the thermovoltage generated by heating the p-n junction equals the sum of the thermovoltages of the individual p-type and n-type films, which is consistent with the description of Eq. (4-13). This
directly demonstrates that optical generation of electron-hole pairs (i.e., a photovoltaic effect) is not necessary to generate a photocurrent in these devices.

To connect the thermoelectric measurements to the photocurrent experiments, we used an infrared camera to measure the temperature rise during illumination with a red laser, as shown in Figure 4.3-3d, e. The results clearly show a significant temperature rise at the location of the laser spot, with the temperature decaying away from this location. In addition, the maximum temperature is found to scale linearly with the laser power (Fig. 4.3-3f). Using Eq. (4-13) and the measured values for the maximum temperature, we obtain a photovoltage of $\Delta V = 1.53 \text{ V/W}$; this value compares favorably with the data presented in Figure 4.3-2d and the responsivities reported above. The photothermoelectric nature of the detector was further confirmed by controlling the thermal environment by putting the SWCNT devices on different substrates: (a) a suspended Teflon substrate, (b) Teflon placed directly on top of an AlN substrate, and (c) an AlN substrate. As shown in Figure 4.3-4d, the THz-induced photosignal drastically decreases as we increase the substrate thermal conductivity, fully consistent with a thermal mechanism.
Existing room-temperature THz detectors have noise-equivalent power (NEP) on the order of 1 nW/Hz$^{1/2}$.\cite{221} For our detector in the open circuit configuration, the noise is limited by Johnson thermal noise which is given by $\sqrt{4k_BT R}$, where $k_B$ is Boltzmann’s constant, $T$ is the temperature, and $R$ the device electrical resistance. The estimated NEP is $\sim 20$ nW/Hz$^{1/2}$, which is promising given the additional attributes provided by the SWCNT detector (e.g., intrinsic polarization sensitivity, flexibility). Furthermore, our combined thermoelectric and optothermal characterization of the detector allows us to assess the prospects for improving the device performance. In fact, much like thermoelectric devices, the performance of PTE detectors is determined by the figure of merit $ZT = S^2 \sigma T / \kappa$, where $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity. We extracted the thermal
conductivity of the SWCNT films by analyzing the temperature profile obtained from optothermal measurements, obtaining $\kappa = 60$ W/m·K. Combined with the above measured values of $S$ and $\sigma = 100$ S/m, this gives $ZT = 2.6 \times 10^{-6}$ at room temperature, a value that is much lower than $ZT \sim 0.08$ recently reported for CNT films.$^{[29]}$ This implies that CNT THz detector performance can be significantly improved by engineering CNT thermoelectric properties. This could be accomplished, for example, by controlling CNT alignment, density, electronic type, or intertube interactions.

In summary, we developed a room-temperature CNT p-n junction THz detector that is powerless, compact, broadband, flexible, large-area, and polarization-sensitive. At the core of the detector is a macroscopic array of highly aligned and ultralong CNTs that strongly absorb THz radiation in a broad spectral range with extreme polarization sensitivity. The device design incorporates the Seebeck coefficient engineering through the formation of a p-n junction by chemical doping and is based on the photothermoelectric mechanism that is firmly supported by direct thermoelectric and optothermal measurements. These results suggest that further engineering of thermal and electronic properties, combined with the superb mechanical strengths and flexibility of CNTs, will lead to the development of novel carbon-based THz detectors.
Chapter 5

Fabrication of aligned and chirality-enriched single-wall carbon nanotube films and devices

One advantage of post-synthetic methods for aligning CNTs is that they can be applied to CNTs that are sorted and chirality-enriched. In this chapter, we present the fabrication of aligned CNT films of enriched chiralities by combining our newly invented technique, the CDPF method (see Chapter 3), with advanced sorting methods. In Section 5.1, we describe the aqueous two-phase extraction (ATPE) method for sorting SWCNTs by type, diameter, and chirality. Using this method, we successfully obtained chirality-enriched SWCNT suspensions. In Section 5.2, we demonstrate successful fabrication of aligned films enriched in (6,5) SWCNTs by combing the ATPE and CDPF methods. Finally, Section 5.3 shows results of characterization experiments of these aligned films and their optoelectronic devices.
5.1. CNT sorting by aqueous two-phase extraction

Over the past decade, a great number of SWCNT sorting techniques have been developed, such as DNA wrapping followed by ion exchange chromatography (IEC),\[115\] selective dispersion by designed polymers followed by normal ultracentrifugation,\[118\] and surfactant encapsulation followed by gel chromatography (GEC)[86] or density gradient ultracentrifugation (DGU).[95] Although these techniques are capable of providing CNTs of nearly-single chiralities, they suffer from various problems, such as high costs and low yields (e.g., DNA-based IEC), selective dispersibility, multiple iterations required to achieve high purity (GEC, DGU), and long separation times. Recently, Khripin et al.[87] reported the ATPE method, which provides an easily accessible and highly scalable route for generating a wide range of enriched chirality CNTs. The simplicity and scalability of this method are ideal for making large-scale aligned films of chirality-enriched SWCNTs, which usually requires a large quantity of purified CNT suspensions. Therefore, we chose ATPE to sort CNTs and then make aligned CNT films by CDPF.

5.1.1. Aqueous two-phase extraction

The ATPE method is based on the spontaneous redistribution of CNTs into two aqueous phases with relatively different hydrophobicities (see Fig. 5.1-1).[87] The two phases are formed by mixing two water-soluble polymers, namely polyethylene glycol (PEG) and dextran, in appropriate concentrations. The top phase, enriched with PEG, is less hydrophilic than the bottom, dextran-rich phase. It was initially
hypothesized that the hydrophobicity difference was determined only by the intrinsic properties of CNTs, including the diameter and metallicity. Zheng et al.\textsuperscript{[115]} previously showed that the hydrophobicity of CNTs is related to their salvation free energy in the aqueous dispersion, which increases linearly with the CNT diameter in the small-diameter regime ($< 1 \text{ nm}$) and saturates in the large-diameter regime ($> 1.2 \text{ nm}$). As a result, in the linear range ($< 1 \text{ nm}$), larger diameter tubes are more hydrophobic because of their larger salvation energy. In addition, because metallic CNTs are more polarizable than semiconducting CNTs, their salvation free energies are lower than those of semiconducting CNTs. In other words, metallic CNTs are less hydrophobic than semiconducting CNTs.
Later studies found that sorting in a wider diameter range can be achieved by controlling the surfactant ratio and concentrations in a co-surfactant system,\cite{110-112} in which the intrinsic hydrophobicity differences of CNTs are largely altered and amplified by micelle structures of surfactants on their sidewalls. Subbaiyan \textit{et al.} studied the preferential encapsulations of various surfactants on CNTs as well as their particular influences on the hydrophobicity of CNTs.\cite{110} Their study 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. More importantly, SC and DOC encapsulated CNTs are relatively hydrophilic, so they tend to stay in the bottom hydrophilic phase (dextran). On the contrary, SDS encapsulated CNTs are much more hydrophobic and therefore go up to the top phase (PEG). Based on these results, they developed a two-step strategy to sort highly enriched single-chirality CNTs by mixing three surfactants in a proper ratio.

Furthermore, Fagan et al. systematically studied diameter-dependent sorting of CNTs using a co-surfactant system (DOC+ SDS). They showed that by keeping DOC at a very low concentration and continuously increasing the SDS concentration one can move CNTs from the bottom phase into the top phase based on their diameters. Larger diameter tubes went up first, and then smaller diameter ones followed. The range of sorted diameters covered from ~0.6 to 1.7 nm by varying the SDS concentration from 0.4% to 1.7% and keeping the DOC concentration at ~0.045%. On the other hand, metal-semiconducting (m-s) separation after diameter sorting was realized by switching to another co-surfactant system (SC+SDS). Highly chirality-enriched CNTs were obtained by orthogonally using m-s sorting and diameter sorting.

More recently, Fagan et al. introduced a redox reaction into the ATPE method and improved the efficiency of m-s separation. In this strategy, CNTs are oxidized by a certain amount of oxidants added into the CNT suspension. The charge transfer from oxidizations leads to re-organization of surfactant micelle structures on the side walls of CNTs, which alters the hydrophobicities of the surfactant-CNT assemblies. Strano et al. found that the oxidization of CNTs depends on their band
structures, i.e., metallic CNTs are more readily oxidized than semiconducting CNTs.[223] After oxidization, the more hydrophilic metallic CNTs stay in the bottom phase while relatively hydrophobic semiconducting CNTs are separated into the top phase. The introduction of redox reaction makes m-s sorting more robust, i.e., less sensitive to environmental factors such as the temperature. In addition, since this type of sorting is based on the band gap of CNTs, it has the ability to separate armchair SWCNTs from non-armchair SWCNTs.[112]

5.1.2. Enrichment of (6,5) SWCNTs by aqueous two-phase extraction

In this section, we present results of our experiments to enrich (6,5) SWCNTs using the ATPE method. Firstly, we performed diameter sorting of SWCNTs using the two-step strategy described above,[110] and then we used m-s separation to further remove metallic tubes. In the two-step strategy, the basic principle is to engineer the subtle difference of hydrophobicities of surfactant-SWCNT assemblies by using a combination of three different surfactants, DOC, SDS and SC, in which the determined factor is the ratio of SDS:DOC.

Four different stock solutions were prepared, including stock 1 (ST₁), stock 2 (ST₂), m-s separation bottom phase (M_B), and m-s separation top phase (M_T). The components of each stock solution are listed in Table 5-1. The function of ST₁ and ST₂ is to sort out (6,5) SWCNTs as well as other SWCNTs (both metallic and semiconducting SWCNTs), which have diameters close to (6,5) SWCNTs (~0.73 nm). The function of M_B is to further remove metallic SWCNTs from the top phase. The function of M_T is to remove metallic SWCNTs from the bottom dextran phase. In this
experiment, only M_B was used because (6,5) SWCNTs were in the top phase after the
two-step diameter sorting process.

<table>
<thead>
<tr>
<th>Diameter</th>
<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_2O [g]</th>
</tr>
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<td>0</td>
<td>0</td>
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</tr>
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</table>

^a^) Metal-semiconducting sorting, ^b^) Metal-semi sorting bottom phase, ^c^) Metal-semi sorting top phase.

In the first-step diameter sorting process, 2.15 mL SWCNT suspension (SG 65i dispersed in 1% DOC), 4.25 mL nanopure water, and 40.8 mL were mixed together, corresponding to a ratio of SDS:DOC ∼ 20.4:1 in the mixture. (6,5) SWCNTs as well as those with smaller diameters were separated into the bottom phase by gentle centrifugation for 5 minutes (4000 rad/minutes). After removing the top phase, the left bottom phase (ST_1^B), which had a volume of ∼ 5 mL, was then mixed with ST_2 of the same volume, leading to an increase of the ratio of SDS:DOC from 20.4:1 to 23.6:1 in the mixture. The second-step diameter sorting process was conducted by increasing the ratio of SDS and DOC. As a result, most of (6,5) SWCNTs went up to the top phase, leaving the majority of SWCNTs of smaller diameters in the bottom phase, such as (6,4), (7,3), etc.

After the two-step separation processes, the top phase (ST_2^T) with the purple color was enriched with (6,5) SWCNTs, but there were small amounts of residual semiconducting tubes of similar or large diameters as well as certain metallic tubes.
In order to remove metallic tubes, we modified the SWCNT suspension into a SDS/SC co-surfactant system by mixing it with an appropriate amount of MB. Furthermore, since the presence of DOC is unfavorable for m-s separation in a SDS/SC co-surfactant system, ST₂T (4.5 mL) was first mixed with the same amount of MB, which increased the volume of the top phase (ST₂TMT) to ∼6 mL. The top phase (ST₂TMT) was then picked out and mixed with the same volume of MB, which led to successful removal of metallic tubes from the top phase.

We characterized the final top phase (ST₂T₂TMT) with the color of light purple was characterized by absorption and photoluminescence excitation (PLE) spectroscopy. As shown in Fig. 5.1-2, the sorted suspension was enriched with (6,5) SWCNTs, with small amounts of residual (9,1) and (8,4) SWCNTs. Because the separation is essentially thermodynamic, CNT species are not able to distribute into one phase by one hundred percent at a given temperature and surfactant concentration, which explains the existence of (8,4) SWCNTs. In order to further remove (8,4) SWCNTs, the diameter sorting steps with ST₁ and ST₂ could be iterated. However, it is difficult to remove (9,1) SWCNTs by simple iteration, because (9,1) and (6,5) SWCNTs have the same electronic type and very similar diameters. Complete removal of (9,1) SWCNTs would require a chiral-angle-sensitive separation method, such as DNA-wrapping-assisted sorting.\[114\]
Figure 5.1-2. Optical characterizations of a (6,5)-enriched suspension prepared by the ATPE method. (a) Photograph, (b) optical absorption, and (c) photoluminescence excitation spectra of the (6,5)-enriched suspension.
5.2. Fabrication of aligned (6,5)-enriched CNT films

Since the sorted (6,5) SWCNTs are in the top PEG phase, the next step was to remove the PEG and a small amount of dextran from the SWCNT suspension. Complete removal of polymers (PEG and dextran) is critical because the formation of alignment could be easily disturbed by their presence. In our experiments, we used two separated strategies to remove PEG: 1) ultrafiltration and 2) precipitation.

**Ultrafiltration:** The principle of ultrafiltration is to filter molecules in aqueous dispersions based on molecular weight (MWs), which is realized by using specialized porous membrane in a sealed cell under strong pressure. Each type of ultrafiltration membrane is characterized by a particular value of MW called molecular weight cut-off (MWCO), and only molecules with MWs smaller than this value can be filtered out. Note that ultrafiltration is different from normal vacuum filtration by two aspects: 1) the pore sizes of ultrafiltration membrane (~ a few nanometers) are much smaller than that of vacuum filtration membrane (~ tens of nanometers to tens of micrometers) and 2) the filtration requires the application of a very strong pressure (in the order of psi) in a sealed stirring cell.

The selection of ultrafiltration membrane with appropriate MWCO is important for the successful removal of polymers from SWCNT suspensions. The MWs of SWCNTs are normally larger than 300 kDa while the MWs of PEG and dextran used in the ATPE method are 6 kDa and 70 kDa, respectively. Therefore, an ultrafiltration membrane with a MWCO of 100 kDa was used for filtering PEG and dextran.
molecules while retaining SWCNTs in the suspension. The removal of PEG was performed by a stirred ultrafiltration cell (Model 8050, 50 mL, Milipore) equipped with ultrafiltration membranes of 100 kDa (ultracel regenerated cellulose, 100 kDa, 25 mm, Milipore). The (6,5)-enriched suspension was first filtered until 10% of the volume remained in the stirred cell. After diluting the remnants by a factor of 10 by refilling the cell with 1% DOC solution, the filtration process was repeated. The cycles of filtration and dilution were repeated at least 15 times in order to get the sample clean enough. After that, SWCNTs were re-suspended in fresh DOC of 1% and ready for the next processes.

**Precipitation:** Depletion-induced interaction and phase separation in polymer–colloid mixtures is a general phenomenon in cell biology and biochemistry.\[224\] The presence of polymers creates a crowding environment in the colloid system, where entropic effects result in an attractive force (depletion force) among colloid particles, driving them to form large size clusters (phase separation). Thus, selective precipitation of colloid particles can be achieved by controlling crowding conditions, such as modifying the concentration of polymers. This method has been applied for length fractionation of DNA-wrapped CNTs in the PEG phase.\[225\] Here, we adopted their method to selectively precipitate SWCNTs for the purpose of removing PGE 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, the aggregation of SWCNTs cannot occur only by increasing the concentration of PEG. The problem can be solved by increasing the salt concentration in the system, which
leads to strong screening of electrostatic forces and allow the formation of clusters among SWCNTs. Once SWCNTs form clusters under the appropriate concentrations of slat and PEG, they can be precipitated and separated from the PEG phase by gentle centrifugation. Compared to the ultrafiltration method, selective precipitation is a relatively time-saving process for cleaning SWCNT suspensions. The only problem with this method is that the concentration of SWCNTs needs to be sufficiently high (normally > 20 μg/mL); otherwise they cannot be precipitated.

In the following, we describe the process of cleaning SWCNT suspensions by the precipitation method. The PEG phase enriched with sorted SWCNTs was collected in a centrifuge tube, and the concentration of PEG was adjusted to 11%. Note that, if the concentration of PEG was lower than 10% in the system, it could not allow SWCNTs to form clusters. A NaSCN (salt) solution was then added into the system, and the final concentration of slat in the suspension was adjusted to 0.25M. The mixture was incubated for 30 minutes and then centrifuged for 15 minutes at a speed of 17000 rad/minute. After centrifugation, SWCNTs were precipitated as pellets at the bottom of the centrifuge tube, and the top PEG phase was removed by a pipette. The centrifuge tube was refilled with 1% DOC surfactant in order to clean any PEG residuals on the surface of SWCNT pellets and the sidewall of the tube. The SWCNT pellets were then re-suspended by adding fresh DOC solution of 1% into the centrifuge tube.

Many SWCNT bundles typically were formed during the cleaning process by ultrafiltration or precipitation, and therefore, short-time tip sonication was needed
to break the bundles. The obtained suspension was sonicated with a tip sonicator (XL-2000 Sonicator from Qsonica, LLC. ¼" probe, ~30 watt) for 30 minutes. Next, the suspension was centrifuged for 1 hour at 40000 rad/minute (Sorvall Discovery 100SE Ultracentrifuge using a Beckman SW-41 Ti swing bucket rotor). After centrifugation, the upper 60% of the supernatant was collected and then diluted with nanopure water.

Before the filtration step, it was necessary to adjust the concentrations of surfactants and SWCNTs to the values appropriate for the formation of alignment. For (6,5)-enriched SWCNT suspensions, the optimized concentrations of SWCNTs and DOC were 4 µg/mL and 0.025%, respectively. The filtration process was straightforward, and we basically followed the procedure described in Chapter 3. In the process, polycarbonate filter membranes with a pore size of 80 nm were used for sample filtration. A weak pressure of 15 Pascal was applied to the filtration system at the beginning, which kept an extremely slow flow rate of ~ 10 minutes per drop. Such a low flow rate was necessary for small-diameter tubes such as (6,5). In the end of the filtration, the speed was increased up to 20 seconds per drop in order to fix and dry the film rapidly.
5.3. Characterization of aligned (6,5)-enriched CNT films and devices

5.3.1. Characterization of aligned (6,5)-enriched CNT films

After filtration, the aligned films were characterized by scanning electron microscopy (SEM), polarized Raman spectroscopy, and photoluminescence excitation (PLE) spectroscopy. Shown in Fig. 5.3-1a is a quarter of an aligned film enriched with (6,5) SWCNTs on a filter membrane, showing that the density of the film is very uniform on a large area. The well-aligned structures of SWCNTs are shown on a SEM image (see Fig. 5.3-1b) for a film transfer onto a SiO₂/Si substrate. Strong anisotropy of Raman scattering was observed between perpendicular and parallel polarization configurations, as shown in Fig. 5.3-1c. The value of $S$ deduced from the Raman spectra was around 0.75. In addition, we measured polarized PL spectra of the film, as shown in Fig. 5.3-2; the intensity ratio of PL between parallel and perpendicular directions is $\sim$3, demonstrating that the PL is mainly polarized along the SWCNT alignment direction. Note that a larger polarization ratio of PL ($\sim$ 6) was reported before on aligned SWCNTs dispersed in stretched gelatin films.[226] Therefore, there is still a large room for us to further improve the film alignment. In fact, the obtained $S$ of (6,5) SWCNT films ($\sim$ 0.75) is much smaller than that of arch-discharge CNT films ($\sim$ 0.96).
Figure 5.3-1. Characterization of aligned SWCNT film made from (6,5) enriched suspension. (a) Photograph of a fabricated large-area aligned film, (b) SEM image of the aligned structure of SWCNTs on the film, (c) polarized Raman spectra of the film under parallel and perpendicular configurations.

As discussed in chapter 3, we suspect the major reason for small values of $S$ for these (6,5)-enriched films is because of the small stiffness of small-diameter tubes, allowing them to be bent easily. Figure 5.3-3a shows an AFM image of (6,5) SWCNTs on SiO$_2$/Si substrate, demonstrating that tubes are entangled with each
other and less straight than large diameter tubes. Note that the average tube length of this sample was ~ 420 nm (see Fig. 5.3-3b), the longest among all types of SWCNTs used in our study. Recent work on liquid crystals (LCs) of CNTs\textsuperscript{[152]} suggested that defects induced by deformed and entangled nanotubes of long lengths are the major reason why CNT LCs cannot be aligned on a large scale. Therefore, further studies are needed to check whether length optimization of (6,5) SWCNT is useful for enhancing the alignment quality.

Figure 5.3-3. (a) AFM image of (6,5) SWCNTs on SiO\textsubscript{2}/Si substrate. (b) The length characterization of (6,5) SWCNTs based on AFM images.

5.3.2. Devices based on aligned (6,5)-enriched CNT films

A polarization-sensitive photodetector was fabricated by using aligned films of (6,5)-enriched SWCNTs (see Fig. 5.3-4a). Aligned films were first cut into ribbons and then transferred to a glass substrate. Then two electrodes were formed by sputtering 50-nm gold using a shadow mask technique 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. A half-wave plate was used to rotate the polarization of the incident light beam. As shown in Fig. 5.3-4b, the generated photo-voltage was polarized with a polarization ratio of ~2:1, which is better than that of polarized photodetectors made by CVD-grown CNT arrays at the same wavelength.[202]

Furthermore, we fabricated field-effect transistors with channels parallel and perpendicular to the CNT alignment direction (see Fig. 5.3-5a). An aligned (6,5) nanotube film with a thickness of ~5 nm was transferred onto a substrate comprised of heavily doped silicon (acting as a global backgate) and 285-nm thick layer of thermal silicon oxide (acting as the dielectric layer). The electrodes and the Hall bar structure on the film were defined and fabricated by photolithography. The electrodes consisted of a bilayer of titanium (1 nm) / gold (30 nm) deposited by electron-beam evaporation. The length and width of the CNT channel were 30 µm and 2 µm, respectively. Electrical measurements were performed 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). As shown in Fig.5.3-5c, the on-
off ratio of the transistor was around $10^{-3}$, which is comparable to transistors made by aligned thin films of semiconductor-enriched SWCNTs in a previous report.\textsuperscript{[141]} Furthermore, strongly anisotropic conductivities were observed between the two CNT channels perpendicular to each other. As shown in Fig. 5.3-5d, the conductivity along the channel parallel to CNT alignment is larger than that along the channel perpendicular to CNT alignment by more than one order.

Figure 5.3-5. The characterization of field effect transistors fabricated by aligned film enriched with (6,5) SWCNTs. (a) False-color scanning electron microscopy image of a transistor with channel width $\sim 5 \mu m$ and channel length $\sim 30 \mu m$ made from aligned film enriched with (6,5) SWCNTs. (b) A scanning electron microscopy image on an area of $\sim 1 \mu m^2$, showing the aligned structures of the SWCNT film. (c) The source-drain current versus gate voltage of the transistor showing large on-off ratio and anisotropic transistor action. (d) The source-drain current versus source-voltage of the transistor showing the strong anisotropic conductivities.
One of the purposes of CNT alignment in transistors is to increase the on-current density by decreasing the number of inter-tube junctions.\[141, 227\] Currently, the device we made had very low current densities ($\sim 12$ pA/µm), indicating that there is much room for further improvement. Besides the degree of CNT alignment and CNT density, a few other factors can also affect the on-current density, such as the ratio of the channel length to the CNT length, the diameter of CNTs, and the gate coupling efficiency.\[12, 62\] A device channel length comparable to the CNT length can minimize scattering by inter-tube junctions to the largest degree and thus increase the current density. On the other hand, recent studies showed that CNT diameters should be around 1.2-1.7 nm in order to achieve a high on-current density as well as the optimal overall performance of transistors.\[228\] In addition, the gate coupling efficiency can be improved by replacing SiO$_2$ with high $\kappa$ (dielectric constant) gate materials such as hafnium oxide (HfO$_2$).\[228\] Therefore, further improvement in transistors based on aligned CNTs will focus on the optimization of the device channel length, CNT lengths and diameters as well as a proper choice of the gate material.
Chapter 6

Summary

We developed two novel methods to prepare macroscopically aligned films of carbon nanotubes (CNTs). The first method is based on rolling down of vertically aligned CNT arrays grown by water-assisted CVD. The second method uses spontaneous global alignment of CNTs during the vacuum filtration of CNTs suspended in aqueous solution. Furthermore, using these aligned films, we made optoelectronic devices including photodetectors, polarizers, and transistors with superb performance characteristics.

Vertically aligned SWCNT arrays of macroscopic sizes were grown on Si substrates by the water-assisted CVD method. A designed water etching process was used to break the chemical bonds between SWCNTs and the substrate. Vertically aligned SWCNTs arrays were then converted into horizontally aligned films with thickness of a few µm and the width of ~ 1cm by skillfully rolling down and dry transferring to desired substrates. Furthermore, vertically aligned SWCNT
films were grown by patterning the catalysts with line-shapes through photolithography. After peeling off from growth substrates, free-standing aligned SWCNT films were obtained with a thickness of \( \sim 1 \mu m \), a width of \( \sim 150 \mu m \), and a length of \( \sim 1 \text{cm} \). These macroscopic aligned SWCNT films were successfully doped into n-type by chemical liquid doping, allowing for the fabrication of p-n junctions of aligned SWCNT films.

An infrared photodetector with intrinsic polarization sensitivity was constructed using a p-n junction made by two horizontally aligned SWCNT films. Zero-biase photocurrent and photovoltage were observed at the junction region with a broadband spectral response spanning from the visible to the mid-infrared. The mechanism of the photodetector was identified as the photothermoelectric (PTE) effect, in which the Seebeck coefficient of SWCNT films plays the key role. By choosing Teflon as the substrate, the photodetector achieved a high responsivity up to \( \sim 1 \text{ V/W} \), which is about 35 times larger than previous PTE detectors based on aligned SWCNT films without p-n junctions.

Furthermore, we developed a room-temperature CNT p-n junction THz detectors based on highly aligned CNT films. At the core of the detector was a single piece of highly-aligned CNT film with an intra-film p-n junction at the center of the device channel. The responsivity of the THz detector was above 2 V/W, and the polarization ratio was as high as \( \sim 5:1 \) in the range from 1 to 3 THz. The PTE mechanism of the detector was confirmed by direct thermoelectric and optothermal measurements, suggesting that further engineering of thermal and
electronic properties will greatly enhance the performance of the detector. Our work on CNT photodetectors provides a new path towards the realization of flexible, compact, polarization-sensitive and ultra-broadband photodetectors that work at room temperature.

We discovered spontaneous global alignment of CNTs during vacuum filtration by accidentally diluting the surfactants below its critical micelle concentration (CMC) in a CNT suspension. We repeated the experiment and optimized the filtration conditions such as the filtration speed, CNT concentration, and surfactant concentration. Eventually, it led to the invention of a novel and simple method for self-assembly of highly aligned CNTs on a macroscopic scale – controlled differential pressure filtration (CDPF). In CDPF, a well-dispersed CNT suspension at a low surfactant concentration is filtered through a smooth filter membrane with a proper pore size under a controlled flow rate (1-2.5 mL/hour). This produces a monodomain, wafer-scale CNT thin film with a high degree of alignment on the surface of filter membrane.

Aligned films of arc-discharge CNTs with controllable thicknesses (from a few nm to ~100 nm) exhibited an exceptionally high degree of alignment (the nematic order parameter $S \sim 1$) and packing density ($\sim 10^6$ nanotubes per cross-sectional area of $\mu m^2$). These films showed strong optical anisotropy in THz region and thus can work as ideal THz polarizers. We also applied the CDPF method to different types of CNTs, such as TUBALL (CVD), CoMoCAT, and HiPco CNTs. Highly aligned CNT films ($S > 0.7$) with monodomain structures were obtained, demonstrating the
universality of the CDPF method. Unlike aligned films made by CVD, the films produced by CDPF are so dense and robust that they can stand any solution-based process, opening the possibility of fabricating various electronic and photonic devices by using standard lithography technologies. Towards this goal, we made aligned films enriched with (6,5) SWCNTs by combining CDPF with the aqueous two-phase extraction method. Using photolithography, we fabricated photodetectors and transistors based on these aligned and chirality-enriched films, which showed great device performances.

CDPF is a unique method, different from both existing two-dimensional (2D) and three-dimensional (3D) assembly techniques. The strikingly high nematic order parameter ($S \sim 1$) is much beyond the theoretical prediction of 3D LC phases of rigid rods ($S = 0.79$). The ability of making films as thick as $\sim 100$ nm also distinguishes this method from previous 2D self-assembly techniques, with which only single or few layers of aligned CNTs can be generated. Furthermore, this method is universal and expected to be applicable to any CNT species and/or any high aspect-ratio, rod-like nanostructures, such as semiconductor nanowires and boron nitride nanotubes, implying a possible route towards the assembly of 3D crystals from one-dimensional nanomaterials. We believe that highly aligned CNT assemblies produced by CDPF will present vast opportunities not only in fundamental research but also in a wide range of applications such as electronics, optoelectronics, sensing and imaging.
Bibliography

carbon nanotube networks for digital, analog, and radio-frequency applications. 


