Carbon dioxide-assisted synthesis of single-walled carbon nanotubes and their thin film properties

Yongping Liao
Supervising professor
Professor Esko I. Kauppinen, Aalto University, Finland

Thesis advisors
Dr. Hua Jiang, Aalto University, Finland
Dr. Qiang Zhang, Aalto University, Finland

Preliminary examiners
Professor Yuan Chen, The University of Sydney, Australia
Dr. Don N. Futaba, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Opponent
Dr. Juan J. Vilatela, IMDEA Materials Institute, Spain
Author
Yongping Liao

Name of the doctoral dissertation
Carbon dioxide-assisted synthesis of single-walled carbon nanotubes and their thin film properties

Publisher School of Science

Unit Department of Applied Physics

Series Aalto University publication series DOCTORAL DISSERTATIONS 162/2019

Field of research Engineering Physics

Permission for public defence granted (date) 22 August 2019 Language English

Abstract
Owing to their unique chemical and physical properties, single-walled carbon nanotubes (SWCNTs) have attracted increasing attention in various fields. The properties of SWCNTs strongly depend on their chirality and geometry. Thus, to realize the applications in desired fields, it is of significant importance to tune the chirality and geometry of SWCNTs.

The floating catalyst chemical vapor deposition (FC-CVD) method, as a dry and continuous process, has been widely used in academic and industrial fields. However, tuning the growth of SWCNTs in FC-CVD is a challenge.

In this thesis, first of all, certain amounts of carbon dioxide (CO2) is introduced to tune the growth of SWCNTs in a FC-CVD reactor, where carbon monoxide (CO) is used as carbon source and ferrocene as catalyst precursor. We found that the SWCNT thin films display different colors with various CO2 concentration, specifically, a green and brown colors are observed. The optical absorption spectrum of the green film shows a distinct absorption peak in visible range. Further analyzing the chirality by electron diffraction reveals that the green film possesses a very narrow chirality distribution near armchair. Besides the chirality, we also studied the geometry, such as tube diameter, bundle length and diameter, modulated by CO2. The SWCNT diameter and bundle length are found to increase with CO2 concentration. In addition, the yield and bundle diameter are also affected by CO2. Accordingly, SWCNT thin film prepared with certain CO2 concentration displays a remarkably reduced sheet resistance. Therefore, employing CO2 offers new strategy to tune the chirality and geometry of SWCNTs in FC-CVD. Furthermore, we also deposited our aerosol SWCNTs on wafer-scale substrates by large-scale thermophoretic precipitator (TP), such SWCNT thin films display ideal uniformity and conductivity. The scale-up deposition method is applicable in industrial productions of SWCNT transparent conductive films.

To further reduce the sheet resistance of SWCNT thin films, we then deposited SWCNTs on graphene by TP. The SWCNTs/graphene hybrid film exhibits improved conductivity. By measuring the temperature dependent conductance, we found that due to the presence of graphene, the tunnelling barrier between tubes has been reduced, which enhances the carrier tunnelling efficiency and thus, improves the conductivity.

Keywords Single-walled carbon nanotubes; carbon dioxide; chirality; geometry; transparent conductive film; graphene; tunnelling


ISSN (printed) 1799-4934 ISSN (pdf) 1799-4942

Location of publisher Helsinki Location of printing Helsinki Year 2019

The work in this thesis was carried out from August 2015 to June 2019, during which I have received lots of support and many people deserve my thanks. First of all, I would like to thank my supervisor professor Esko I. Kauppinen, for accepting and funding me as a doctoral student in Nanomaterials Group. His supervision on my research not only let me see the big picture, but also the details and fundamentals. His attitude of keeping learning and being curious on new knowledge always inspires me. In addition, I wish to thank my thesis advisors, Dr. Hua Jiang and Dr. Qiang Zhang. Hua’s expertise in transmission electron microscopy helps me a lot, from learning how to operate the equipment to interpreting the results. Qiang’s experience in synthesis also helps me find better solutions to improve the reactor’s stability and synthesize the desired samples. Both Hua and Qiang contributed so much to my papers, whose comments and corrections are of great importance to me.

I also wish to give many thanks to my collaborators Dr. Kimmo Mustonen and Dr. Viera Skakalova from University of Vienna, for their tremendous contributions in the last paper of this thesis. My former group members Sabbir A. Khan, Dr. Patrik Laiho and Dr. Ying Tian also deserve many thanks. I wish to particularly thank Patrik for his design and creation of several setups in our lab, bringing so much convenience for my research work.

The time of working in lab together with my colleagues was unforgettable, so I wish to thank my current group members Aqeel Hussain, Saeed Ahmed, Er-Xiong Ding, Taher Khan, Dr. Nan Wei and Dr. Mohammad Tavakkoli. We worked together to build or modify a reactor and discuss the problems we met and find the solutions in lab. Without your contributions, this thesis work can hardly go so smoothly. I also wish to especially thank Taher, with whom I shared an office, for many interesting talks besides research discussion.

I thank my parents for their infinite love and support on me during my whole life, and I thank my brother and sister for taking care of the family.

The most important one I wish to thank is my wife Yujie, whose love and support always encourages me to move forward and be a better man.

Espoo, June 3rd, 2019
Yongping Liao
# Contents

Acknowledgements

List of Abbreviations and Symbols

List of Publications

Author’s Contribution

Other featured publications

1. Introduction

2. Single-walled carbon nanotube
   2.1 Structural and electronic properties
   2.2 Optical properties
   2.3 Synthesis
     2.3.1 Different methods for SWCNT synthesis
     2.3.2 Carbon precursors
     2.3.3 CO$_2$ effect on CNT growth
     2.3.4 Synthesis of SWCNTs with narrow chirality

3. Transparent conductive films
   3.1 SWCNT transparent conductive films
   3.2 SWCNTs/graphene hybrid transparent conductive films

4. Methods
   4.1 SWCNT synthesis and deposition
   4.2 Doping of SWCNT thin films
   4.3 Characterization
     4.3.1 Differential mobility analyzer
     4.3.2 Optical spectroscopy
     4.3.3 Scanning electron microscopy
     4.3.4 Transmission electron microscopy and electron diffraction
     4.3.5 Sheet resistance measurement
     4.3.6 Temperature dependence conductance measurement

5. Results and discussion
   5.1 Chirality and thin film colors modulated by CO$_2$
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>CO$_2$-modulated geometry of SWCNTs</td>
<td>30</td>
</tr>
<tr>
<td>5.3</td>
<td>Thin film performances affected by CO$_2$</td>
<td>32</td>
</tr>
<tr>
<td>5.4</td>
<td>Proposed role of CO$_2$ in SWCNT growth</td>
<td>35</td>
</tr>
<tr>
<td>5.5</td>
<td>Improving film performance by SWCNTs/graphene hybrid</td>
<td>37</td>
</tr>
</tbody>
</table>

6. **Conclusion and outlook** .......................................................... 45

References .......................................................................................... 47

Publications 1-4
## List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0D</td>
<td>zero-dimensional</td>
</tr>
<tr>
<td>1D</td>
<td>one-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>two-dimensional</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>CPC</td>
<td>condensation particle counter</td>
</tr>
<tr>
<td>DMA</td>
<td>differential mobility analyzer</td>
</tr>
<tr>
<td>ED</td>
<td>electron diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive spectroscopy</td>
</tr>
<tr>
<td>FC-CVD</td>
<td>floating catalyst chemical vapor deposition</td>
</tr>
<tr>
<td>FCE</td>
<td>faraday cup electrometer</td>
</tr>
<tr>
<td>FAT</td>
<td>fluctuation assisted tunnelling</td>
</tr>
<tr>
<td>ΔG</td>
<td>change in Gibbs free energy</td>
</tr>
<tr>
<td>HiPco</td>
<td>high pressure carbon monoxide disproportionation</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>MWCNT</td>
<td>multi-walled carbon nanotube</td>
</tr>
<tr>
<td>MFC</td>
<td>mass flow controller</td>
</tr>
<tr>
<td>MAADF</td>
<td>medium angle annular dark field</td>
</tr>
<tr>
<td>OAS</td>
<td>optical absorption spectrum</td>
</tr>
<tr>
<td>Rs</td>
<td>sheet resistance</td>
</tr>
<tr>
<td>RBM</td>
<td>radial breathing mode</td>
</tr>
<tr>
<td>SWCNT</td>
<td>single-walled carbon nanotube</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscopy</td>
</tr>
<tr>
<td>S-CVD</td>
<td>substrate chemical vapor deposition</td>
</tr>
<tr>
<td>TCF</td>
<td>transparent conductive film</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TFT</td>
<td>thin film transistor</td>
</tr>
<tr>
<td>T&lt;sub&gt;550&lt;/sub&gt;</td>
<td>optical transmittance at 550 nm wavelength</td>
</tr>
<tr>
<td>UV-vis-NIR</td>
<td>ultraviolet-visible-near infrared spectroscopy</td>
</tr>
<tr>
<td>vol%</td>
<td>volumetric percent</td>
</tr>
</tbody>
</table>
List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals.

1. Liao, Yongping; Jiang, Hua; Wei, Nan; Laiho, Patrik; Zhang, Qiang; Khan, Sabbir A.; Kauppinen, Esko I. 2018. Direct synthesis of colorful single-walled carbon nanotube thin films. American Chemical Society. *Journal of the American Chemical Society*, volume 140, issue 31, pages 9797-9800. ISSN 1520-5126. DOI: 10.1021/jacs.8b05151.

2. Liao, Yongping; Hussain, Aqeel; Laiho, Patrik; Zhang, Qiang; Tian, Ying; Wei, Nan; Ding, Er-Xiong; Khan, Sabbir A.; Nguyen, Nguyen Ngan; Ahmad, Saeed; Kauppinen, Esko I. 2018. Tuning geometry of SWCNTs by CO2 in floating catalyst CVD for high-performance transparent conductive films. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. *Advanced Materials Interfaces*, volume 5, issue 23, pages 1801209 (10 pages). ISSN 2196-7350. DOI: 10.1002/admi.201801209.

3. Laiho, Patrik; Rafiee, Mahdi; Liao, Yongping; Hussain, Aqeel; Ding, Er-Xiong; Kauppinen, Esko I. 2018. Wafer-scale thermophoretic dry deposition of single-walled carbon nanotube thin films. American Chemical Society. *ACS Omega*, volume 3, issue 1, pages 1322–1328. ISSN 2470-1343. DOI: 10.1021/jacs.9b01836.

Author’s Contribution

Publication 1: Direct synthesis of colorful single-walled carbon nanotube thin films

The author co-designed the synthesis reactor. Then the author carried all the experiments and measurements apart from the scanning transmission electron microscopy. The author also analysed and interpreted all the data and wrote the whole manuscript. The co-authors gave comments on the manuscript.

Publication 2: Tuning geometry of SWCNTs by CO$_2$ in floating catalyst CVD for high-performance transparent conductive films.

The author constructed and optimized the synthesis reactor with co-authors. The author did all the experiments and analysed all the data and wrote the whole manuscript. The co-authors gave comments on the manuscript.

Publication 3: Wafer-scale thermophoretic dry deposition of single-walled carbon nanotube thin films

The author mainly contributed to the SWCNT sample preparation and deposition on large-scale TP, as well as SWCNT thin film on filter and the film performance measurement. The author also contributed to the manuscript writing on the synthesis part.

Publication 4: Enhanced tunnelling in a hybrid of single-walled carbon nanotubes and graphene

The author was mainly responsible for preparing and depositing the SWCNT samples, optimizing the optoelectronic performances of thin films and measuring optical absorption spectra and scanning electron microscopy. The author also contributed to analyze the corresponding data and co-write the manuscript.
Other featured publications

The author has also contributed to the following publications:

- Ahmad, Saeed; **Liao, Yongping**; Hussain, Aqeel; Zhang, Qiang; Ding, Er-Xiong; Jiang, Hua; Kauppinen, Esko I. Systematic investigation of the catalyst composition effects on single-walled carbon nanotubes synthesis in floating-catalyst CVD. *Carbon* 2019, 149, 318-327.

- Hussain, Aqeel; **Liao, Yongping**; Zhang, Qiang; Ding, Er-Xiong; Laiho, Patrik; Ahmad, Saeed; Wei, Nan; Tian, Ying; Jiang, Hua; Kauppinen, Esko I. Floating catalyst CVD synthesis of single walled carbon nanotubes from ethylene for high performance transparent electrodes. *Nanoscale*, 2018. 10, 9752-9759.


- Tian, Ying; Wei, Nan; Laiho, Patrik; Ahmad, Saeed; Magnin, Yann; **Liao, Yongping**; Bichara, Christophe; Jiang, Hua; Kauppinen, Esko I. Cutting floating single-walled carbon nanotubes with a ‘CO₂ blade’. *Carbon* 2019, 143, 481-486.

- Ding, Er-Xiong; Jiang, Hua; Zhang, Qiang; Tian, Ying; Laiho, Patrik; Hussain, Aqeel; **Liao, Yongping**; Wei, Nan; Kauppinen, Esko I. Highly conductive and transparent single-walled carbon nanotube thin films from ethanol by floating catalyst chemical vapor deposition. *Nanoscale* 2017, 9, 17601–17609.
1. Introduction

Since the discovery in 1991, single-walled carbon nanotube (SWCNT) has drawn tremendous attentions due to its unique chemical and physical properties. The properties of SWCNTs critically depend on the chirality and geometry (i.e. diameter, length and bundle size etc.) of SWCNTs. Thus, to adequately realize the applications in various fields, such as transparent conductive films (TCFs) or thin film transistors (TFTs), controlling the chirality and geometry of SWCNTs is essential.

In last decades, researchers have developed a series of methods of producing SWCNTs, such as arc discharge, laser ablation and chemical vapor deposition (CVD). In particular, the floating catalyst CVD (FC-CVD), owing to the continuous process, high-yield and direct deposition on various substrates of high-quality SWCNTs, has been widely used in academic and industrial fields. HiPco is well-known FC-CVD method developed by Smalley et al. for SWCNT synthesis, where the carbon monoxide (CO) is used as carbon source and decomposed at high pressure. In 2006, Kauppinen et al. developed a new FC-CVD system, where the CO could be used as carbon source at ambient pressure for SWCNT synthesis. After which, with the similar system more synthesis conditions were investigated and the SWCNT quality has been significantly improved by the same group. For instance, Kaskela et al. could directly deposit the SWCNTs on the membrane filter as a thin film and the SWCNT length can be tuned using reactors with different sizes. However, more details of the synthesized SWCNTs, such as the chirality, still remain unclear. In addition, more controllable synthesis of SWCNT is demanding and the thin film performances have room for improvement.

In addition, earlier researchers reported that employing certain amount of promotors during growth, such as H₂O, CO₂, S, is efficient to grow SWCNTs with high selectivity on chirality or geometry. CO₂, as a small gas molecule containing both C and O elements, may act as indirect carbon source and oxidizing agent for SWCNT growth. Some research have been conducted using CO₂ as promoter and hydrocarbon as carbon source for CNT synthesis, and the structure of SWCNTs, such as diameter and length, can be modulated by CO₂. Tian et al. employed certain amount of CO₂ in FC-CVD where CO was used as carbon source, they find that the SWCNT diameter increases with CO₂ concentration. However, some other parameters of SWCNTs tuned by CO₂, such as chirality, bundle length and bundle diameter and the corresponding film performances, call for further study.
Thus, in this thesis, firstly, we introduce certain amount of CO$_2$ in FC-CVD using CO as carbon source and ferrocene (FeCp$_2$) as catalyst precursor to tune the growth of SWCNTs. The chirality of SWCNTs could be modulated by CO$_2$. By carefully analyzing the chirality of SWCNT using electron diffraction (ED), we found that the obtained SWCNTs with certain amount of CO$_2$ possess very narrow chirality distribution. Due to the narrow chirality distribution and suitable diameter of SWCNTs, the thin film can display specific color. For instance, with 0.25 volumetric percent (vol%) of CO$_2$, we obtained SWCNT thin film with a green color. Furthermore, we also gained SWCNT thin films displaying brown color. To the best of our knowledge, this is the first report on direct synthesis of colorful SWCNT thin films. The SWCNT thin films with narrow chirality have great potential application in electronics, such as touch sensors or thin film transistors.

In addition to the chirality, the geometry of SWCNTs also critically depends on CO$_2$ concentration. Both the tube diameter and bundle length are found to be significantly increased by increasing CO$_2$ concentration. Moreover, the yield can also be boosted over two times with a proper amount of CO$_2$. The SWCNTs with optimized geometry were used as TCFs, exhibiting a sheet resistance as low as of 86.8 $\Omega$/sq. by AuCl$_3$ doping at 90% T$_{550}$ (transmittance at 550 nm wavelength). The enhanced performance of SWCNT TCFs essentially ascribes to the optimized geometry, including large tube diameter, small bundle diameter and long bundle length. Furthermore, we also tried to scale-up our SWCNT thin films using large-size thermophoretic precipitator (TP). The synthesized SWCNTs can be successfully deposited on wafer-scale substrates, such as glass and polyethylene terephthalate (PET). The corresponding SWCNT thin films also show good uniformity and conductivity.

Finally, we attempted to further improve the conductivity of SWCNT films by manufacturing SWCNTs/graphene hybrid thin films. The conductivity of SWCNT film is limited strictly by the charge tunneling between individual tubes$^{22}$. Hence, we deposited aerosol SWCNTs on graphene by small-size TP$^{23}$ or filter-press transfer$^{11}$ methods. Due to the strong $\pi-\pi$ stacking between SWCNTs and graphene, the charge tunnelling between the tube junctions is significantly enhanced. As a result, a sheet resistance as low as 36 $\Omega$/sq. at 90% T$_{550}$ after AuCl$_3$ doping has been achieved.
2. Single-walled carbon nanotube

2.1 Structural and electronic properties

As one of the low-dimensional carbon allotrope families (Figure 2.1.1), single-walled carbon nanotubes (SWCNTs) possess their unique geometrical and electronic structures. A SWCNT can be considered as a hollow cylinder rolled up from a graphene sheet. The diameter of SWCNT varies from sub-nanometer to few nanometers, and the length from tens of nanometer to hundreds of millimeter. Similar to graphene, the carbon atom in SWCNTs form the strong σ bond with its neighbor carbon atom by a sp² orbital hybridization, and the remaining pz orbital forms a π bond with another pz of its neighbor carbon atom. The π and σ bond determines the SWCNTs’ unique electrical (such as the high electron mobility) and mechanical (such as the high Young’s modulus) properties, respectively.

![Figure 2.1.1. The low-dimensional carbon allotropes, (a) zero-dimensional (0D) fullerene, (b) one-dimensional (1D) single-walled carbon nanotube and (c) two-dimensional (2D) monolayer graphene.](image)

As mentioned above, the vector of rolling up the graphene sheet into a tube is called the chiral vector \( \mathbf{C} \), it determines the structure of a SWCNT. As seen in Figure 2.1.2, the chiral vector \( \mathbf{C} \) can be expressed by the basis vector \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \), \( \mathbf{C} = n \mathbf{a}_1 + m \mathbf{a}_2 \), the integer pair (n,m) is called the chirality of SWCNT. The intersection angle \( \theta \) (0° ≤ θ ≤ 30°) between \( \mathbf{C} \) and \( \mathbf{a}_1 \) is known as the chiral angle.

Accordingly, the chirality (n,m) can determine the structure of SWCNTs, including the diameter and chiral angle shown in equation 2.1.1 and 2.1.2, respectively.

\[
d = \frac{a_{cc}}{\pi} \sqrt{3(n^2 + nm + m^2)} \quad (2.1.1)
\]

where \( a_{cc} = 0.142 \) nm is the distance between two neighboring carbon atoms.

\[
\cos \theta = \frac{2n + m}{2\sqrt{n^2 + nm + m^2}} \quad (2.1.2)
\]
Based on different \((n,m)\), the SWCNTs can be classified as “zigzag” when \(m\) or \(n = 0\) and “armchair” when \(n = m\), otherwise, the “chiral” nanotubes (Figure 2.1.3). Furthermore, the SWCNTs can behave semiconducting or metallic properties, depending on the \((n,m)\) as well. In the case of \(n-m = 3i\) \((i\) is an integer), the SWCNT exhibits metallic properties, otherwise the semiconducting properties. In Figure 2.1.3, we list three representative SWCNTs with different chirality and their corresponding one-dimensional density of state.

Owing to rolling up from a graphene sheet, the SWCNT’s band structure can be explored according to the graphene’s. Theoretically, the energy dispersion in graphene follows the equation \(2.1.3^{28}\),

\[
E = \pm \gamma_0 \sqrt{1 + 4 \cos(\frac{\pi k_x a_x}{2}) \cos(\frac{k_y a_y}{2}) + 4 \cos^2(\frac{k_y a_y}{2})}
\] (2.1.3)
where \( k_x \) and \( k_y \) are the wave vectors, \( \gamma_0 \) is the transfer integral between the neighboring carbon atoms and \( \alpha = 2.46 \, \text{Å} \) is the lattice constant of graphene.

According to this equation, the surface and contour plots of energy dispersion for graphene are displayed in Figure 2.1.4a and b. We can see that the valence \( \pi \) and conduction \( \pi^* \) meets at six points in the Fermi points (K and K’ points at the first Brillouin zone), resulting in graphene acting as semimetal or zero-gap semiconductor.

\[
\mathbf{k}_{\parallel} \mathbf{C} = \pi d \mathbf{k}_{\perp} = 2\pi m, \quad (2.1.4)
\]

where \( \mathbf{C} \) is the chiral vector, \( d \) is the diameter of SWCNT and \( m \) is an integer. As a result of quantized values of allowed \( \mathbf{k}_{\perp} \), the energy band of graphene is cut into a series of 1D sub-bands which are parallel to the tube axis (Figure 2.1.4c).
Therefore, the 1D band structure of SWCNT is determined by the spacing $2/d$ between allowed $k_\perp$ and their angles. The band structure near the Fermi level is given by the allowed $k_\perp$ states near the K points. In the case that the allowed $k_\perp$ states directly pass through the K points (Figure 2.1.4d), the energy dispersion displays two straight line across the Fermi level with a zero-bandgap, which is called the metallic SWCNT. Otherwise, it is known as semiconducting SWCNT\textsuperscript{25} (Figure 2.1.4e).

### 2.2 Optical properties

The optical absorption spectrum (OAS) of SWCNTs, which is closely related to the SWCNT diameter or band structure\textsuperscript{30}, has been widely used to study the properties of individual SWCNT or thin film. Due to the unique band structure mentioned above, the OAS of an individual SWCNT should display several sharp peaks in the ultraviolet-visible-near infrared (UV-vis-NIR) region. Each peak corresponds one energy transition between interbands. Generally, for semiconducting individual SWCNTs (diameter < 2.5 nm) the interband transition peaks, $V_1-C_1$, $V_2-C_2$, $V_3-C_3$, $V_4-C_4$, labeled as $S_{11}$, $S_{22}$, $S_{33}$ and $S_{44}$ can be observed in UV-vis-NIR region, while for metallic individual SWCNT, only the $M_{11}$ and $M_{22}$ peak can be seen (Figure 2.2.1a and c). However, SWCNTs are commonly synthesized as the bulk materials, such as SWCNT thin films, with CNT bundles and mixture of semiconducting and metallic tubes. Thus, unlike individual SWCNT, the OAS of bulk SWCNTs displays both semiconducting and metallic transition peaks (Figure 2.2.1b). Importantly, in the bulk SWCNTs, the broadening of peaks appear due to the broad chirality distribution and the bundle effect\textsuperscript{31-33}. And peaks at higher energy regions, such as $S_{33}$ or $S_{44}$, would be difficult to distinguish because of the existence of mixed chirality. In addition to the electronic transition peaks, a strong-intensity $\pi$ plasmon absorption peak can be detected as well. This peak mainly attributes to the collective oscillation of $\pi$ electrons in carbon but still remains elusive. It also contributes to the background of SWCNT transition peaks in the high-energy region\textsuperscript{34, 35}.

Since the band gap is critically related to tube diameter as discussed in previous chapter, the peak position in OAS will thus be affected by tube diameter. According to the Kataura plot\textsuperscript{34}, which depicts the relation between transition energy and tube diameter (Figure 2.2.1c), the approximate mean diameter of SWCNTs in a thin film sample can be determined based on the peak positions. For example, in Figure 2.2.1b the $S_{11}$ and $S_{22}$ peaks correspond transition energy of 0.77 eV and 1.39 eV, respectively. Thus, we can estimate the mean diameter \~1.3 nm of this sample using Kataura plot. Furthermore, with this plot, we can also assign the chirality for sample with highly individual tubes.

As the electron density near the Fermi level is sensitive to the covalent or non-covalent doping of SWCNT by chemicals, the transition peaks can also be modulated by doping. Hence we can study the SWCNT doping using absorption spectra. For instance, dopants like $\text{AuCl}_3$ and $\text{HNO}_3$ can deplete the electrons from valence band of SWCNT\textsuperscript{36-39}, resulting in the suppression of transition peaks.
Figure 2.2.1. (a) A schematic illustrating the first (S₁₁) and second (S₂₂) optical transition energy of semiconducting SWCNT (top), and first optical transition (M₁₁) of metallic SWCNT (bottom), where \( v \) and \( c \) represent the valence band and conduction band, respectively. (b) A representative optical absorption spectrum of a SWCNT thin film studied in Publication 1, displaying the S₁₁, S₂₂ and M₁₁ peaks. (c) The Kataura plot for optical transitions, we can estimate the mean diameter of SWCNTs based on the transition energies using this plot. It can be also used to assign the chirality \((n,m)\) in Raman spectroscopy.

Besides the optical absorption spectrum, Raman spectroscopy, based on the inelastic scattering of a photon in a molecule, has been widely used to analyze the diameter, chirality and defects of SWCNTs. Resonance Raman scattering means the intensity enhancement or decrease when the incident photon energy match with the optically allowed electronic transition energy of the material. The Raman spectroscopy of SWCNT can reflect the \((n,m)\) information at the resonant condition since each \((n,m)\) carbon nanotube has a unique electronic structure. In a typical Raman spectrum, two important features, the radial breathing mode (RBM) and the G and D bands, are vital to revealing the structural information of SWCNT.

The RBM peaks in the frequency region 100-300 cm\(^{-1}\) provide information of SWCNT diameter and chirality \((n,m)\) based on Kataura plot (Figure 2.2.1c). The diameter of SWCNTs \((d)\) calculated from the RBM frequency \((\omega)\) with \(\omega = \frac{234}{d} + 10\), and each point in Kataura plot represent one \((n,m)\) of SWCNT. However, for the \((n,m)\) abundance assignment in a mixed chirality sample, we have to consider the cross section dependence. Researchers find that the nanotube diameter and chiral angle can change the Raman intensities by about one order of magnitude. In short, RBM can be used to identify partial rather than complete \((n,m)\) in a sample.

The dominant peak located at ~1590 cm\(^{-1}\) is called G band, it refers to the graphite-like band. Due to the curvature, the G band of SWCNT splits into a lower energy G\(^-\) and higher energy G\(^+\) peak. The G\(^+\) peak corresponds to lattice vibrations in the SWCNT axis direction, while the G\(^-\) to the vibration in the circumferential direction, and G\(^-\) peak is found to be sensitive to whether the nanotube is semiconducting or metallic. In addition to the G band, the peak located at ~1350 cm\(^{-1}\) is known as D band, referring to the disordered properties caused by the vacancies, hetero-atoms, or any defects. Thus, it is common to use the intensity ratio of G to D band (I\(_G\)/I\(_D\)) to evaluate the purity of \(sp^2\) bonded carbon in SWCNTs.
2.3 Synthesis

2.3.1 Different methods for SWCNT synthesis

Currently, there are three common approaches to prepare SWCNTs (Figure 2.3.1), including arc discharge, laser ablation and chemical vapor deposition (CVD). Therein, the chemical vapor deposition method in this thesis is divided into substrate chemical vapor deposition (S-CVD) and floating catalyst chemical vapor deposition (FC-CVD).

Arc-discharge, normally requiring high temperature (over 1700 °C) for CNT growth, is the first method to produce CNTs established by Iijima in 1991. In this method, two electrodes with a distance (1-2 mm) are placed in a vacuum chamber filled with inert gas, such as helium or argon (Figure 2.3.1a). When the current passes through the positive and negative electrodes, the high temperature can turn the gas into plasma, evaporating the electrode materials with charged nanoparticles. In arc discharge, the electrodes are usually made of graphite, with the assistance of arc discharge, the evaporated anode carbon will deposit on the cathode.

In practice researchers found the wall number of CNT depends on the composition of electrodes, the pure graphite electrodes normally will lead to the MWCNTs, while the metal-doped graphite electrodes to SWCNTs. The metal-doped graphite has been proved more efficient to control over the diameter of SWCNTs. For instance, Bethune et al. and Ajayan et al. studied the composition of cobalt and carbon towards synthesis of very small diameter SWCNT (1.2 nm). Some other catalyst-doped graphite have also been investigated, such as Fe, Ni, and platinum-group metals.

The laser ablation approach for SWCNT synthesis, which in principle has similar mechanism to the arc discharge, was firstly developed by Smalley et al. in 1995 (Figure 2.3.1b). In this approach, a laser bombards the metal/graphite target in a high-temperature furnace filled by inert gas. The vaporized carbon and metal particles will reassemble into the form of carbon nanotubes with the assistance of laser plume, the generated carbon nanotubes are then deposited on a cooled surface. Researchers have found that the laser source and the transition metal composition will have dominant effect on the growth of carbon nanotubes.

Generally speaking, both arc discharge and laser ablation are very practical methods for CNT synthesis since they can yield highly graphitized nanotubes at high temperature. However, the extensive energy consumed for high reaction temperature in both methods leads to a big challenge in large-scale production of SWCNTs. In addition, many by-products appear along with the SWCNTs, such as MWCNTs, amorphous carbon and metallic particles, requiring further treatment to obtain high-purity SWCNTs. Further, it is also difficult to finely control the chirality of SWCNTs using these two methods.

Chemical vapor deposition (CVD), on the other hand, has been considered as a more advanced approach for large-scale production of SWCNTs with both high quality and selectivity. In principle, the carbon source decomposes on the catalyst surface at high temperature or plasma, followed by the nucleation and
growth of SWCNTs. Currently, two growth models, the tip growth\(^5\) and base growth\(^6\), are generally accepted, although the real growth mechanism remains elusive. Based on how the catalyst is introduced, we divide the CVD into two types, the substrate CVD (S-CVD, Figure 2.3.1c) where the catalysts are firstly spread on the surface of substrate, and the floating catalyst CVD (FC-CVD, Figure 2.3.1d), where the catalysts are carried by gas (as an aerosol form) into the furnace.

In S-CVD, the pre-made catalysts, such as transition metals (Fe, Co and Ni etc.) or even some noble metals, are deposited on substrate, followed by catalytic decomposition of carbon precursor at high temperature furnace (700-1200 °C). This method is beneficial for preparing the CNT forest\(^7\) and the horizontally aligned CNTs\(^8\). However, the large-scale production for the S-CVD is limited by the substrate size and catalyst activity.

![Figure 2.3.1.](image)

In 1998, FC-CVD method was first-time used to synthesize CNTs by Cheng et al.\(^9\). Smalley et al. also developed a FC-CVD system where the CO was used as carbon source at high pressure in 1999\(^8\) (known as the HiPco SWCNTs), after which Kauppinen et al. developed this method so that SWCNTs can be produced in ambient pressure\(^9\). In this thesis, all the SWCNTs are synthesized by ambient pressure FC-CVD method. In FC-CVD the catalysts, such as some low-vapor pressure organometallic compound like ferrocene or nanoparticles generated by spark, are suspended in gas phase. Then the SWCNTs grow in aerosol phase without any supports, making the growth process more complicated. A schematic of catalyst formation and SWCNT growth was proposed by Moisala et al.
using CO as carbon source and ferrocene as catalyst precursor. In detail, as illustrated in Figure 2.3.2, the ferrocene vapor firstly decomposes and then fast nucleates into iron nanoparticles due to collision. Then, the disproportionation of CO molecule takes place on the nanoparticle surface until saturation. After that, the carbon atoms start to form the $sp^2$ bonds, until a carbon cap is formed on the nanoparticle surface. With continuous incorporation of $sp^2$ carbons into the cap, the SWCNT can grow longer. In reality, the termination of SWCNT growth is possibly determined by the dynamic temperature zone in reactor, and the inactivity of catalyst due to their size or over saturation, as well as the bundling due to the collision between SWCNTs. In Publication 2, we have developed this schematic and discussed more about the role of CO$_2$.

![Figure 2.3.2](image.png)

**Figure 2.3.2.** The schematic of SWCNT growth process in FC-CVD using CO as carbon source and ferrocene as catalyst precursor. Partially adapted from Moisala *et al.*

Notably, compared to arc discharge and laser ablation or S-CVD methods, FC-CVD is a continuous process. The acquired SWCNTs, especially as a form of thin film, can be directly applied in high-performance thin film transistors or touch sensors without any further solvent purifications, avoiding the contaminations, defects or shortening from solution process.
Thus, FC-CVD method has attracted much attention in academic filed. In FC-CVD the SWCNT parameters can be well controlled by modulating the feeding or reactor conditions. For example, the bundle diameter of SWCNTs can be tuned by controlling the catalyst feeding rate\(^6^2\); and the bundle length of SWCNTs can be modulated by scaling up the reactor dimension\(^1^1\); the chirality distributions can be also controlled\(^6^3\).

Besides the fundamental research, FC-CVD method has also been considered as a promising approach in industry for high-yield and large-scale production of SWCNTs, due to the continuous feeding of carbon source and catalysts. In fact, recently the FC-CVD method has enabled the industrial productions of SWCNT thin films\(^6^4\), showing great potential to replace the conventional indium tin oxide (ITO) materials.

### 2.3.2 Carbon precursors

In the CVD method, a variety of carbon sources have been used for SWCNT growth, such as hydrocarbon (methane, ethylene or toluene etc.), ethanol and carbon monoxide. In this thesis, all the SWCNTs are synthesized using carbon monoxide (CO, \textit{Publications 1-4}) as carbon source.

The key factor of selecting carbon source is the thermodynamics, meaning that the chemical reaction of making the solid carbon must be thermodynamically allowed under the given temperature and pressure\(^6^5\). The change in Gibbs free energy (\(\Delta G\)) can be used to address this issue (Figure 2.3.3, calculated data from CRC Handbook of Chemistry and Physics\(^6^6\)). For instance, the \(\Delta G\) for \(\text{CH}_4\) decomposition is below zero when the temperature is over 600 °C, meaning its decomposition is only favored above 600 °C, while it's above 100 °C for \(\text{C}_2\text{H}_4\). Therefore, the \(\text{CH}_4\) is more stable than \(\text{C}_2\text{H}_4\) and in preparation of CNTs the temperature is set higher when using \(\text{CH}_4\) than using \(\text{C}_2\text{H}_4\). Unlike the endothermic decomposition of hydrocarbon, the decomposition of CO (Boudouard reaction 2.3.1) on catalyst is an exothermic reaction. This reaction is kinetically slow below 700 °C and thermodynamically limited above 700 °C and thus, normally high pressure is required to displace the equilibrium (such as the HiPco method with 30–50 atm at 900–1100 °C\(^7,^6^7\)) for improved yield of SWCNTs. Nevertheless, in \textit{Publication 2} of this thesis, we find that at ambient pressure, introducing little amount of CO\(_2\) can also promote the SWCNT production.

\[2\text{CO} \leftrightarrow \text{C} + \text{CO}_2 \quad (2.3.1)\]

In addition to thermodynamics, other factors of carbon precursor, such as cost of gases and byproducts of decomposition, should be also taken into consideration for CNT synthesis. For example, Compare \(\text{CH}_4\) and \(\text{C}_2\text{H}_4\), the cost of CO is lower, though is higher than that of ethanol. However, ethanol decomposition would produce more byproducts by multi-path\(^6^8\), which can affect CNT synthesis. On the other hand, CO decomposition into carbon and \(\text{CO}_2\) is main reaction path, moreover, the produced \(\text{CO}_2\) can act as an etchant to remove the amorphous carbon from catalysts\(^6^9\).
Figure 2.3.3. Gibbs free energies of carbon decomposition reactions from different carbon sources. Data calculated from CRC Handbook of Chemistry and Physics (the energies are normalized to the number of solid carbon atoms).

2.3.3 CO₂ effect on CNT growth

Besides the main roles of catalysts and carbon source in CNT growth, small molecules, such as O₂, CO₂, H₂O, NH₃, and others, are commonly employed as promoters to grow CNTs. CO₂, as a molecule containing C and O atoms, might achieve different CNT productions from other promoters. It might act as indirect carbon source or etchant to improve the yield or selectivity of CNTs. In addition, using CO₂ as promoter will not bring alien atoms in a CO-based CVD process. In fact, based on experimental and simulation results of previous research, CO₂ can interact with catalyst nanoparticles, CNTs and carbon precursor, resulting in various micro-structure of CNTs.

Moisala et al. proposed that role of CO₂ is expected to “etch” amorphous carbon from the catalyst particle surfaces at the CNT nucleation and growth stages. The etching effect prevents particle from deactivation and maintains conditions for CNT nucleation and growth. Qian et al. claimed that in S-CVD method, where the Fe/Mo/MgO catalysts were used for decomposing methane for CNTs synthesis, a small amount of added CO₂ was effective on removing amorphous carbon to regenerate the catalysts, as well as decreasing the size of the MgO support and increasing the specific surface area of the catalyst.

Tian et al. proposed that CO₂ can also etch the graphitic cap (a CNT embryo). CNT embryo with low curvature have a higher possibility of survival, and vice versa, CNT embryo with higher curvature can be etched away more easily by CO₂. Consequently, the diameter of as-prepared SWCNT increased when increasing CO₂ concentration.
When hydrocarbon was chosen as the carbon source for CNT synthesis, CO\textsubscript{2} can not only remove amorphous carbon from catalyst, but also react with hydrocarbon to form intermediates which can be used as carbon source for CNT synthesis, the later role was even dominated. Therefore, many studies were conducted by introducing CO\textsubscript{2} in S-CVD using hydrocarbon as carbon source. Magrez \textit{et al.} proposed that when equimolar ratio of CO\textsubscript{2} and C\textsubscript{2}H\textsubscript{2} were introduced into S-CVD at low temperature (680 °C), two chemical processes are possible for the reaction of acetylene with CO\textsubscript{2} for the synthesis of carbon nanotubes (reactions 2.3.2 and 2.3.3). The regeneration of CO\textsubscript{2} is resulted from CO disproportionation (reaction 2.3.1) or the water gas shift reaction (reaction 2.3.4). These reactions prefer to take place around area metal-support interface\textsuperscript{13}.

\begin{equation}
\text{C}_2\text{H}_2 + \text{CO}_2 \leftrightarrow 2\text{C} + \text{H}_2\text{O} + \text{CO} \\
(2.3.2)
\end{equation}

\begin{equation}
\text{C}_2\text{H}_2 + \text{CO}_2 \leftrightarrow \text{C} + 2\text{CO} + \text{H}_2 \\
(2.3.3)
\end{equation}

\begin{equation}
\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{CO}_2 + \text{H}_2 \\
(2.3.4)
\end{equation}

Although CO\textsubscript{2} was proven to react with hydrocarbon or other molecules to enhance CNT synthesis, whether it acts as direct carbon source to incorporate the CNT growth still remains unclear. Plata \textit{et al.} utilized \textsuperscript{13}C labeling CO\textsubscript{2} in S-CVD with C\textsubscript{2}H\textsubscript{2} as carbon source. Coupling with Raman spectroscopy, they identified that CO\textsubscript{2} did not serve as carbon source for CNT growth in the equimolar CO\textsubscript{2}-C\textsubscript{2}H\textsubscript{2} reaction\textsuperscript{14}.

Despite the role of CO\textsubscript{2} has been proposed by researchers, more systematic studies are demanded on the microstructure and electronic properties of CNTs modulated by CO\textsubscript{2}. Thus, in \textbf{Publications 1 and 2}, we investigated the chirality and geometry of SWCNTs tuned by CO\textsubscript{2}, and the role of CO\textsubscript{2} has been explored systematically.

\textbf{2.3.4 Synthesis of SWCNTs with narrow chirality}

As discussed above, the excellent properties of SWCNT critically depend on the chirality, thus, it is meaningful to produce SWCNTs with narrow distributions. To achieve this goal, researchers have taken much effort in last few years and many progresses have been achieved.

At present, mainly two methods are taken for producing SWCNTs with narrow chirality distribution or even single chirality, the direct growth and post synthesis purification. The post synthesis purification method is primarily based on solution process, such as ion-exchange chromatography separation (IEX) of DNA-wrapped SWCNTs\textsuperscript{73}, density gradient ultracentrifugation\textsuperscript{74}, gel chromatography\textsuperscript{75} and aqueous two-phase separation techniques\textsuperscript{76}. Those approaches have been proven to separate pristine SWCNTs efficiently and over 10 types of single-chirality tubes have been obtained\textsuperscript{75}. However, one cannot avoid the contamination and damage (\textit{i.e.} cutting of tubes) caused by the chemicals in solution process, which suppresses the intrinsic properties of SWCNTs. In addition, the cost (\textit{i.e.} DNA in IEX method) and yield should be also taken into consideration for the scale-up process. On the other hand, direct growth of SWCNTs with
narrow chirality distribution can efficiently retain the intrinsic properties. Generally, three approaches have been developed for direct growth: the use of CNT segments as seeds, the growth initiated from carbonaceous molecular seeds and use of well-designed catalysts for (n,m)-selective growth. The method using CNT segments as seeds, however, is limited to the yield and purification of the initial CNT segments. As for carbonaceous molecular seeds method, the challenge is to control the seed diameter, as well as precisely control the diameter and chirality of as-grown SWCNTs over the seeds. Nevertheless, the catalysts with specific chemical composition, structure and size for growth of SWCNTs with narrow chirality distribution have been studied extensively. The most commonly used catalysts are alloys such as W6Co, FeRu, FeNi, FeCu and CoMo etc. However, issue for this method is that the chirality distribution mainly clustered around (6,5) and can hardly be tuned to other ranges. Due to the use of S-CVD method, other drawbacks, such as low yield and post-purification of SWCNTs, also matter for further applications.

Problems mentioned above could be solved using FC-CVD method as its unique advantages, such as solvent free process and direct depositions of thin film. However, due to the existence of unsupported catalysts in aerosol phase, it is a big challenge to selectively grow SWCNTs with narrow chirality distribution in FC-CVD. Only few works about controlling chirality distribution in FC-CVD were reported. Zhu et al. found that appropriate amount of NH3 can narrow the chirality distribution in FC-CVD. But in this case, SWCNTs could be doped as the existence of NH3 at high temperature.

In Publication 1, we report a method to selectively and directly grow SWCNTs with tuneable and narrow chirality distributions, in which a certain amount of CO2 was introduced in FC-CVD using CO as carbon source.
3. Transparent conductive films

Transparent conductive films (TCFs) is one of the key components in modern technologies, such as photovoltaics, touch panel, liquid crystal displays (LCD) or organic light-emitting diodes (OLED)\(^8\). A TCF should display a very low sheet resistance \(R_s\) at high light transmittance \(T\). The \(R_s\) could be measured by a 4-point probe and the \(T\) is measured using optical absorption spectroscopy. Theoretically, we can combine these two parameters to define the figure of merit \(K\) of TCF as,

\[
K = \left( R_s \times \ln T \right)^{-1} \quad (3.1)
\]

and a higher \(K\) value represents the better performance of TCFs.

Currently, indium tin oxide (ITO) is the most widespread material for TCFs as it has low sheet resistance (from 10 to 100 \(\Omega\)/sq.) at high transmittance (>85\%)\(^8\).\(^8\). However, the drawbacks of ITO, such as the brittle nature\(^8\) and the low reserve of indium element\(^8\), have limited its further application for flexible TCFs in future. Thus, it is of significant importance to seek new alternatives. In recent years, researchers have found a series of novel materials showing great potential of replacing ITO, such as silver nanowire\(^8\)\(^9\)\(^-\)\(^1\)\(^1\), graphene\(^9\)\(^2\)\(^-\)\(^9\)\(^4\) and SWCNTs\(^3\)\(^-\)\(^1\)\(^1\), \(^9\)\(^5\)\(^-\)\(^9\)\(^6\). In terms of silver nanowire, the main disadvantages are high cost of raw materials, the oxidation in air and the increased reflection with wavelength\(^9\)\(^7\). Graphene as TCF mainly suffers from the defects (grain boundary, wrinkles, folds or cracks)\(^9\)\(^8\) and the difficulties of transfer\(^9\)\(^9\). Single-walled carbon nanotubes, on the other hand, have been considered as a promising candidate due to their easy production, superior electrical conductivity, flexibility and chemical stability.

3.1 SWCNT transparent conductive films

In general, a SWCNT network consists of both metallic and semiconducting tubes with various dimensions. Figure 3.1.1 shows a scanning electron microscopy image of SWCNT network and its utilization as transparent conductive film on PET from Ding et al\(^1\)\(^0\). SWCNT network can be thought of a quasi-two-dimensional (2D) system\(^1\)\(^1\) since the film is rather thin (from sub-nanometer to tens of nanometer). The interconnectivity of network can be explained by a well-known 2D percolation theory as described in

\[
N_c = 4.236^2 \pi L_s^2 \approx \frac{1}{L}, \quad (3.1.1)
\]
where the $N_c$ is the threshold of network, $L_a$ and $L$ are the length and aspect ratio of individual SWCNTs, respectively. The aspect ratio is very high since a SWCNT has several micrometer in length and 1-3 nm in diameter, indicating that the threshold of a SWCNT network is low. Thus, the required amount of materials is low to form an interconnected path for carrier transport, leading to the high light transmittance. Above the threshold, the sheet resistance of SWCNT-TCF decreases dramatically with increasing SWCNT thickness according to equation 3.1.

![Figure 3.1.1.](image)

According to literature, besides the different fabrication methods (wet or dry) of SWCNT thin films$^{5,102}$, the conductivity of TCFs varies in a wide range due to the different geometric and chiral structure of SWCNTs.

We can use a simplified model to understand the carrier transport within the network, where the carriers transport along a SWCNT and then “jump” to another SWCNT through their junction, although the real case is much more complex. It has been proven that the resistance of SWCNT-TCF mainly attributes to the tube-tube junction resistance, while the resistance along the individual tube contributes quite mildly$^{22,103}$. The junction resistance not only depends on the SWCNT bundle length and diameter, but also the electronic types of SWCNT (semiconducting or metallic).

Under the same transmittance, the longer bundles will form fewer junctions than the shorter ones, resulting in the improved conductivity. Simien et al.$^{104}$ and Hecht et al.$^{105}$ have studied the effect of bundle length on the conductivity of CNT thin films. In addition, Hecht et al. proposed a relation between the film conductivity ($\sigma$) and the average bundle length ($L_{av}$), $\sigma \propto (L_{av})^{1.46}$. However, Li et al. found that for CNT with length of 0.4 cm, the resistance along the tube is dominated rather than the junction resistance$^{106}$. Besides the bundle length, the bundle diameter also plays a key role in film conductivity. The charge transport is proposed to mainly takes place on the surface of bundles, while the tubes inside bundle could contribute to the light absorption$^{107}$. Thus, preparing SWCNTs with small bundles is necessary for highly conductive films. Mustonen et al. systematically studied the bundle diameter effect and obtained highly individual SWCNTs by FC-CVD. The corresponding TCF exhibits 63 $\Omega$/sq. at 90% transmittance after HNO$_3$ treatment$^{108}$. Jiang et al. synthesized carbon-welded
and non-bundled SWCNT network and achieved a sheet resistance of 25 Ω/sq. at 90% transmittance after HNO₃ doping⁹⁶.

Additionally, modulating the metallic and semiconducting SWCNT ratio is another strategy to improve the conductivity of TCF. Researchers have shown that the junction resistance for metal-metal or semiconducting-semiconducting nanotubes is 200-400 kΩ, while it is two orders of magnitude higher for a metal-semiconducting junction which forms a Schottky barrier¹⁰⁹. Topinka et al. simulated the conductance of SWCNT thin film with different metallic and semiconducting SWCNT ratio. Their results imply that for a mixed-metallicity SWCNT film, the conductance decrease with increasing semiconducting SWCNT ratio until it reaches 80%, after which it increases¹¹⁰. In the real preparation, however, selective growth of SWCNTs with enrichment of semiconducting or metallic tubes is still a big challenge. Although we can obtain the high ratio of metallic tubes by post-separation¹¹¹, the problems, such as the low yield, the tube damage or contaminations caused by post-treatment, still remain.

In Publication 2 of this thesis, we succeeded in tuning the bundle length and diameter using CO₂ as promoter in FC-CVD, where the SWCNTs with bundle length of ~7.5 μm, small bundle diameter ~7.1 nm and large tube diameter ~1.9 nm along with a metallic tube ratio of 46.3%. The thin films made by filter-press method present improved conductivity (86.8 Ω/sq. at 90% transmittance). In Publication 3, we studied the scale-up deposition of prepared aerosol SWCNTs on 50 mm wafers or the PET using a large-size thermophoretic precipitator (TP). The corresponding TCFs show a comparable uniformity and conductivity to the filter-press transfer films.

### 3.2 SWCNTs/graphene hybrid transparent conductive films

Furthermore, combing other materials with SWCNTs, such as the silver nanowire¹¹²,¹¹³ and graphene¹¹⁴-¹¹⁶, to form the hybrid is another strategy to improve the SWCNT TCF performance. As discussed above, the SWCNT film conductivity is mainly limited by the inefficient carrier tunneling between tubes. Thus, besides the optimization of CNT geometry during synthesis, hybridizing SWCNTs with other conductive materials is expected to reduce the tunneling barrier by enhancing the tube-tube contact. Specifically, when the conductive materials directly connect the tube-tube junction, the M-S Schottky contact could be converted into near-ohmic one⁹⁶. In principle, for example, due to the outstanding optical and electrical merits of SWCNTs and graphene, the SWCNTs/graphene hybrid should have exhibited excellent conductivity. However, the reported results for SWCNT/graphene hybrid are not as good as expected. For instance, Tung et al. used a solution-based method to fabricated CNT/graphene film and achieved a sheet resistance of 240 Ω/sq. at 86% transmittance¹¹⁷. Yan et al. prepared a rebar graphene, where CNTs were interconnected with graphene using an approach of annealing the functionalized CNTs, the hybrid displayed ~600 Ω/sq. at 95.8% transmittance¹¹⁸. The unsatisfactory conductivity mainly emerges from the weak interaction between the SWCNT and graphene due to the fabrication methods.
In **Publication 4**, we deposited SWCNTs on graphene by small-size thermophoretic precipitator (TP) or filter-press transfer methods. Due to the strong van der Walls interaction between graphene and SWCNTs, the charge tunneling barrier is reduced between SWCNTs. Thus we obtained a pristine sheet resistance as low as 180 Ω/sq. at 90% transmittance (36 Ω/sq. after Au₃ doping).

In Table 3.1, we list the performance of representative SWCNT and SWCNTs/graphene thin films from this thesis and literature.

### Table 3.1. Performance of representative SWCNT and SWCNT/graphene films from literature and this thesis.

<table>
<thead>
<tr>
<th>Films</th>
<th>Fabrication</th>
<th>Pristine Rs (Ω/sq.)</th>
<th>Dopant</th>
<th>Final Rs (Ω/sq.)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT</td>
<td>Disperse commercial HiPCo CNTs in superacid chlorosulfonic acid and obtained the film by vacuum filtration.</td>
<td>−</td>
<td>HSO₃Cl</td>
<td>60/90.9%</td>
<td>Hecht et al.¹¹⁹</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD using CO as carbon source and ferrocene as catalyst precursor, with a semi-industrial reactor to prepare the longer (9.4 μm) CNT bundles.</td>
<td>820/90% HNO₃</td>
<td>110/90%</td>
<td>−</td>
<td>Kaskela et al.¹¹</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD with a spark reactor, which can control size and concentration of pre-made catalysts. The SWCNTs have highly individual (&gt;80%) tubes.</td>
<td>−</td>
<td>HNO₃</td>
<td>60/90%</td>
<td>Mustonen et al.¹⁰⁸</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD with feedstock of ferrocene dissolved in ethanol, obtaining SWCNTs with mean bundle length ~27 μm.</td>
<td>320/90% AuCl₃</td>
<td>95/90%</td>
<td>−</td>
<td>Ding et al.¹²⁰</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD using CO and C₂H₄ as mixture carbon source to get long (17 μm) SWCNT bundle.</td>
<td>291/90% AuCl₃</td>
<td>73/90%</td>
<td>−</td>
<td>Anoshkin et al.¹²¹</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD using C₂H₄ and toluene (ferrocene dissolved), growth with high feeding rate, SWCNTs are long (mean 62 μm) and highly individual welded by graphite carbon.</td>
<td>41/90% HNO₃</td>
<td>25/90%</td>
<td>−</td>
<td>Jiang et al.¹²⁶</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD using CO as carbon source, CO₂ as growth promoter to modulate tube diameter and length etc.</td>
<td>273/90% AuCl₃</td>
<td>86/90%</td>
<td>−</td>
<td>Publication 2</td>
</tr>
<tr>
<td>SWCNT</td>
<td>FC-CVD using CO as carbon source, CO₂ as growth promoter to modulate SWCNT growth, thin films deposited by large TP on glass or PET.</td>
<td>200/87.8% HNO₃</td>
<td>60/87.8%</td>
<td>−</td>
<td>Publication 3</td>
</tr>
<tr>
<td>SWCNT/graphene</td>
<td>Direct annealing of functionalized SWCNTs on Cu foil without extra carbon source, obtaining the SWCNT toughened graphene.</td>
<td>600/95.8%</td>
<td>−</td>
<td>−</td>
<td>Yan et al.¹¹⁸</td>
</tr>
<tr>
<td>SWCNT/graphene</td>
<td>SWCNT films made by FC-CVD were transferred on quartz substrate, followed by the spray-coating of commercial graphene oxide (GO), and finally reduced GO to rGO.</td>
<td>365/90% AuCl₃</td>
<td>73/90%</td>
<td>−</td>
<td>Gorkina et al.¹¹⁸</td>
</tr>
<tr>
<td>MWCNT/graphene</td>
<td>CVD growth of Graphene on Cu foil, put the aligned self-supporting MWCNT sheets on graphene, then the Cu foil was etched in solution, finally the hybrid was transferred on target substrate.</td>
<td>220/85%</td>
<td>−</td>
<td>−</td>
<td>Kholmanov et al.¹¹⁵</td>
</tr>
<tr>
<td>SWCNT/graphene</td>
<td>SWCNTs from FC-CVD were dry-deposited on commercial graphene (on quartz) by TP.</td>
<td>180/90% AuCl₃</td>
<td>36/90%</td>
<td>−</td>
<td>Publication 4</td>
</tr>
</tbody>
</table>
4. Methods

4.1 SWCNT synthesis and deposition

In this thesis, all the SWCNTs are synthesized using FC-CVD method, where the CO is used as carbon source and ferrocene as the catalyst precursor, certain amount of CO₂ is employed to tune the growth of SWCNTs.

As seen in Figure 4.1.1a, a vertical furnace (Entech, Sweden, length, 87 cm) equipped with a quartz tube (inner diameter, 22 mm) and kept at 850 °C is used for high temperature SWCNT growth. Ferrocene (99.0%, Alfa Aesar) is used as catalyst precursor and CO (99.0%, AGA) as carbon source, CO₂ (99.9993%, AGA) plays a role of growth modulator. Each gas flow is controlled by a mass flow controller (MFC, Aalborg, USA). In a growth process, 50 ccm CO passes through the cartridge, where the ferrocene mixed with silica sand (99.9%, Balzers Materials, weight ratio ferrocene : SiO₂ = 1 : 4) is stored at ambient temperature. The ferrocene-containing gas is then injected through a water-cooled injector probe maintained at a constant temperature of 24 °C. Another 250 ccm CO flow is introduced from the main inlet and 100 ccm from bypass inlet (to avoid the turbulence across the probe). Accordingly, the SWCNTs will grow in a laminar flow and be collected in the outlet of reactor. CO₂ was used to tune the growth of SWCNTs. In this work, the CO₂ flow rate was set to 0.0, 1.0, 1.25, 1.5, 2.0, 2.5, 3.0 and 5.0 ccm, corresponding to the volumetric fraction of 0, 0.25, 0.31, 0.37, 0.50, 0.62, 0.74 and 1.23 vol%, respectively.
Methods

Figure 4.1.1. (a) The schematic of SWCNT synthesis reactor in Publications 1-4 of this thesis, where CO is used as carbon source and ferrocene as catalyst precursor, CO₂ is employed to tune the growth of SWCNTs. (b) The schematic of sample holder, which is designed to deposit aerosol SWCNTs on a membrane filter with assistance of vacuum.

The aerosol SWCNT samples are collected using two different technics, the filter-press transfer\textsuperscript{102} and the thermophoretic precipitator (TP)\textsuperscript{23}.

As shown in Figure 4.1.1b, a filter (Millipore, USA) with 0.45 μm pore size is placed in a cone-shaped holder, one top of the filter an O-ring is used for sealing. After which, the aerosol SWCNTs are collected on the filter with the assistance of vacuum, the SWCNT film thickness can be controlled by varying the collection time. Then the obtained SWCNT films on filter can be directly transferred on various substrates by pressing.
The TP method (Figure 4.1.2) is based on the thermophoresis theory, which describes the force derived from a temperature gradient in a gas medium. In aerosol, the thermophoresis force of a particle depends on the temperature gradient in the surrounding gas. As shown in Figure 4.1.2a, the gas molecules from the hot zone ($T_2$) have greater velocity than those from cool zone ($T_1$), resulting in a total momentum of the particle pointing from $T_2$ to $T_1$. Therefore, the net force (thermophoresis force) will lead to the overall movement of nanoparticle from $T_2$ to $T_1$. Using this principle, we develop a TP setup (Figure 4.1.2b) to deposit the aerosol SWCNTs. The TP consists of two parallel aluminum plates separated by a polytetrafluoroethylene (PTFE) plate (0.5 mm in thickness), in which the top aluminum plate is heated up to ~120 °C and the bottom one is kept at ~20 °C. After which, with the assistance of vacuum, the aerosol SWCNTs could be deposited on various substrates, such as quartz, wafer or mica. In addition, using the same principle, we also design a large-size TP for scale-up deposition of SWCNT thin films (Figure 4.1.2c and d).
4.2 Doping of SWCNT thin films

To further improve the conductivity of SWCNT thin film, the doping is generally employed. Doping improves SWCNT conductivity in two ways. First, the carrier concentration in the networks can be increased. Second, the tube-tube junction resistance can be reduced. Different dopants, such as HNO$_3$, AuCl$_3$, SOCl$_2$, and MoO$_x$ have been used for SWCNT doping. In this thesis, we mainly used AuCl$_3$ as dopant (HNO$_3$ was used in Publication 3). As shown in Figure 4.2.1, after measuring the pristine SWCNT film, the sample is placed in fume hood, followed by several drops of AuCl$_3$ in acetonitrile solution (16 mM). After 5 min, the film will be rinsed by pure acetonitrile and then dried by compressed air. Right after doping, the sheet resistance will be measured again.

![Doping process of SWCNT thin film by AuCl$_3$](image)

Figure 4.2.1. The doping process of SWCNT thin film by AuCl$_3$.

4.3 Characterization

4.3.1 Differential mobility analyzer

The aerosol particles can be classified by differential mobility analyzer (DMA) based on their electrical mobility. The charged poly-disperse aerosol particles flow into the DMA, where a voltage is applied so that an electric filed is built. Therefore, only the particles with certain electrical mobility (dynamic diameter) can be flowed out and thus, a monodisperse aerosol is obtained. In practice the voltage applied in the DMA varies with time in order to classify the particles with different size. After DMA, a condensation particle counter (CPC) or Faraday cup electrometer (FCE) is used to analyze the size distribution.

DMA+CPC/FCE is powerful to real-time analyze the size distribution or monitor the growth process for the aerosol SWCNTs. In Publication 2, we mainly used the SMPC + E system (Grimm Aerosol Technik, Germany) consisting of a DMA and a FCE to monitor and compare the SWCNT yield affected by CO$_2$.

4.3.2 Optical spectroscopy

Optical absorption spectroscopy (OAS) is handily to study many properties of SWCNTs, including mean diameter, metallic/semiconducting tube ratio or doping level. In Publications 1-3, the OAS was recorded by a Perkin-Elma Lambda 950 UV-vis-NIR spectrometer with wavelength ranging from 175 to 3300 nm, the SWCNT thin film is deposited on quartz substrate (20×35×1 mm, Finnish Specialglass) by filter-press transfer. While in Publication 4 it was
conducted using a Agilent Cary 5000 (175-3300 nm), the SWCNT is deposited on (graphene-coated) quartz substrate (10×10×0.5 mm, Graphenea Inc, Spain) by TP or filter-press transfer. Both the equipment are calibrated without samples and reference, after calibration the measurement will be conducted by placing the sample in beamline center and a bare quartz substrate as reference.

Raman spectroscopy is mainly used to investigate the quality and doping level of SWCNT films in this thesis. In Publications 1 and 2, the Raman spectroscopy was carried out using a Horiba LabRAM HR 800 equipped with four excitation lasers of 488, 514, 633 and 785 nm. Similar to the OAS measurement, in Raman the SWCNTs were also transferred on quartz substrate. While in Publication 4, Raman experiments were conducted (at University of Vienna) using a Witech Alpha 300 R combined confocal Raman spectroscope and atomic force microscope using 532 nm diode and 633 nm helium-neon laser sources.

4.3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) is widely used to observe the morphology of SWCNTs. In Publications 1-3, the SEM experiments were performed by a ZEISS Sigma VP. Due to the fact that SWCNTs are very small and were deposited on an insulating substrate, such as Si/SiO₂ or quartz, the samples have to be observed by an in-column-type (in-lens) secondary electron detector at 1.0 kV. In order to study the SWCNT bundle length by SEM, the aerosol SWCNTs were deposited on Si/SiO₂ substrate by TP with a proper density (below percolation). Then the bundle length distribution was analyzed using software ImageJ by counting all the SWCNTs shown in SEM image. In addition, we also analyzed the SWCNT network by SEM. In Publication 4, however, we mainly used SEM (at University of Vienna) to compare the contrast of the thin SWCNT network on different substrates. SWCNTs were deposited on bare quartz or graphene-coated quartz by TP, followed by a SEM characterization. The images were acquired by a Zeiss Supra 55 VP analytical SEM with beam energy of 5.0 kV using the in-lens secondary electron detector.

4.3.4 Transmission electron microscopy and electron diffraction

Transmission electron microscopy (TEM) is powerful to analyze the nanoscale structure of SWCNT. To prepare a TEM sample, the TEM grid is placed on the membrane filter, followed by putting them in the holder and harvesting SWCNTs with the assistance of vacuum. In Publications 1 and 2, a world-class aberration-corrected high-resolution TEM (HR-TEM, JEOL JEM-2200FS) was employed to investigate the tube and bundle diameter and, more importantly, the chirality of SWCNTs. The equipment can work with imaging mode and electron diffraction (ED) mode under 200 or 80 kV, respectively. Compared to other approaches for chirality identification, such as Raman or photoluminescence, ED is the most direct and unambiguous method to determine the chirality of SWCNTs. Jiang et al. developed a non-dimensional method for identifying chirality based on the ED patterns of SWCNTs. As shown in Figure 4.3.1, an individual SWCNT is focused and displayed the ED pattern where...
the intrinsic equatorial line and layer lines are clearly seen. The pseudo-period of equatorial line ($\sigma$, non-unit) and layer-line spacing ($d_2$ and $d_3$, non-unit) can be acquired using the software Gatan DigitalMicrograph. Based on these three parameters, the chirality $(n,m)$ can be calculated using Jiang's method [126].

**Figure 4.3.1.** (a) A typical transmission electron microscopy (TEM) image of individual SWCNT and the corresponding electron diffraction (ED) pattern. (c) The corresponding profile image of equatorial line in ED pattern by software Gatan DigitalMicrograph.

### 4.3.5 Sheet resistance measurement

Sheet resistance ($R_s$) is commonly used to characterize the electrical properties of a thin film, such as metal or doped semiconducting thin films. It is well known that for a regular three-dimensional conductor, the resistance $R$ follows

$$R = \rho \frac{L}{A} = \rho \frac{L}{WT} = \rho \frac{L}{tW} = R_s \frac{L}{W}, \quad (4.3.1)$$

where $\rho$ is the resistivity, $L$ is the length, $A$ is the cross-section, $W$ is the width and $t$ is the thickness of thin film.

The 4-point probe measurement is commonly used to acquire the sheet resistance of thin film (Figure 4.3.2). In **Publications 1-3**, the sheet resistances of SWCNT film were measured by a Hewlett Packard 3485A multimeter with a 4-point probe head (Jandel, UK), consisting of four in-line tungsten tips with a 100 $\mu$m curvature and 1.0 mm separation. While in **Publication 4**, the sheet resistance was measured by a Jandel test unit (model, RM3000) equipped with a 4-point probe head (Jandel, UK), consisting of four in-line tungsten tips with a 300 $\mu$m curvature and 1.0 mm separation.

**Figure 4.3.2.** An illustration of 4-probe setup. A constant current is supplied from outer probes, and the voltage drop in the middle probes is recorded. The sheet resistance can be calculated according to equation 4.3.2 when the thickness $t$ is small compare to the probe distance $s$. 

For the sheet resistance measurement, the SWCNT thin films were transferred on quartz substrate by filter-press or TP, then the 4-point probe system was applied. The sheet resistance can be calculated$^{127}$ according to

$$R_{sh} = \frac{U}{I} \approx 4.53 \frac{V}{I}. \quad (4.3.2)$$

### 4.3.6 Temperature dependence conductance measurement

To further understand the carrier transport mechanism of the SWCNT and the SWCNT/graphene hybrid in Publication 4, we performed the temperature dependence conductance measurement (at University of Vienna). These measurements were conducted on networks deposited on SiO$_2$ substrates with the size of $4 \times 4$ mm) by TP with nominal transmittance of ~80%. The four symmetrically placed contact electrodes were fabricated by evaporating gold through a slit mask and manually wire-bonded to a Kyoreca chip carrier. The measurement apparatus consisted of a liquid helium tank with custom-built vertically movable sample arm including a thermocouple for temperature readout and a Keithley 2635B sourcemeter for 4-point conductivity measurements. Before slowly immersing the sample arm into liquid helium (He), the volume was evacuated to a pressure of $10^{-3}$ mbar and finally filled with He gas. The cooling rate was kept at ~10 K min$^{-1}$ from 4 to 350 K.
5. Results and discussion

5.1 Chirality and thin film colors modulated by CO₂

CO₂ effect on chirality of SWCNTs was carefully studied in Publication 1. The first interesting phenomenon we observed, as demonstrated in Figure 5.1.1a, was that the SWCNT thin films produced with various CO₂ concentrations display different colors. Particularly, a green and brown colors were observed from the thin film with CO₂ concentration of 0.25 and 0.37 vol%, respectively. To the best of our knowledge, this is the first report on direct synthesis of colorful SWCNT thin films. The colors should be reasonably related to the optical properties. Thus, we then performed the optical absorption spectroscopy for these thin films. Indeed, with an increase of CO₂ concentration, the transition peaks $S_{11}$ and $S_{22}$ from semiconducting tubes and the $M_{11}$ peaks from metallic tubes have an obvious redshift (Figure 5.1.1b), implying an enlargement of SWCNT diameter. More importantly, we believe the color of the film is mainly determined by absorption peaks in the visible region (mainly the $M_{11}$ peaks). For instance, the green film displays a distinct and sharp absorption peak from $M_{11}$ at a wavelength of ~610 nm. While the brown film mainly results from the relatively flat $M_{11}$ peak at ~760 nm. Other samples with no obvious absorption peaks (0.50 vol% CO₂) or very weak peaks (0 vol% CO₂) in the visible region display a normal grey color.
Results and discussion

The distinct absorption properties, especially for SWCNTs with 0.25 vol% CO$_2$, is correlated to their chirality distribution. To further uncover the correlation between the colors and SWCNT structures, we carried out the ED for both individual SWCNTs and bundles. Based on the ED, we calculated the chirality (n,m) using the method developed by Jiang et al.\textsuperscript{126} Figure 5.1.2 shows the chirality distributions of SWCNTs produced by various CO$_2$ concentrations. It shows the mean SWCNT diameter increases with CO$_2$ concentration, which is consistent with the optical absorption results. Notably, the SWCNTs with 0.25 vol% CO$_2$ possess much narrower chirality (as well as diameter) distribution than those with 0 and 0.50 vol%. This narrow distribution and suitable tube diameter may account for the sharp and narrow optical absorption peaks as mentioned above and thus, the corresponding thin film displays a distinct color.
Results and discussion

All the three samples exhibit similar chirality preference near armchair with dominant chiral angle between 20-30° (Figure 5.1.3a-c). In addition, by analysing the chiral angle of SWCNT bundles (Figure 5.1.3d-f), we find that the chiral angle distribution of bundles shows a similar trend to the individual tubes. This implies the identical global chiral angle distributions over the SWCNTs.

As temperature also plays a key role in chirality distribution\textsuperscript{128}, it is possible to further narrow the chirality by optimizing the furnace temperature based on the results obtained by 0.25 vol% CO\textsubscript{2}. In our work, increasing temperature from 850 up to 880 °C can reduce the CO decomposition and accordingly, lead to a more controllable synthesis towards narrow chirality distribution. Figure 5.1.4 presents the chirality distribution of SWCNTs with 0.25 vol% CO\textsubscript{2} at 880 °C. A narrower chirality distribution clustered around (11,9) has been achieved (Figure 5.1.4a) and over 98% of tubes have the diameter in the range of 1.2-1.5 nm (Figure 5.1.4b).

Figure 5.1.2. (a) Chirality distributions measured from individual SWCNTs with CO\textsubscript{2} concentration of (a) 0 vol%, (b) 0.25 vol% and (c) 0.50 vol%. M and S represent metallic and semiconducting tubes, respectively. (d) The corresponding diameter distributions extracted from a-c. Copyright © 2018 American Chemical Society, used with permission.
Results and discussion

Figure 5.1.3. Chiral angle distributions measured from (a-c) individual SWCNTs and (d-f) SWCNT bundles with various CO\textsubscript{2} concentrations. The SWCNT bundles show the similar chiral angle distributions to the Individual tubes, implying the global chirality distributions over the SWCNTs. Copyright © 2018 American Chemical Society, used with permission.

Figure 5.1.4. (a) Narrower chirality distributions of SWCNTs synthesized at 880 °C with 0.50 vol% CO\textsubscript{2} and (b) its corresponding narrow diameter distributions. Copyright © 2018 American Chemical Society, used with permission.

5.2 CO\textsubscript{2}-modulated geometry of SWCNTs

In addition to the chirality, we also systematically studied the geometry (diameter, length and bundle) of SWCNTs modulated by CO\textsubscript{2} in Publication 2. As shown in Figure 5.2.1a, more CO\textsubscript{2} conditions were investigated here and the SWCNT diameter likewise increases with the CO\textsubscript{2} concentrations. The mean diameters were estimated by Kataura plot, and from results we see it enlarges from 1.1 up to 2.0 nm when increasing CO\textsubscript{2} from 0 to 0.74 vol%. Further increasing CO\textsubscript{2} up to 1.23 vol%, however, results in a rather flat absorption profile, suggesting a lower content of SWCNTs in this sample. The Raman spectroscopy
also identifies the increment of SWCNT diameter with CO\textsubscript{2} according to the RBM peaks (Figure 5.2.1b and c). In addition, the intensity ratio of G and D band (I\textsubscript{G}/I\textsubscript{D}) can reflect the purity of SWCNTs as we discussed above. Seen from Figure 5.2.1d, the I\textsubscript{G}/I\textsubscript{D} values of SWCNTs with CO\textsubscript{2} are much higher than the one without CO\textsubscript{2}. This means the purity of SWCNTs has been significantly improved with the presence of CO\textsubscript{2}.

Figure 5.2.1. (a) Optical absorption spectra (OAS) of SWCNT thin film synthesized with different CO\textsubscript{2} concentration, inset: the calculated mean diameter using Kataura plot based on OAS. The RBM peaks of SWCNT thin films with laser wavelength of (b) 488 nm and (c) 633 nm. G and D bands excited by 633 nm laser and their intensity ratios. Copyright © 2018 WILEY-VCH, used with permission.

Figure 5.2.2. The typical SEM images and length distributions of SWCNT bundles prepared with (a, d) 0 vol\%, (b, e) 0.31 vol\% and (c, f) 0.50 vol\% CO\textsubscript{2}. Samples are deposited by TP method on Si/SiO\textsubscript{2} substrate. Copyright © 2018 WILEY-VCH, used with permission.
The bundle length, as one of the key factors for improved TCF performance, can be elongated by CO$_2$ as well. Figure 5.2.2 shows the representative SEM images of SWCNT bundles and their bundle length distributions (~300 bundles counted for each condition). The bundle length elongates from 2.7 to 7.5 µm when increasing CO$_2$ from 0 to 0.50 vol%. The SWCNTs with longer bundle length, as we discussed above, possess fewer contact junctions between tubes and thus, show potential for better TCF performance.

Bundle diameter can also be tuned by CO$_2$ during growth. The bundle diameter of SWCNTs with various CO$_2$ is investigated by TEM (~200 bundles for each condition). As illustrated in Figure 5.2.3, the as-prepared SWCNTs are clean with little amorphous carbon (Figure 5.2.3b-d). The relatively small mean bundle diameter of 7.5 nm at 0 vol% CO$_2$ (Figure 5.2.3b, e) increases up to 9.5 nm at 0.31 vol% CO$_2$ (Figure 5.2.3c, f). However, it reduces to 7.1 nm as CO$_2$ concentration increases to 0.50 vol% (Figure 5.2.3d, g). Considering that higher yield results in the higher possibility of collision between SWCNTs in the aerosol phase, we are expecting a strong relationship between yield and bundle diameter. Here we calculate the yield based on the transmittance of thin films, since the thicker the film is, the higher yield it indicates. As illustrated in Figure 5.2.3a, the yield with 0.31 vol% CO$_2$ is much higher (over twice) than that without CO$_2$. Correlating the bundle diameter with the yield, we then find that the higher yield is, the larger the bundle diameter will be.

Figure 5.2.3. (a) The transmittance of SWCNT thin film with 20 min of collection on filter and the normalized yield with CO$_2$ concentrations. The typical TEM images and the diameter distributions of SWCNT bundles produced with (b, e) 0 vol%, (c, f) 0.31 vol% and (d, g) 0.50 vol% CO$_2$. Copyright © 2018 WILEY-VCH, used with permission.

5.3 Thin film performances affected by CO$_2$

SWCNTs with various electronic and geometric structures should have dramatic influence on thin film conductivity. Later on we fabricated SWCNT thin films
with different CO$_2$ concentration by filter-press transfer method and studied their sheet resistance. The conductivity of pristine TCFs with different CO$_2$ varies from each other (Figure 5.3.1a). The sheet resistance of SWCNT films at 90% T$_{550}$ decreases from 1075.6 to 273.4 $\Omega$/sq. when increasing CO$_2$ from 0 to 0.50 vol%. However, SWCNT films synthesized at 1.23 vol% CO$_2$ show inferior conductivity. To further reduce the sheet resistance of SWCNT TCFs, AuCl$_3$ was used as an efficient dopant. While doping by AuCl$_3$ increases the conductivity of all SWCNT TCFs, the trend is not different (Figure 5.3.1b). In fact, our best sample is the doped SWCNT film synthesized at 0.50 vol% CO$_2$ with a sheet resistance as low as 86.8 $\Omega$/sq. at 90% T$_{550}$.

As mentioned above, contact junctions play a critical role in the conductivity of SWCNT TCFs. The SWCNTs with 0.50 vol% CO$_2$, owing to the long length, the number of junctions will be fewer than those with 0 vol% CO$_2$. In addition, though the SWCNTs with 0.50 vol% CO$_2$ have similar bundle diameter to those with 0 vol% CO$_2$, the tube diameter is larger, indicating fewer tubes in one bundle and thus, more tubes could contribute to the conductivity. Accordingly, SWCNT films with 0.50 vol% CO$_2$ exhibit the best conductivity among all samples.

In addition, the doping factor (pristine $R_s$/doped $R_s$) also varies from films prepared with various CO$_2$ concentrations. As illustrated in Figure 5.3.2,
SWCNT thin films prepared without CO2 show a mean doping factor ~6.0, this factor decreases to ~5.4 and 3.1 with 0.31 and 0.50 vol% CO2, respectively. However, it rises to ~3.8 and 5.4 for films synthesized with 0.62 and 0.74 vol% CO2, respectively. This trend can be also interpreted by the junction resistance. Znidarsic et al. have proven that the junction resistance, specially the metallic-semiconducting (M-S) tube junction, plays the dominant role in thin film conductivity, and the chemical doping could significantly reduce the junction resistance while the resistance along tubes remains unaltered22. In our work, due to the larger bundle diameter and smaller diameter for SWCNTs with 0 vol% CO2, the pristine junction resistance is higher than those with 0.50 vol% CO2. In addition, SWCNTs with 0 vol% CO2 have shorter bundle length and lower ratio of metallic tubes, resulting in higher ratio of M-S junctions. Consequently, the AuCl3 doping will have more significant reduction of junction resistance for SWCNT film with 0 vol% CO2 and thus, a higher doping factor. On the other hand, at higher CO2 concentration, such as 0.74 vol%, due to the presence of amorphous carbon or nanoparticles, the pristine junction resistance is high. Thus, the AuCl3 could also reduce the junction resistance dramatically, leading to a higher doping factor.

![Figure 5.3.2](image)

**Figure 5.3.2.** The doping factor of thin film versus CO2 concentration. Copyright © 2018 WILEY-VCH, used with permission.

In **Publication 3**, to show the potential applications in industry, we also tried to scale-up the SWCNT deposition using a large scale TP (Figure 4.1.2). In this way we have successfully deposited the aerosol SWCNTs on glass and PET. Depending on substrates, the thin film performance also varies (Figure 5.3.3a and b). The pristine TP SWCNT films display a bit lower sheet resistance than the filter-press transferred, while after doping the sheet resistance shows little difference. SWCNT films deposited on glass and PET both exhibit reasonable uniformity, as evidenced by transmission spectra in Figure 5.3.3c and g. This scale-up demonstration is a readily design for high yield production of SWCNT thin films or other aerosol nanomaterials.
5.4 Proposed role of CO$_2$ in SWCNT growth

Now let us discuss the role of CO$_2$ on SWCNTs growth, including the effect on yield, tube diameter and length. First of all, we should pay our attention on the catalysts since the catalyst size and composition will significantly affect the SWCNT growth. From the statistics of the catalyst size by TEM, the catalysts are found to have same diameter ~2.7 nm (Figure 5.4.1a-c), regardless of various CO$_2$ concentration. However, the diameter of SWCNT grown on catalyst varies with CO$_2$ concentration. Fiawoo et al. proposed two possible growth modes on the catalysts with same size, the perpendicular and tangential modes. In our case, without CO$_2$ SWCNT grows in a perpendicular mode, while with 0.50 vol% CO$_2$ a near-tangential mode is preferred. The energy dispersive spectroscopy (EDS) results acquired from transmission scanning electron microscopy (STEM) further reveal the similar chemical composition of catalysts in all three samples with different CO$_2$ concentration (Figure 5.4.1d-f). Therefore, CO$_2$ was found to have no dominant effect on catalyst diameter and the chemical composition.
Results and discussion

Figure 5.4.1. The catalyst size distributions and the catalyst chemical composition in SWCNTs with CO\textsubscript{2} concentration of (a, d) 0.50, (b, e) 0.31 and (c, f) 0 vol\%. This indicates CO\textsubscript{2} has no effect on catalyst size and chemical composition. Adapted from Publication 2.

We propose the main function of CO\textsubscript{2} is to remove the amorphous carbon on catalyst and a schematic is illustrated in Figure 5.4.2. In principle, in the aerosol phase, particles can deposit on the quartz wall surface by diffusion\textsuperscript{130}, the deposition ratio depends on the size of aerosol particles at a given temperature, quartz tube length and flow rate. However, as soon as the nanoparticles start to quickly catalyze the nucleation and growth of carbon nanotubes, the deposition ratio will decrease due to the increase of mobility diameter. In our work, when no CO\textsubscript{2} is employed, the CO disproportionation on catalyst is very low, leading to a high deposition ratio of inactive catalysts and a slow growth kinetics and thus, the final SWCNTs are short and low yield. While with 0.31 vol\% CO\textsubscript{2} introduced, the amorphous carbon on catalysts can be removed, enhancing the CO disproportionation. Thus, more catalysts will catalyze the SWCNT growth and finally, a higher-yield synthesis with longer tubes is achieved. When increasing the CO\textsubscript{2} concentration up to 0.50 vol\%, more catalysts will be activated and the growth kinetics is strongly enhanced, resulting in longer tubes. However, the excess of CO\textsubscript{2} will shift the Boudouard reaction backward and the CO decomposition will be reduced modestly, leading to a decreased yield.
5.5 Improving film performance by SWCNTs/graphene hybrid

As we have discussed above, the inefficient tunnelling between contact junctions are the key factor influencing the SWCNT thin film conductivity. To solve this problem, besides optimizing the geometry of SWCNTs during growth, bridging the junction by suitable working function metal\textsuperscript{131} or graphite\textsuperscript{96} is another strategy. In the same principle, we combine graphene, a material with excellent electrical and optical properties, with our SWCNT thin film to improve the conductivity. In this work, the SWCNTs were synthesized using similar condition in Publication 2, where CO was used as carbon source and 0.50 vol\% CO\textsubscript{2} was employed. Then the SWCNTs were deposited on both bare quartz and graphene-coated quartz substrate by two methods, the filter-press and TP. Thus, four different types of thin films, SWCNTs on bare quartz by filter-press and TP, SWCNTs on graphene by filter-press and TP, were investigated on their optoelectronic properties (Figure 5.5.1).

The deposition methods will slightly influence the sheet resistance. For example, at 90\% transmittance the pristine SWCNTs collected by TP exhibit a sheet resistance of ~450 $\Omega$/sq., while a value of ~330 $\Omega$/sq. is gained by the filter-press method (Figure 5.5.1a). In addition, at higher transmittance (>92\%), the TP deposited SWCNTs show higher sheet resistance than the predicted results by fitting (Figure 5.5.1a). However, this issue does not appear for the filter-press SWCNTs. This implies the interactions of individual tubes might differ with different collection methods, which remains discussion later. Deposition of SWCNTs on graphene significantly reduces the sheet resistance, yielding ~180 $\Omega$/sq. at 90\% $T_{550}$ for pristine TP deposited SWCNTs on graphene. Meanwhile, the filter-press transferred SWCNTs on graphene shows a sheet resistance of ~215 $\Omega$/sq. at 90\% $T_{550}$. 

![Figure 5.4.2. A schematic indicating the SWCNT growth with CO\textsubscript{2} concentrations of 0 vol\% (left), 0.31 vol\% (middle) and 0.50 vol\% (right). Copyright © 2018 WILEY-VCH, used with permission.](image-url)
Results and discussion

Figure 5.5.1. Optoelectronic performance of (a) SWCNT thin films on quartz deposited by filter-press and TP methods, and (b) SWCNT thin films on graphene-coated quartz deposited by filter-press and TP methods.

AuCl₃ was used as dopant to further improve the film conductivity. After doping, all the films exhibit the reduced sheet resistance and the doping factor (pristine Rs/doped Rs) is nearly constant, regardless of the film thickness. Accordingly, the lowest sheet resistance is gained with TP deposited SWCNTs on graphene, showing average ~50 Ω/sq. at 90% Tₕ₅₀ (the best result is ~36 Ω/sq.), better than filter-press transferred SWCNTs on graphene with ~65 Ω/sq. at 90% T. Nevertheless, the filter-press transferred SWCNTs on bare quartz (~95 Ω/sq.) is still better than the TP SWCNTs on quartz (~115 Ω/sq.).

We then attempted to interpret our results using a simple parallel resistor model, where the graphene and SWCNTs are considered as two parallel resistors. For example, the hybrid thin film with 90% T equals to a graphene film with 97.5% Tₕ₅₀ (~650 Ω/sq.) adding a SWCNT film with 92.5% Tₕ₅₀ (~750 Ω/sq. for TP). After calculation, the predicted sheet resistance of hybrid films is ~350 Ω/sq., which is much higher than our measured result ~180 Ω/sq. Therefore, we have achieved a highly conductive SWCNTs-graphene hybrid film, and the parallel resistor model fails to interpret this conductivity.
Nevertheless, we can uncover the improved conductivity by studying the carrier transport of SWCNT thin films. According to previous reports, the charge transport, including tunnelling efficiency between individual tubes can be illustrated by temperature dependence of conductance. The fluctuation-assisted tunnelling (FAT)\textsuperscript{132} model integrating with a quasi-1D transport mechanism\textsuperscript{133, 134} can interpret the carrier transport. For sheet resistance it can be written as:

\[ R(T) = A \times \exp \left( -\frac{T_m}{T} \right) + B \times \exp \left( \frac{T_b}{T_s + T} \right), \quad (5.5.1) \]

where A and B are constants. The first term represents the quasi-1D metallic conduction involving the resistivity suppressing at lower temperature while at higher temperature the backscattering by lattice vibration with the phonon energy \( k_b T_m \) (\( k_b \) is the Boltzmann constant), and the second term \( T_b \) represents the temperature at which the thermal voltage fluctuations become large enough to raise the energy of electronic state over the barrier, and \( k_b T_b \) is the tunnelling barrier; \( T_s \) is the tunnelling efficiency without fluctuations near \( T = 0 \) K.

The results of conductance versus temperature for various thin films has been shown in Figure 5.5.2. We can clearly see that the graphene’s conductance is one order of magnitude lower than the SWCNT or hybrid films. In addition, the SWCNT or hybrid films exhibit a rapid increase with temperature then a decrease after reaching a maximum. More interestingly, combining SWCNTs with graphene shows a similar effect in conductivity to the AuCl\textsubscript{3} doped SWCNTs. To fit this plot, we can also write the equation conductance (G) as a function of temperature (T):

\[ G(T) = G_0 + G_1 \times \left[ \exp \left( -\frac{T_m}{T} \right) + \exp \left( \frac{T_b}{T_s + T} \right) \right]^{-1} \quad (5.5.2) \]

where \( G_0 \) and \( G_1 \) are constants with units (S), the parameters extracted from fitting are listed in Table 5.1.

The \( T_m \) (\( k_b T_m \) represents the phonon energy), varies from films. For example, the pristine SWCNT/graphene hybrid thin film shows the lowest \( T_m = 726 \) K, indicating the lowest phonon energy with the maximum conductance at 118 K. This is even lower than the AuCl\textsubscript{3} doped SWCNT film with a \( T_m = 806 \) K and maximum conductance at 162 K. However, the pristine SWCNT film shows a much higher \( T_m = 970 \) K with maximum conductance at 190 K. Thus, combining with graphene and doping by AuCl\textsubscript{3} can both reduce the phonon energy of SWCNT. In addition, the tunnelling barrier heights can be also affected, for example, compare to the bare SWCNTs, a \( \sim 29\% \) reduction of \( T_b \) for SWCNT/graphene hybrid is observed, being similar to the AuCl\textsubscript{3} doped SWCNTs. Therefore, it evokes a question whether the graphene acts as dopant similar to AuCl\textsubscript{3}.
Results and discussion

Table 5.1 The parameters extracted by fitting data in Figure 5.5.2 with equation 5.5.2

<table>
<thead>
<tr>
<th>Films</th>
<th>$G_0$, S</th>
<th>$G_0$, S</th>
<th>$T_m$, K</th>
<th>$E_m$, eV</th>
<th>$T_s$, K</th>
<th>$T_n$, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>0.0002</td>
<td>0.0004</td>
<td>1078</td>
<td>0.093</td>
<td>2.10</td>
<td>14.85</td>
</tr>
<tr>
<td>SWCNTs</td>
<td>-0.0411</td>
<td>0.0549</td>
<td>970</td>
<td>0.084</td>
<td>5.36</td>
<td>20.72</td>
</tr>
<tr>
<td>SWCNTs+Graphene</td>
<td>-0.0196</td>
<td>0.0372</td>
<td>726</td>
<td>0.063</td>
<td>3.81</td>
<td>12.48</td>
</tr>
<tr>
<td>SWCNTs+AuCl$_3$</td>
<td>-0.0104</td>
<td>0.0279</td>
<td>806</td>
<td>0.069</td>
<td>4.17</td>
<td>11.34</td>
</tr>
</tbody>
</table>

Figure 5.5.2. The temperature dependent conductance of TP deposited SWCNTs, graphene and SWCNT/graphene hybrid thin films with (a) linear axis and (b) log-log axis.

To answer this question, we first did Raman spectroscopy measurement. A tiny broadening of RBM peaks for SWCNTs is shown after combining with graphene, this is due to the strong van der Waals interaction between SWCNTs and graphene. The peak broadening of RBM was also found after SWCNTs form bundles$^{31}$. On the other hand, the RBM peaks of AuCl$_3$ doped SWCNTs are completely different from pristine SWCNT because of the resonant conditions (Figure 5.5.3a). Additionally, the G band mode ($\sim$1580 cm$^{-1}$) has a blue-shift about 4 cm$^{-1}$ due to the prominent charge transfer between AuCl$_3$ and SWCNTs. For the SWCNTs/graphene hybrid, however, no such shift was observed (Figure 5.5.3b), implying no substantial charge transfer between SWCNTs and graphene. The optical absorption spectroscopy can further identify this (Figure 5.5.3c). The transition peaks including $S_{11}$, $S_{22}$ and $M_{11}$ are all suppressed after AuCl$_3$ doping, resulting from the fermi level shift$^{36}$. Combining graphene with SWCNTs, however, did not show the similar spectrum to AuCl$_3$ doped. Only a minor suppression of $S_{11}$ peak is observed, indicating a mild charge transfer but still incomparable to AuCl$_3$ doping. Furthermore, the $S_{22}$ peak becomes broader and has a red-shift after integrating graphene, accounting from the strong interaction between SWCNTs and graphene. From the earlier contributions we know the bundling effect of tubes can result in the broadening and red-shift of transition peaks$^{31, 32, 135}$ and thus, the strong-interaction interface between SWCNTs and graphene can be considered as a similar effect to the bundling.
Hence, we reveal that graphene does not play a role of dopant in the SWCNTs-graphene hybrid.

Figure 5.5.3. (a) RBM peaks of SWCNTs on SiO$_2$, on graphene and AuCl$_3$ doped SWCNTs, and (b) the corresponding G bands and (c) optical absorption spectra of these films.

To reveal the interfacial microstructure between graphene and SWCNTs, we performed the scanning transmission electron microscopy (STEM). Similar to the previous findings that the SWCNTs form hundreds of nanometer long stacking interface with graphene$^{136}$, our SWCNT bundles also stack firmly with graphene, evidenced by the STEM results that all SWCNTs share common Z-height in Figure 5.5.4a. A close-up image in Figure 5.5.4b can further prove it. We also note that in the scanning electron microscopy (SEM), the contrast for SWCNTs on SiO$_2$ (Figure 5.5.4c) is more obvious than those on graphene (Figure 5.5.4d). This is due to, as also discovered by others, the charge effect from poor contact between SWCNTs and the dielectric substrate$^{137}$.
Figure 5.5.4. (a) A STEM/MAADF overview of SWCNTs on graphene. (b) A magnified zone where a SWCNT bundle closely contacts with graphene substrate. (c) The SEM images of SWCNT network on (c) Si/SiO₂ and (d) graphene substrates under beam energy of 5.0 kV.

Finally, previous research claimed that the Y-junctions in the SWCNT network is more conductive than the X-junctions\(^\text{138}\). In fact, in our work the SWCNTs-graphene interface can be resembled as the Y-junctions, where the contact is long and firm. This could also explain the enhanced tunnelling and high conductance of TP deposited SWCNTs on graphene. In addition, the anomalously high sheet resistance for TP deposited SWCNTs on bare quartz can be interpreted. As demonstrated in Figure 5.5.5a, a low density TP deposited SWCNT film is completely dominated by X-junctions, resulting a poor interaction with substrate without graphene and thus a poor conductance. Nevertheless, with longer deposition time the thicker film exhibits more Y-junctions (Figure 5.5.5b), indicating the morphology or roughness will affect the formation of Y-junctions. We then believe that the SWCNTs deposited on filter by vacuum prefer to form Y-junctions due to the higher surface roughness, exhibiting superior conductance to TP deposited SWCNTs on bare quartz.
Figure 5.5.5. STEM/MAADF images of SWCNTs deposited on graphene by TP with (a) low density and (b) higher density.
In summary, in floating catalyst chemical vapor deposition, the chiral and geometric properties of SWCNTs have been successfully tuned by employing CO₂ as promoter in a carbon monoxide-ferrocene system. The CO₂ concentration plays a key role in tuning the diameter and chirality distributions. With certain CO₂ concentration, the SWCNTs show a very narrow diameter and chirality distribution, leading to a dominant absorption peaks in visible region and thus, a specific color of thin film is exhibited. Moreover, optimizing reactor temperature can further narrow the distribution. In addition, the metallic tube ratio could be increased from 29.8% to 46.3% when increasing CO₂ from 0 to 0.50 vol%. In addition to chirality, the geometry, including tube diameter, bundle length and diameter, can be also modulated by CO₂. The tube diameter increases from 1.1 to 2.1 nm by raising CO₂ from 0 to 0.74 vol%, along with increment of bundle length from 2.7 to 7.5 μm. The SWCNT yield is found to be dependent on CO₂ as well, being over twice higher with 0.31 vol% than that without CO₂. And at higher yield, the bundle diameter will also be larger due to the higher possibility of collision in aerosol phase. Based on the study on geometry affected by CO₂, a role of CO₂ is proposed, CO₂ mainly affect the catalyst and the CO decomposition, leading to the change of the carbon dissolution and diffusion. As a result, the transparent conductive film consisting of SWCNTs with optimized geometry, including large diameter (1.9 nm), long bundle length (7.5 μm) and small bundle diameter (7.1 nm), exhibit reduced pristine sheet resistance as low as 273.4 Ω/sq. at 90% transmittance. After AuCl₃ doping, it reduces to 86.8 Ω/sq. We ascribe the excellent conductivity to the reduced both junction numbers and junction resistance due to the optimized geometry. Furthermore, we demonstrated the scale-up deposition of SWCNT thin films, such films show good uniformity and TCF performance. The method implies great potential for roll-to-toll production of SWCNT TCFs. In short, the use of CO₂ in this work blaze new trail for the in situ growth of SWCNTs with geometric and chiral structure control, and it offers great chances for scale-up productions of high-performance SWCNT TCFs. Furthermore, the colorful thin films also show potentials for the touch screen or transistor applications.

Finally, to further improve the conductivity of SWCNT thin films, we fabricated the SWCNTs/graphene hybrid thin films. The TP deposited SWCNTs on graphene display a reduced pristine sheet resistance of 180 Ω/sq. (36 Ω/sq. after AuCl₃ doping), being over twice lower than SWCNTs on quartz. We further iden-
tified the improved conductivity slightly results from the band alignment between graphene and SWCNTs, but mainly from the enhanced interactions between them by van der Waals stacking. The temperature dependent conductance measurements indicate the hybrid film shows a lower tunnelling barrier, leading to the improved conductance.

For the future research, further improving the conductivity of SWCNT thin film is still one of the goals. Although we can achieve highly conductive thin film by combining SWCNTs and graphene, the high cost and the complicated fabrication process are the challenges for real applications. On the other hand, we can improve the film conductivity by further optimizing the SWCNT growth process. For example, some active hydrocarbon, such as toluene or ethanol, can be used as carbon sources to grow longer tubes, along with a low yield or high total flow rate to gain highly individual tubes. This might be promising to achieve the goal.

In addition, some other small molecules, such as H₂O, H₂S or NH₃, could be employed during SWCNT growth. It would be interesting to investigate more effects by these molecules on the geometry and chirality, as well as the film conductivity. Furthermore, introducing molecule like NH₃ has been reported to obtain nitrogen doped SWCNTs. Although the conductivity was reported to be more inferior after nitrogen doping, it might be a good candidate for electro-chemistry applications, such as oxygen reduction reaction.

Last but not least, as we know that the semiconducting SWCNT films are of great importance for thin film transistors, however, the selective synthesis of semiconducting SWCNTs has been a challenge for years. In the FC-CVD this goal could be easier to achieve. Since the SWCNTs are suspended in aerosol, thus, one possible approach is to selectively etch by post treatment in aerosol phase. For instance, we can connect another reactor to the synthesis reactor. Then some etchants, such as O₂ or H₂O, could be introduced into the second reactor to selectively etch SWCNTs. To finely control the etching process, the SWCNTs from the first reactor should be highly individual and the etchant concentration should be controlled carefully, and the DMA can be used for real-time monitor. By this manner, we might obtain the semiconducting SWCNT thin films and utilize them for high-performance thin film transistors.
References


Carbon dioxide-assisted synthesis of single-walled carbon nanotubes and their thin film properties

Yongping Liao