DIAMETER MODULATION AND INTEGRATION OF VERTICALLY ALIGNED SINGLE WALLED CARBON NANOTUBES FOR UNDERSTANDING OF MASS TRANSPORT IN CARBON NANOTUBES

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presented by

SEUL KI YOUN

MSc. Chemistry,
Korea Advanced Institute of Science and Technology (KAIST), Daejeon
Born on 27. 02 1983 citizen of Republic of Korea

accepted on the recommendation of

Prof. Dr. Hyung Gyu Park, examiner
Prof. Dr. Christofer Hierold, co-examiner
Prof. Dr. John Robertson, co-examiner
Dr. Aleksandr Noy, co-examiner

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Abstract

Carbon nanotubes (CNTs) are the prototypical one-dimensional nanomaterial that has been highly touted for their superior properties beneficial for a wide range of applications. In particular, a membrane with pores of the CNT interior promises to facilitate and enhance mass transport and poses great potential for applications such as energy-efficient purification, desalination, demineralization and hydroelectric energy generation.

Nevertheless, simulations and experiments are not in agreement about the mass transport enhancements. In order to provide indisputable evidence about the flow enhancements in relation to their key physical factors, such as nanotube diameter, it is crucial to establish reliable methodologies for diameter modulation of vertically aligned (VA) CNTs and for membrane manufacturing. Processes that integrate small-diameter, single-walled CNTs (SWCNTs) into a membrane matrix should maintain the original alignment, spatial uniformity, and defect density of the as-grown nanotubes.

Here, the precise control of the average diameter of VA-SWCNTs ranging from 1.2 nm, which is the state-of-the-art minimum value for VA-SWCNTs, to 4.67 nm with a 1-3 Å resolution is demonstrated. The two-fold strategies that enabled this wide range and fine average diameter modulation are the rational design of catalyst and the parameter optimization of chemical vapor deposition (CVD) process.

The former influences the size distribution of catalyst particles formed from the dewetting process of a thin metal film on a support. First, controlling the nominal deposition thickness of Fe with ~1Å resolution finely tunes the size distribution and number density of nanoparticles. Next, the size matching of Al₂O₃ support asperities and deposited catalyst particles is found critical to suppress the diffusion and coarsening process. Following, Mo deposited between Fe and Al₂O₃ support is found effective to reduce and narrow the dewetted particle size range and shift CNT formation window to smaller size range, thereby producing smaller diameter CNTs. Lastly, a few-tens-of-nm-thick layered Fe/Mo/Al₂O₃ catalyst is developed that generates dense nanosized bimetallic particles on surface upon a sufficient thermal annealing, which hints weakening of an otherwise strong
correlation between catalyst size and resultant CNT diameter. This new type of catalyst would especially be very promising for large scale uniform production of small diameter VA-SWCNTs.

The latter, CVD process parameters influence the dewetting process as well as the CNT formation window, thereby altering the diameter distribution of VA-SWCNTs: lower acetylene partial pressure, lower growth temperature, and catalyst preannealing for a short duration and sufficient metal catalyst reduction in a hydrogen-rich environment prior to the growth produce smaller diameter CNTs. All these parameters simultaneously affect the other structural properties of VA-SWCNTs such as defect density and vertical alignment. Therefore, CVD condition and a type of catalyst to grow high quality and sufficiently dense VA-SWCNTs for membrane application have been carefully adjusted and chosen depending on the targeted CNT diameter range.

Also reported is a new approach to CNT membrane manufacturing that is the conformal coating of each SWCNT bundle by a few-tens-of-nanometer-thick metal oxide layer via atomic layer deposition (ALD) in order to reinforce their mechanical strength prior to the subsequent gap-filling process. Thanks to the mechanical stability and chemical compatibility of the reinforced nanotube arrays, crack and pinhole-free membranes are obtained that preserve the morphology and properties of as-grown VA-SWCNTs. This conformal reinforcement method can be broadly applicable to various types of VACNTs and matrix materials.

Finally, flow rates of gases and water are measured through these SWCNT membranes whose average diameters are 1.93, 2.15, 2.39, 3.62, and 4.15 nm. The measured gas flow rates are one-to-two order-of-magnitude higher than the Knudsen model prediction and for the first time demonstrate the diameter dependency of gas transport inside CNTs: a decreasing trend of the flow enhancement with increased diameter. The gas flow enhancement greatly agrees with simulations and provides an evidence of the curvature effect on atomic smoothness of CNT wall. Obtained water flows for the pore diameter of 3-4 nm show around two-order-of-magnitude enhancement compared with a continuum hydrodynamic model prediction, updating a map of water flow enhancement with respect to the diameter of CNT. The compilation of transport data can help to
reconcile the discrepancy issue among previous experimental results and serve as a reference in designing a membrane for targeted permeance values for practical applications. Also, a challenge of the current definition of flow enhancement is claimed in association with both CNT lengths and flow impedances during the flow-to-CNT-channel entrance event.
Zusammenfassung


In dieser Arbeit wird die gezielte Synthese von vertikal ausgerichteten Kohlenstoffnanoröhrchen demonstriert, deren mittlerer Durchmesser von 1.2 nm bis 4.67 nm mit 1-3 Å Auflösung eingestellt werden kann und damit ein neuer Stand der Technik definiert. Durch die Optimierung, sowohl der Katalysatorschicht, als auch der Parameter des chemischen Gasphasenabscheideprozesses (CVD), konnte der Durchmesser der CNT innerhalb eines großen Bereiches präzise eingestellt werden.

Das Katalysatordesign hat einen starken Einfluss auf die Größenverteilung der Katalysepartikel, die bei der Entnetzung der Unterlage von der Metalldünnschicht entstehen. Zu Beginn dieser Arbeit wird gezeigt wie durch die Kontrolle der nominellen Abscheidedicke mit einer Auflösung von \(~1\) Å die Größenverteilung und Dichte der Nanopartikel eingestellt werden kann. Darüberhinaus konnte gezeigt werden, dass unter Berücksichtigung der Rauigkeit der \(\text{Al}_2\text{O}_3\) Unterlage eine passende Metalldünnfilmschichtdicke die

Die Prozessparameter im CVD Prozess beeinflussen nicht nur den Entnetzungsprozess der Katalyse-Lagen, sondern verändern auch das Prozessfenster für die Formation von CNT und ermöglichen daher auch eine Veränderung der Durchmesserverteilung der CNT. Insbesondere führen ein niedriger Partialdruck von Acetylen, niedrigere Wachstumstemperaturen, eine kurze Temperaturbehandlung des Katalysators und eine ausreichende Reduktion der Metallfilme in wasserstoffreicher Atmosphäre vor dem Wachstum der CNT, zu CNT mit kleinerem Durchmesser. Gleichzeitig haben alle genannten Parameter auch einen Effekt auf andere Eigenschaften der VA-SWNT wie deren Defektdichte als auch die Ausrichtung der CNT. Daher wurden die Konditionen für den CVD-Prozess und die Katalyse-Lagen gemeinsam optimiert um VA-SWNT mit hoher Qualität und ausreichender Dichte für eine Membrane mit definierter Porenröße zu synthetisieren.

Darüberhinaus wird eine neuer Ansatz für die Herstellung von CNT Membranen präsentiert, bei dem die SWCNT Bündel mit einem Metalloxid beschichtet werden. Die mehrere 10nm dicke Beschichtung, durch einen Atomlagenabscheideprozess (ALD), verstärkt die CNTs bevor die Zwischenräume zwischen den CNT Bündeln mit einer Matrix gefüllt werden. Dank der mechanischen Stabilität und der chemischen Kompatibilität der verstärkten CNT Wälder, können riss- und defektfreie CNT Membranen hergestellt
werden, die die ursprüngliche Morphologie und die Eigenschaften der gewachsenen Kohlenstoffnanoröhren beibehalten. Diese verstärkende und homogene Beschichtung kann universal auf VA-CNT angewendet werden und ermöglicht die Verwendung verschiedenster Matrixmaterialien für die Membranesynthese.

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Introduction
1 Introduction

1.1 Brief Overview and Motivation

1.1.1 Carbon nanotubes

Carbon nanotubes (CNTs) have a one-dimensional tubular structure, a concentrically rolled up form of one or more graphene sheets, with diameters in the range from a few angstroms to tens of nanometers and often high aspect ratios. The way the graphene sheet is wrapped is described by a pair of indices (n,m) called the chiral vector, where the integers n and m indicate the number of unit vectors along two directions (a_1 and a_2) in the honeycomb crystal lattice of graphene. If n=m and m=0, “armchair” and “zigzag” nanotubes are formed, respectively. In other cases, “chiral” nanotubes are formed (Figure 1.1). Depending on the number of graphene layers, CNTs are classified as single-walled CNTs (SWCNTs) whose diameters are in the range from 0.4 nm up to around 10 nm [1, 2] and multiwalled CNTs (MWCNTs) whose wall numbers range from two to less than a hundred and diameters from 1 nm up to around 100 nm. In case of MWCNTs, the intertube distance is around 0.35 nm, close to the interlayer distance of graphite. [3, 4]

Since Iijima’s discovery of the microtubules of graphitic carbon in 1991, CNTs have attracted great attentions due to their many intriguing and superior chemical, mechanical, electrical, optical, field emission properties, which could be beneficial to many applications; for instance, 100 time stronger than steel—“mechanical reinforcement”, 100 times more conductive than copper over distances in the order of a micron—“interconnect”, metallic and semiconducting behavior depending on diameter and helicity of CNTs—“transistor, band-gap modulation, detector”, thermal conductivity twice as good as diamond—“heat sink”, strong UV-Vis-NIR absorption—“solar cell” and one dimensional structure with possibly very high aspect ratios—“nanofluidic membrane” (Figure 1.1). [4-6] In particular, SWCNTs can exhibit metallic (semimetals) or semiconducting behaviors, depending on their chirality. [7] When synthesized without special chirality control, it is generally accepted that one third of the nanotubes are metallic (when n-m is a multiple of 3) and two third of
the nanotubes are semiconducting. [8] Given the metallic to semiconducting ratio for SWCNTs, MWCNTs can be assumed to be metallic because it is likely that at least one of the walls will be metallic. [8] For both fundamental studies and practical applications of CNTs, SWCNTs have attracted more interest due to their ultimately small diameter, perfect $sp^2$ bonding (higher crystallinity, lower defect density) and relevant superior properties compared to MWCNTs.

![Graphene roll-up and chirality](image)

**Figure 1.1** Schematic representation of the different types of CNTs, rolled up forms of one or more two dimensional graphene sheet of lattice vectors $a_1$ and $a_2$, the roll-up chiral vector $C_h = n \cdot a_1 + m \cdot a_2$, and the chiral angle $\theta$ between $C_h$ and $a_1$. The chiral vector $(n,m)$ determines the tube helicity-armchair, zigzag, and chiral. Some superior properties of CNTs are listed in the table. [6]

<table>
<thead>
<tr>
<th>Properties</th>
<th>CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture strength (Gpa)</td>
<td>45</td>
</tr>
<tr>
<td>Area Density (/cm$^2$)</td>
<td>$10^{10}$ - $10^{12}$</td>
</tr>
<tr>
<td>Thermal conductivity (W/m$\cdot$K)</td>
<td>3000</td>
</tr>
<tr>
<td>Electrical conductivity (S/cm)</td>
<td>5000</td>
</tr>
<tr>
<td>Charge mobility (cm$^2$/V$\cdot$s)</td>
<td>100,000</td>
</tr>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>400</td>
</tr>
</tbody>
</table>

Various methods (i.e., electric arc discharge, laser ablation, chemical vapor deposition (CVD) with/without assistance of laser or plasma, etc.) have been developed and used to produce CNTs, which in common include a carbon source, catalyst particles, and an energy input. [6] At the macroscopic level, CNTs can grow, either in aligned and non-aligned structures. Although arbitrarily grown CNTs are for some applications good enough, aligned CNTs can be beneficial to many applications using the nanotubes as mass or energy conductor. Various approaches for the structure-controlled synthesis of vertically
aligned CNTs (VACNTs or also called CNT forest) have been widely investigated during the past two decades. Above all, the growth of VACNTs requires densely packed catalyst particles, which allow the collective growth of CNTs in the direction perpendicular to the substrate. [9] The synthetic methods for the growth of VA-MWCNTs have been known for many years. However, the selective growth of VA-SWCNTs has only recently been realized due to the difficulties in catalyst preparation and high susceptibility of the small catalyst nanoparticles to extreme synthesis conditions.

Figure 1.2 State of the art techniques for the growth of VA-SWCNTs, adapted from (a) ref. [10]: water-assisted APCVD, (b) ref. [11]: APCVD with decoupled thermal treatment of feedstock gas and catalyst, (c) ref. [12]: APCVD without the help of water growth enhancer by maintaining low acetylene partial pressure and (d) ref. [13]: APCVD with gas dwell time control.

Recent progress in catalytic CVD (CCVD) and the use of supported catalyst nanoparticles have enabled the efficient growth of VA-SWCNTs. The CCVD process in most cases indicates the catalytic conversion of gaseous carbon precursors into solid graphitic materials.
at the surface of reactive particles or of granular film, which can act as templates for growing tubular structure. This CCVD process has become the prevailing technique for CNT synthesis today because it allows higher degree of process control and potentially a large scale, batch production. Several state-of-the-art techniques for the growth of VA-SWCNTs are described in Figure 1.2. Among them, a water-assisted CVD method, so-called super-growth, has realized a remarkably rapid and long growth of millimeter-tall VA-SWCNTs in 10 min growth time (Figure 1.2a). [10] It has been suggested that water may help retain the catalyst activity by removing the amorphous carbon \((a-C)\) coating from catalyst surface. [14] Similar approaches employing various oxygen-containing molecules for the same purpose have followed. [15, 16] On the other hand, reports on the highly efficient synthesis of VA-SWCNTs without using moisture do also exist, enabled by modification of a CVD system to allow precise control of process parameters (Figure 1.2a-d). [11, 13] Despite the great efforts and achievements, two of the most important challenges still remain elusive in the CNT research community: the structure-controlled synthesis of SWCNT forests and the large-scale growth and application of CNTs. To solve the key scientific and technological issues related to these challenges, particularly in relation to the application of VA-CNTs for the membrane applications, research efforts on catalyst design and CVD process optimization are made in this thesis work. Detailed update on current understanding and achievements and the major technical difficulties of catalyst design and CVD process for controlled growth of VA-SWCNTs will be further provided in chapter 2 and 3.

1.1.2 Carbon nanotube membranes

CNT based membranes have emerged as a promising technology in water desalination and purification applications, [17-19] mainly owing to the advantageous features of fast water transport, large surface area, and ease of surface or end functionalization of the fluid channel. For instance, the water permeability through the interiors of CNTs could be about two to three orders of magnitude higher than that predicted by Hagen-Poiseuille equation. [20, 21] The significant enhancement of water permeability together with the low biofouling potential, CNT membranes are believed to solve many issues
currently encountered when using the conventional membrane separation process such as meticulous maintenance, and high energy consumption. [17] The origins of such intriguing nanofluidic phenomena in CNT membranes are attributed to the interiors of CNTs that are atomically smooth and hydrophobic as well as the extreme spatial confinement at nanoscale. Both are considered to enable the concerted motion of water chains (i.e., one dimensional single file water) based on strong hydrogen bondings between water molecules and minimal friction of water molecules at the CNT inner wall. [22, 23] However, the so-far reported water flow enhancement, defined as a ratio between the rate of liquid water transmission in CNT and the predicted rate of Hagen-Poiseuille flow formalism, shows marginal agreement between theoretical calculations and experiment and even between the very limited numbers of experiments. [21] The bottleneck in experimental demonstrations arises from the fabrication of CNT membranes with finely controlled and well-defined structures.

On the other hand, molecular dynamics (MD) simulations have reported that curvature (i.e., inverse of tube radius) effects on the fluid transport through CNT membrane drastically diminish with an increase of tube diameter. Intriguing nanofluidic phenomena such as superfast water or proton conduction, molecular sieving of hydrated ions and altered water-ice phase transition can only be verified in the extreme confinement regime. From the viewpoint of nanotube synthesis, VACNTs with smallest possible diameters are most likely to be single-walled with areal density in the $10^{11}$-$10^{12}$ cm$^{-2}$ range, and thus a new fabrication method should be developed to incorporate the CNTs of these features into an impermeable matrix with the retention of initial alignment. [1, 24]

CNT membranes can be classified into two major groups according to the fabrication methods (in turn resulting in great differences in the spatial density and the arrangement of CNT channels). (i) The first group is a VACNT membrane (type I) where membrane pores made of the CNT interior are aligned more or less perpendicular to the membrane surface. To this end, the CNTs had better be grown in the vertically or laterally aligned manner and the inter-tube spacings need to be thoroughly filled, blocking any leakage through cracks or voids across the membrane. So far, several polymeric and inorganic
materials have been tried as the gap-filler material. (ii) The second group is a CNT/polymer mixed-matrix membrane (type II) in which CNTs are randomly oriented and sparsely dispersed, often in an asymmetric configuration where the thin top layer containing CNTs are placed over a relatively thick porous support. Figure 1.3 shows conceptual and exemplary images of the two types of CNT membranes. There are several different fabrication approaches such as the template growth of carbonaceous tubular materials inside preformed ordered porous membrane (i.e., anodized alumina) [25] and the capillary force driven shrinkage of freestanding VACNTs which uses both the interior and exterior spaces of the tubes as channels. [26, 27] However, precise control of pore dimension and clean graphitic surface for the low frication at the interface between molecule and channel wall cannot be achieved by these methods.

Finally, the most desirable method of integrating a large number of CNTs into a membrane configuration without creating unwanted defects and losses in density or alignment of the active nanochannels is to embed VACNTs in a certain matrix and subsequently open their

![Figure 1.3](image_url) Conceptual and exemplary images of the two major types of CNT membrane; (a) VACNT membrane: the first CNT membrane made up of MWCNTs and polystyrene filler (scale bar: 2.5 µm), adapted from ref. [28] (b) CNT/polymer mixed matrix membrane: the first SWCNT based membrane fabricated by filtering solution-dispersed nanotubes through polytetrafluoroethylene (PTFE) membrane (pore size: 0.2 µm) and spin-coating the surface with a diluted polysulfone (PSf) solution, adapted from ref. [29]
both ends (type 1). Since the first prototype for VACNT membrane reported in 2004 by Hinds et al. [28], many research groups have been attempting to reproduce or scale up the results and develop the better methods to fabricate VACNT membranes whose various structural features (i.e., pore size, channel length, tortuosity, areal density, etc.) are better controlled for studying various nanofluidic phenomena as well as commercializing the technology. The common methods of filling the inter-tube gaps with either a polymeric or a ceramic matrix materials such as polystyrene, polysulfone, epoxy, parylene and silicon nitride [28-32], are known to seriously suffer from the capillarity-driven agglomeration of VACNTs, mechanical deformation and detachment from substrate of the collapsed CNTs or, in the case of vapor phase deposition of silicon nitride, the hindered access of gas precursor in the forest structure, as well as silicon nitride’s high brittleness and low Young’s modulus. [33-35] These issues are found more critical for the VA-SWCNTs with small diameters due to their low bending stiffness and high areal density and none of existing methods has been proven to work for VA-SWCNTs. [36-38] Also, because the industrially meaningful value of membrane permeance highly depends on the pore density per membrane area, further efforts in increasing the packing density of VACNTs during growth process or post-growth method for the densification of the VACNTs are also needed. [18, 20, 28, 39-41]

Owing to the difficulties and complexities in the CCVD, membrane fabrication processes as well as the characterization of nanocomposite materials, obtaining SWCNTs with small diameters and integrating them in a certain membrane configuration still remain challenging. [42] Various efforts to solve the current technological issues in fabricating the membrane based on VA-SWCNTs are made in this thesis work. An update on the state-of-the-art techniques in CNT membrane fabrication and the previous experimental and simulation results in CNT nanofluidics will be further introduced in chapter 4.
1.1.3 Enhanced mass transport inside a CNT

The inner channels of CNTs have the potential as a fast mass transporter owing to the atomically flat surface that would not interrupt the flowing fluids and to the large non-interacting van der Waals (vdW) distance (i.e., a depletion region) between the travelling molecules and the inward surface of the strongly curved graphitic layer. Falk et al. recently have reported the detailed physical mechanism on the origin of low interfacial frictions of water at graphitic interfaces that exhibit strong curvature dependence. [22] The flat graphitic surface felt by water molecules generate rather corrugated energy landscape despite hydrophobicity and weak carbon-water interaction. The interaction energy landscape of inward CNT surface is further smoothened out at higher curvature, thereby imposing lower resistance to water molecules.

This mechanism is strongly linked to the molecular ordering unseen in bulk water, in particular, in a strong confinement regime. The confined water molecules inside the orifice of CNTs with sub-nanometer diameters tend to organize themselves into a highly and long-lasting hydrogen-bonded network, so-called a single-file structure. Unlike bulk water, each water molecule has two hydrogen bonds, one donated to and one accepted from a neighboring water molecule. Hummer and colleagues have shown a single-file water wire in a 0.8 nm diameter CNT that conducts rapidly in a concerted motion along the CNT axis (ca. 17 H₂O per nanosecond), when driven by thermal fluctuation. [23] In their following work, the single file water flow has revealed a flow rate of 5.8 H₂O per nanosecond under an osmotic gradient, comparable to those of the transmembrane protein aquaporin-1. [43] These high flow rates are observed practically independent of the length of the nanotube in contrast to the prediction of conventional hydrodynamics theories.

In case of gas transport, such a collective motion of strongly bound molecular network is unlikely to occur. The atomically smooth surface of a CNT channel allows the gas molecules to collide almost elastically to preserve the tangential forward momentum. In such a case, transport can occur in a specular manner, thereby increasing the gas diffusivities to an extent higher than the prediction of Knudsen diffusion. [44] At the same time, the nanoscale confinement is
expected to lead to significant differences in adsorption and to promote surface diffusion based on adsorption, which can also contribute to a highly diffusive and selective transport. Skoulidas et al. have revealed that even at a relatively low pressure of 1 bar, almost all the gas molecules inside a CNT reside close to the wall. With an increase of pressure the molecules tend to form a layered structure within the effective van der Waals interaction range of the wall. Accordingly, if surface diffusion becomes a dominant transport mechanism, gas diffusivity would be virtually independent of the pressure gradient. [45]

In the past decade, several experimental studies using various types of CNT membranes have provided evidence for enhanced gas and water flow rates through CNTs. Despite the intensive researches, experimental demonstrations are still limited. Currently available experimental data are not sufficient to determine the detailed flow properties and governing mechanisms. Sometimes they even show inconsistency with the abundant simulation results, [21] which will be addressed in detail in section 4.2 and 4.6.1. Clearly, there are significant differences in the transport conditions considered in these simulation and experimental studies. Perfectly straight and defect-free VACNTs are hardly achievable in reality. Also, controlling the nanotube diameter, a key parameter for flow enhancement, still remains a challenge. The pore entrance and exit effects on the experimentally measured flow rates may not be completely controlled or decoupled from the other sources of flow resistance. Using the newly developed fabrication method of CNT membrane, we attempt here to tune the CNT diameter with minimizing the variation in the other factors which potentially affect the transport behavior. New findings about the enhanced gas transport inside pore-size controlled CNTs and new observations in the enhanced water transport inside the CNT of unreported diameters will be discussed in section 4.6.
1.2 Objectives

This PhD thesis focuses on developing a novel fabrication method for CNT membranes incorporating the diameter-controlled VACNTs and investigating the confinement effect on the mass transport through CNT channels. The major challenges and principal goals are: to understand the mechanism of the diameter modulation of VACNTs; to establish practical strategies for the CVD of diverse VACNTs with tailored structures; to develop and fabricate a robust membrane platform for the nanofluidic experiments; and to evaluate mass transport characteristics of gases and water through the fabricated CNT membranes.
1.3 Thesis Structure

This thesis charts the author’s work on the development and investigation of diameter-controlled, facile synthesis of VA-SWCNTs and CNT membrane as well as nanoscale mass transport across it, for potential applications to separation processes and energy conversion technology.

This thesis work has begun with the study of VACNT growth via thermal CVD with an intention of developing strategies for catalyst and process design that would enable reliable and controllable synthesis of the VACNTs with structural properties desirable for the fabrication of CNT membrane. In the course of the investigation, it was apparent that fundamental understanding in the growth of the VACNTs and improvements in control of the CVD process are critical to achieve diverse VACNTs with tailored features that can meet the various demands of the membrane applications. While limitations in the reduction of SWCNT diameter to sub-nm still exist, significant advancements in diameter control, wall-number selectivity, nanotube crystallinity, amorphous carbon content, process repeatability and scalability were accomplished towards facile diameter control of high quality VACNTs. Each of these topics, along with relevant results demonstrating controlled growth of VACNTs is presented in chapter 2 and 3:

Chapter 2 presents state of the art and motivation for rational catalyst design aimed at achieving the selective growth of VA-SWCNTs with small diameters and narrow distributions. Critical role of a catalyst support, size-engineered Fe catalyst, a synergistic effect of Mo addition in Fe catalyst and transformation of a multilayered metal film into nanometer-sized catalysts via metallic interdiffusion across interfaces are discussed in the context of diameter distribution of VACNTs. Finally, wide-range diameter modulation of high quality VA-SWCNTs is demonstrated using a variety of catalysts and the current minimum average diameter of 1.25 nm is achieved for VA-SWCNTs.

Chapter 3 presents the background knowledge on the basic principles of CCVD process, with a specific emphasis on the critical parameters influencing the structural properties of VA-SWCNTs. Systematic investigations on a thermal gradient developed in the precursor gas
mixture that rearranges its chemical composition, pretreatment condition affecting catalyst state and morphology, and precursor partial pressure controlling activation and deactivation of catalytic nanoparticles are discussed, in addition to their impacts on the growth dynamics of VACNTs. Finally, dominant mechanisms responsible for the diameter selection during VACNT CVD as well as significant process parameters are unveiled, which will help synthesize VA-SWCNTs for the CNT membrane manufacturing.

The second part of the thesis aims at realizing ideal graphitic nanochannels for the investigation of the unique physics behind the nanofluidic phenomena observed in biological protein channels, or nature’s pumps. Initial attempts for constructing CNT membranes by use of current existing methods in the literatures turn out to be non-working, for VA-SWCNTs are susceptible to compressive stresses and can undergo severe structural deformation and microscopic collapse. New ideas in membrane design and advances in fabrication and characterization methods will be desired for employing these VA-SWCNTs of tailored structural properties.

Chapter 4 embodies the new design, fabrication procedure and structure analysis of the first VA-SWCNT membrane and its molecular transport characteristics. Along with an in-depth discussion of the strategic selection of VACNT structure, novel design and fabrication procedure of CNT membrane are presented. Transport properties of various gases and liquid water through the fabricated VA-SWCNT membranes are characterized experimentally and compared with classical models and other simulations and experiments.

Chapter 5 summarizes the findings of this thesis work and highlights their key contributions to the field of CNT synthesis and Carbon Nanofluidics. Future directions from the CNT synthetic point of view, unresolved issues in the fabrication, scale-up and application of CNT membranes and key questions of Carbon Nanofluidics are formulated, along with ongoing and future work towards answering these questions.
Rational Catalyst Design for the Diameter Controlled Growth of VACNTs
2 Rational Catalyst Design for the Diameter Controlled Growth of VACNTs

2.1 Background Knowledge

CCVD is currently the most popular method of synthesizing CNTs where the decomposition of a carbon source supplied mostly in gas or liquid form and the templated growth of a CNT are achieved in the presence of a metallic catalyst particle when a sufficient energy exists in a system (Figure 2.1). This process involves many parameters such as hydrocarbon, catalyst, temperature, pressure, reactor geometry, wall condition and pre-conditioning, gas flow rate and dwell time, carrier and additive gases, et cetera. In this section, we first consider catalyst design that is the primary factor governing the formation and the size control of catalyst particles.

![Figure 2.1. Three key components in the CVD growth of CNTs.](image)

2.1.1 Catalysts for CNT growth via CVD

Catalyst particles play roles in the CVD growth of CNTs by (i) catalyzing the adsorption and dissociation of carbon precursors or their pyrolysis products, (ii) assisting the bulk and/or surface diffusion of the carbonaceous species as well as further interactions and reactions among them, (iii) instigating the nucleation and keeping the nanotube rim reactive for a continued growth of a nanotube. Accordingly, the structure of resultant CNTs such as wall
number, diameter, chirality, and terminal height are strongly tied up with the configuration and composition of the catalyst.

Nanometer-sized particles made up of transition metals such as Fe, Ni, and Co are commonly used as key catalyst components for CCVD of CNTs. Besides Fe, Ni, and Co, SWCNT growth has also been reported using sub-3-nm-sized particles of other late transition metals (i.e., Pd, Pt, Ru) [46, 47], noble metals (i.e., Cu, Ag, Au) [48, 49], early transition metals (i.e., Mn, Cr, Mo) [50, 51], carbon family (i.e., diamond, Si, Ge, Sn, Pb) [52, 53], lanthanides (Gd, Eu) [54] and other mixed compounds (FeSi₂ [55], SiC [52], SiO₂ [56], Al₂O₃ [56], TiO₂ [56], Er₂O₃ [56], ZnO [57], ZrO₂ [58]). However, the transition metals have shown far better activities for catalyzing the CNT growth.

On the other hand, there is a synergetic effect of having more than two catalytically active metals in the catalyst nanoparticles. [59] Such bi- and trimetallic catalysts have been widely studied and reported to show a higher activity in the CCVD of CNTs than the pure elements. [60, 61] Addition of non- or less active elements such as Mo and Mg as co-catalysts to transition metal elements are also frequently used, notably to prevent or control the catalyst coarsening behavior. [62-64]

### 2.1.2 Chemical and physical states of catalyst particles

How the different chemical and physical properties of a variety of catalysts can influence the CNT growth is summarized hereafter. First, the physical state of catalyst, whether catalyst is in the solid or liquid form, can affect carbon solubility and surface or bulk diffusion rate of the carbon. [65, 66] Under CVD experimental conditions, the melting points of catalyst particles can be significantly lowered due to the dissolved carbon [67, 68] and the high surface energy with respect to the bulk materials by Gibbs-Thomson effect for small particles. [69, 70] The former applies to particularly for the metallic element that has eutectic and eutectoid points in their phase diagram with carbon such as Fe, Co, Ni, Pt, Pd, Rh, Ru, Ir and Re. [71, 72] The eutectic point, at which all three phases can exist simultaneously, shifts not only toward lower temperature but also toward lower content of carbon. Meanwhile, the presence of substrate such as Al₂O₃ can raise the melting point by reducing the surface and interface energies of catalyst particles via attractive interactions. [68, 73]
When considering the aforementioned list of active catalyst reported for SWCNT growth, the melting point of the bulk phase ranges from 327.46 (Pb) to 3550 °C (diamond). Even if we consider the competing effects of melting-point depression and elevation, it is likely that at standard CVD temperatures (600-1000 °C) particles of some species are in liquid state (i.e., Pb) while those of other species are in solid state (i.e., diamond). Experimentally, several in-situ monitoring studies of metal-catalyzed CNT growths (i.e., Fe, Co, Ni, FeCo, FeMo, etc.) using environmental TEM have demonstrated that catalyst nanoparticles are in the fluctuating crystalline state, alternating between rounded and elongated throughout the growth of a nanotube. [74, 75] Note that, since rather large particles (> 4 nm) were used in these works, it is unclear whether the physical states of smaller catalyst particles may show the same behavior.

Secondly, the chemical state of catalyst, whether catalyst particle is metallic or carbidic, covered with metal oxides or fully reduced, whether carbonaceous species are dissolved in the bulk or subsurface sites, or if they reside only on the surface of the particle, can also influence the CNT growth. The answer to these questions would depend on the kind of metal chosen, its carbon affinity and tendency to form carbides. Transition metal has stronger affinity to carbon as the number of unfilled d-orbitals increases. [76, 77] For example, metals without d-vacancies (i.e., Cu and Zn) show a negligible affinity for carbon. Metals with few d-vacancies (i.e., Ni, Fe, and Co) exhibit finite carbon solubilities. Metals with many d-vacancies (i.e., Ti and Mo) can form strong chemical bonds with carbon leading to stable carbide compounds. [78]

Fe, the most widely used catalyst is an exceptional case: the carbon solubility is relatively low for α-Fe (~0.1 at% at 700 °C) but substantial for γ-Fe (~4 at% at 800 °C), and Fe can form metastable carbide (Fe₃C) simultaneously. In general, carbon can precipitate out when the incorporated carbon concentration exceeds the carbon solubility of the catalyst particle. However, for the stable carbide-forming metals (i.e., Al, Sc, Ti, V, Cr, Mn, Fe, Y, Zr, Nb, Mo, Hf, Ta, W and U), the carbon concentration must exceed the carbon content of the most stable carbide for the nanotube growth. [79, 80]

The size of catalyst nanoparticle influences not only the physical state but the chemical state. Many studies have predicted and observed an
increase of the solubility of impurities inside catalyst nanoparticles as their size decrease. [81-83] Diarra et al. have reported an interesting simulation result that at a given carbon chemical potential and temperature, smaller Ni nanoparticles can absorb a larger fraction of carbon than larger ones due to the larger carbon solubility in subsurface than in the bulk. [84]

2.1.3 Catalytic activity of metal nanoparticles

The catalytic activity of a metal strongly depends on its electronic structure. This catalyst property not only controls the decomposition of the carbon source, but also the formation and stability of metal carbides and, more importantly the release of carbon atoms. When a molecule is adsorbed on a metal, the activation barrier for the dissociation of carbonaceous molecules is lowered. Activation energy for self-decomposition of acetylene, for example, is 5.58 eV but can be significantly reduced to 1.4 eV with the help of Ni catalyst. [85] Molecules adsorbing on transition metals preferentially interact with the d-states near the Fermi level, and thus the strength of the bonding between adsorbate and catalyst surface is proportional to the degree of d-band vacancies. [86] From the viewpoint of chemical reaction, such strong interactions allow a transition state of lower energy and therefore accelerate CNT growth. This trend is experimentally reflected in the heat of adsorption, the latent heat given off by a material as it adsorbs onto metal. Because too strong interactions hold back the reaction intermediates on the surface and block the continuous uptake of reactant molecules, metals forming bondings of intermediate strength with adsorbate are optimal as catalysts for the growth of CNTs. Consequently, catalytic efficiency of transition metals in heterogeneous catalysis for CNT growth shows a volcano relation to the metal d-orbital energy (Figure 2.2). [87-89]

In the volcano plot, noble metals (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au, Re, Cu and Hg) are inefficient due to their poor ability in the dissociation of adsorbed carbon species, while early transition metals (Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, Ta and W) are inefficient because their catalytic surface sites become all covered by absorbed carbon and cannot release the nanotube. Finally, metals that can dissociate the feedstock readily and release the nanotube is considered as optimum catalysts.
Teschner et al.’s work pointed out that the modification of catalyst subsurface region for instance by carbon (from fragmented feed molecules) enabled selective hydrogenation on Pd catalysts. Similarly, the degree of subsurface occupation by carbon even in metals of low carbon solubility can strongly influence the catalytic activity and the conversion selectivity to nanotube. [90]

On the other hand, carbides or carbide-forming metals have shown catalytic activities for CNT growth in CCVD. In general, the bonds between adsorbate and carbides are weaker than the bonds between adsorbate and metals. [91, 92] Therefore, carbides can be considered as having no or weak catalytic activity. Exceptionally, however, carbides of group IV-VI metals have been found to rival the catalytic performance of the Fe-group metals. These carbides are often as active as transition metals for (de)hydrogenation and used for catalysis in extreme conditions due to their high hardness and melting points, as compared to transition metals. [93, 94]

Experimentally, all transition metal particles are observed to undergo carburization. During CNT growth, higher transition metal carbides (i.e., Ni\textsubscript{3}C) tend to decompose while lower transition metal carbides (i.e., WC) remain stable. Other metal carbides (i.e., Mo\textsubscript{2}C) are found stable but inactive for CNT growth. [95, 96] In-situ observations of
SWCNT growth using ultrahigh vacuum TEM and XPS have provided direct evidences that Fe, Co and Ni catalyst particles remain metallic, instead of going through carbide formation. [97, 98] In contrast to these results, several other groups have reported that the nanotubes nucleate and grow from Fe\(_3\)C nanoparticles. [74, 99] On the other hand, He et al. [72] and Wirth et al. [71] have found out that both Fe and Fe\(_3\)C particles can be the active catalyst although their catalytic performances are not the same. At low temperature or α-rich Fe catalyst Fe\(_3\)C phase is found more abundant, which leads to the formation of short bamboo-like CNT structure.

Besides the bond strength between adsorbate and catalyst surface, the size and the surface structure of catalyst particles can also influence the catalytic activity. Classically, the structural sensitivity of a catalytic reaction is related to a modification of the population of surface reactive sites (terraces, steps, kinks, defects) by the size and shape of the catalyst particles. Reducing the size of nanoparticles can lead to an enhanced catalytic activity by decreasing the density of states at the Fermi level and modifying the shape and position of the valence band, which is revealed by large heat of adsorption. For instance, Meier et al. have suggested that for Au nanoclusters the metal to non-metal transition, the increase in heat of adsorption and the onset of catalysis occur concomitantly with the size reduction. [100]

### 2.1.4 Supported metal nanoparticle catalysts

The growth of VACNTs requires a complicated system of a group of small nanoparticles distributed over a support. Vertical alignment can be achieved as a result of the densely packed catalyst particles, which allow the collective growth of CNTs in the direction perpendicular to the substrate. [9] Properties of the supported metal catalyst systems are dominated by catalyst-substrate interactions as well as catalyst surface energy effects. Catalysts are metals with large surface energy, support layers are typically ionic oxides with low surface energies. Namely, \(\gamma_{\text{metal}} + \gamma_{\text{metal-support}} > \gamma_{\text{support}}\), where \(\gamma_i\) denote surface free energies. [101, 102] When thermally treated to induce a dewetting process, therefore, catalyst in the form of thin film breaks up into a large number of nanoparticles to lower its total surface energy by
exposing the support of low surface energy. [103, 104] Based on the information about the heat of sublimation of the metal ($\gamma_{\text{metal}}$) and the heat of formation of the stable metal oxide ($\gamma_{\text{metal-support}}$), one can predict the wetting behavior of the supported metal catalysts (Figure 2.3). The most frequently used support materials is Al$_2$O$_3$ due to its characteristic feature of restricting the surface mobility of metal atoms. However, support materials itself sometimes show the catalytic activity, although they do not dissolve carbon. For instance, Al$_2$O$_3$ is known to catalyze the decomposition of acetylene. Noda et al. have observed the hidden role of Al$_2$O$_3$ support in balancing the concentration of carbon adsorbates on the catalyst surface. [105, 106]

![Figure 2.3](image.png)

**Figure 2.3.** (a) Schematic representation of the force balance equilibrium for a liquid catalyst on a flat catalyst support at the catalyst-support-air triple interfaces and (b) description of the heat of metal oxide formation and the heat of metal sublimation for various metals on TiO$_2$ support where black squares (■) and red circles (●) represent experimentally observed particle and layer formations. When the metal-metal lateral interactions are stronger than metal-TiO$_2$ interfacial interactions, surface metal atoms tend to form three dimensional islands instead of two dimensional layer structures. [107, 108]

Interactions of metal nanoparticles with support can influence the chemisorption process on the catalyst surface. [100] For instance, strong catalyst-support interaction between Au and Al$_2$O$_3$ is found unhelpful and simply lowers the catalytic activity. [109, 110] Such catalytic degradation is attributed to the change in the electronic structure of catalyst caused by both the interfacial charge transfer and the catalyst encapsulation with a thin oxide layer via atomic diffusion.
at the interface. [111] The surface properties of the oxides (stoichiometry, defects, oxidation state, acid-base character and termination) and the difference of electronegativities between metal catalyst and oxide support can induce the charge redistribution at the interface. [112] Electronegativity is the tendency of an element to attract electrons towards itself. For instance, Bayer et al. have reported the use of metallic Ta support, which is more electronegative compared to Fe, for solid-state reduction of Fe catalyst. Ohashi et al. have proposed the use of Ti co-catalyst, which has stronger oxygen affinity than the Al support and Fe catalyst. [113-115] Encapsulation (or decoration) of metal surface with a thin oxide layer would be favored because it can lower the total surface energy, but it can also have a deleterious effect on the catalytic activity.

During the CVD process at elevated energies, catalyst particles on the support can encounter the competing effects of coarsening (Ostwald ripening and migration-coalescence, also known as Smoluchowski ripening) and diffusion of the catalyst into the surface. [116, 117] Ostwald ripening occurs due to the higher vapor pressure of the smaller particles. Therefore, metal atoms escape quickly from small particles than from larger ones, eventually resulting in the bimodal size distribution. Migration-coalescence (Smoluchowski ripening), on the other hand, takes place through particle motions and simply leads to increase in average particle size and decrease in particle number density. This process will be accelerated with an increase in the areal density of particles and in temperature. Several studies have reported that the dominant mechanism changes from migration-coalescence at low temperatures and short times to Ostwald ripening at high temperatures and longer times. [118-120] This phenomenon in part depends on the nature of the catalyst support. Amama et al. have shown that the use of different types of Al$_2$O$_3$ supports having a wide range of porosity can significantly affect the evolution, activity and lifetime of the Fe catalyst. [102]
2.1.5 Diameter modulation by catalyst design

Preparation of VA-SWCNTs with controlled nanotube diameters is critical for many applications because the nanotube diameter can affect their mechanical, thermal, chemical and particularly electronic properties. The diameter of SWCNTs ranges from 0.4 nm to several nanometers. [121] It is commonly accepted that the CNT diameter is primarily determined by the sizes of initial catalyst nanoparticles, though what should not be neglected is that the sizes of nanoparticles and nanotubes are most likely to alter during the typical energy-intensive CVD processes. This relationship has been supported by observations of catalyst nanoparticle while templating the nanotube formation at its tip or base and by other experimental demonstrations. [122, 123] In addition, there exists a strong correlation between size of catalyst particle and wall number of nanotube in that the larger the particle sizes, the more the CNT wall numbers. It is related to the shift in the growth mode from base to tip, the size effect on surface-to-volume ratio, reactivity and binding energy toward substrate. [1, 124]

There have been considerable attempts for the diameter modulation of VA-SWCNTs. In 2006, Yamada et al. reported the selective growth of VA-SWCNTs with diameters in the range of 0.4-4.0 nm using sub-1-nm-thick Fe catalyst (Figure 2.4a). [125] More recently, Hata et al. have shown successful control over the diameters from 5 to 10 nm and the wall numbers for SWCNT and MWCNTs using Fe catalyst films with thickness in the range of 1.6-5 nm (Figure 2.4b). [24] However, reduction of the diameter range of VA-SWCNTs to less than 2 nm has been very challenging subject due to the difficulties in preparation of the very small catalyst particles. Instead of controlling the deposited catalyst size, many recent studies have attempted to develop new catalyst designs, which can limit the size of catalyst particles for growing small diameter SWCNTs. For example, Zhong et al. have proposed a nanolaminate Al₂O₃, Fe, and densified Al₂O₃ trilayered catalyst, which allowed the use of thinner Fe catalyst. Dense VA-SWCNTs with the diameters of 0.5-2.1 nm were achieved in this method, showing a great promise for their application to interconnects (Figure 2.4c). [126] Further, Xiang et al. have achieved even smaller average diameter VA-SWCNTs of 1.4 nm by wet chemical synthesis of Co-Mo bimetallic particles of a tailored composition (Figure 2.4d). Distinctly from these approaches, Sakurai
et al. have proposed an indirect method of controlling the nanoparticle size and density by decoupling the catalyst formation and SWCNT growth processes. [127] Thurakitseree et al. have found out that the addition of acetonitrile to an ethanol carbon feedstock during CVD process is effective in reducing the average SWCNT diameter from 2.1 nm to 0.7 nm by the incorporation of nitrogen into the sp² carbon network of the nanotubes (Figure 2.4e). [128, 129] Yao et al. have introduced a unique technique so called a ‘cloning’ growth by extending the nanotube from the open-end of pre-grown SWCNTs. [130]

Besides, evolution in catalyst morphology via lateral and vertical diffusion induces particle coalescence, and Ostwald ripening can result in the increase and broadening of nanotube diameter along the length during the long growth time. This influence should be kept in mind when comparing the effectiveness of different approaches in diameter modulation of CVD-grown CNTs. For instance, Hasegawa et al. have reported a gradual increase in diameter on average from 1.7 nm at the top to 3.7 nm at the bottom of VA-SWCNTs, revealing the necessity of developing methods of suppressing the catalyst coarsening not only at the nucleation stage but throughout the entire growth process. [12, 131]
Figure 2.4. Diameter modulation of VA-SWCNTs; (a) adapted from ref. [125], histograms of the type and diameter of CNTs grown from thin Fe catalysts; red, blue and green bars denote SW-, DW-, and MWCNTs, (b) adapted from ref. [24] average diameter and wall-number of CNTs grown from Fe catalysts with thicknesses of 1.6-5 nm, (c) adapted from ref. [126]: SIMS depth profile of the newly developed Al₂O₃, Fe, and densified (impermeable) Al₂O₃ trilayered catalyst, which can grow VA-SWCNTs with diameters in the range of 0.5-2.1 nm, (d) adapted from ref. [64]: The use of Co-Mo bimetallic catalyst, leading to the growth of VA-SWCNTs with an average diameter of 1.4 nm, and (e) adapted from ref. [129]: heteroatom (nitrogen atom from acetonitrile, CH₃CN)-mediated diameter control.
2.2 Size-engineered, Alumina-supported Fe Catalysts


2.2.1 Brief description of section 2.2

This section describes a diameter-controlled growth of VA-SWCNTs via CCVD, enabled by ultrathin Fe catalysts on Al$_2$O$_3$ and low C$_2$H$_2$ partial pressure, $P_{C_2H_2}$. A long, sub-3-nm SWCNTs up to one millimeter in height could be obtained without addition of hydrogen or moisture, and precise control of the SWCNT diameters was successfully established. Key to the efficient growth of such arrays of narrow SWCNTs is threefold: (a) growth temperature low enough to suppress catalyst agglomeration and Ostwald ripening, (b) $P_{C_2H_2}$ below a certain level to extend the catalyst lifetime, and (c) size-matching at nanometer scale between Fe catalyst seeds and Al$_2$O$_3$ support asperities in order to mitigate the surface migration and undesirable enlargement of catalyst particles. These findings can contribute to the facile growth of uniform, dense arrays of high quality VA-SWCNTs with narrow diameter distributions.

2.2.2 Experimental details: catalyst deposition & CCVD

Sub-0.5 nm ultrathin Fe catalysts on 20-nm-thick Al$_2$O$_3$ supports were deposited by electron beam evaporation (Univex 500, Leybold). Both depositions of Fe and Al$_2$O$_3$ films were conducted at the chamber pressure in the range of 0.75–2.0 $\times$ 10$^{-6}$ mbar with a deposition rate of 0.033 Å/s and 0.2 Å/s, respectively. The CCVDs of VACNTs were carried out in a vertical CVD reactor (Black Magic Pro™, Aixtron) adopting the rapid heating cold-wall method. After cleaning the chamber with O$_2$ plasma, catalyst substrates were loaded on the sample stage, 41 mm below the gas shower head at a substrate temperature above 200 °C to avoid moisture condensation, and the chamber was evacuated below 0.2 mbar. The sample stage was then heated to 750 °C at a ramp rate of 300 °C/min and kept for 5 min in
an Ar atmosphere at a flow rate of 8000 sccm at a chamber pressure of 70–80 mbar. The CNT growth step began by additionally flowing 5 sccm of the C₂H₂ gas (purity >99.6%, Pan Gas). Growth conditions such as annealing time, growth temperature, and hydrogen concentration during annealing were chosen to allow all the ultrathin catalysts to show sufficient activities and yield uniform VACNTs all the time (Figure 2.5a,b). For a stop-and-start (pulsed) growth to obtain SWNT growth kinetics, the C₂H₂ gas was injected discontinuously with a short time interval. For example, C₂H₂ pulses were given for 3, 5, 20 and 30 min, each pulse separated by a 15 s interval (Figure 2.5c).

**Figure 2.5.** (a) A standard CVD condition corresponds to the growth temperature of 750 °C, the short preannealing of 5 min, the very low \( P_{C_2H_2} \) of around 0.035 mbar and the total chamber pressure of around 70 to 80 mbar throughout the entire process. (b) The TEM diameter histograms of VA-SWCNTs grown from 0.2 nm-thick Fe catalysts with different H₂ concentrations during preannealing step are shown with log-normal fittings. Diameter range tends to shift to lower values as the catalyst nanoparticles become reduced and thus smaller but the growth rate decreases. It hints the excessive surface coverage by H species may inhibit the continuous supply of carbonaceous species. In order to rule out the effect of H₂ on gas pyrolysis, the growths for comparing different Fe catalysts were performed without it. (c) The variation in C₂H₂ flow rate during the stop-and-start (pulsed) growth of VA-SWCNTs to obtain the SWCNT growth kinetics.
2.2.3 Catalyst analysis techniques: AFM and XPS

Surface topography and roughness of the as-deposited and annealed catalyst substrates was analyzed with AFM (Asylum Research, MFP-3D™), operating in the tapping mode with a scan rate of 1 Hz and a cantilever oscillation frequency of ~279 kHz for a scan size of 1×1 µm². A supersharp tip with tip radius of smaller than 5 nm (Nanosensors™, SSS-NCHR) was used for an enhanced resolution. The AFM images were processed using WSxM 5.0 software. [133]

A PHI Quantum 2000 microprobe spectrometer with base pressure of 8×10⁻⁷ Pa and monochromatic Al Kα (1486.6 eV) radiation was used to obtain the XPS spectra. The spectrometer energy scale was calibrated using the Au 4f⁷/₂, Ag 3d⁵/₂, and Cu 2p⁵/₂ photoelectron lines at 83.96 eV, 368.21 eV, and 932.62 eV, respectively. The full width half maximum (FWHM) of the Ag 3d⁵/₂ lines were 1.62 and 0.6 eV at 117.4 and 11.75 eV of pass energy, respectively. The elemental composition was determined using the MULTIPAK software package (Physical Electronics) that uses proprietary relative sensitivity factors to calculate element concentrations in atomic percentages.
RESULTS AND DISCUSSION

2.2.4 Diameter modulation of VA-SWCNTs

Figure 2.6. Diameter-controlled synthesis of VA-SWCNTs obtained from 1 \times 1 \text{cm}^2 size ultrathin Fe catalysts of sub-5 nm in nominal thickness supported on e-beam deposited alumina. Each histogram was made based on counting more than 100 individual nanotubes from TEM images and shown with log-normal fittings. The numbers on the right hand side are average value and standard deviation of CNT diameters. The inset (upper left) shows a linear relation between the average diameter of CNT and the nominal thickness of Fe catalyst.

The primary objective is to precisely control the diameters of CVD-grown VA-SWCNTs at small values with narrow distributions. In addition, we aim at minimizing changes in the diameter distribution over long nanotube lengths. Since the growth window depends on both the catalyst and CVD conditions, we first established the CVD conditions effective to activating ultrathin Fe catalysts and growing VACNTs as described in section 2.2.2. Ultrathin Fe catalysts all with sub-0.5-nm nominal thicknesses were prepared and used for CCVDs. The actual thickness of these catalyst cannot be defined because the form discrete islands rather than a continuous film. Instead, the
variations in surface roughness by catalyst deposition will be further discussed in section 2.2.7. The resultant samples were examined by TEM and the results in Figure 2.6 show a good control of the CNT diameter. Average CNT diameter ($d_{\text{CNT}}$) is found linearly proportional to the nominal Fe thickness ($t_{\text{CNT}}$): $d_{\text{CNT}} \text{ (nm)} = 4.72 \ t_{\text{CNT}} \text{ (nm)} + 0.65$.

All CNTs obtained from Fe catalysts of sub-0.5 nm in thickness are single-walled and their diameters are smaller than 3.8 nm. The prevalence of SWCNT is attributed mainly to the sizes of catalyst nanoparticles formed from the ultrathin Fe catalysts that are too small to nucleate nanotubes with multiple graphitic layers. [1] Figure 2.7 presents representative TEM images of diameter controlled SWCNTs, also revealing the cleanness and straightness of the nanotubes. Corroborating TEM analysis results, Raman spectroscopy also underpins the size controllability of the narrowly distributed, small diameters of as-grown SWCNTs (Figure 2.8). When Raman spectra of the VA-SWCNTs from various catalyst thicknesses were compared, the RBMs in the 100–250 cm$^{-1}$ frequency range were clearly observed in all samples. The intensities of higher frequency RBMs above 250 cm$^{-1}$ corresponding to sub-1 nm SWCNTs gradually decreased with increasing Fe thickness until it disappeared for the catalysts thicker than 0.2 nm. For Fe thicknesses larger than 0.2 nm, only the lower frequency RBMs corresponding to CNT diameters in the range of 1–2 nm were visible, in good agreement with the TEM results.
Figure 2.7. Low and high magnification TEM images of diameter controlled SWCNTs vertically grown from ultrathin Fe catalysts of sub-5 nm in thickness; (a) 0.1 nm, (b) 0.15 nm, (c) 0.2 nm, (d) 0.3 nm and (e) 0.4 nm.
Figure 2.8. Raman spectra of diameter controlled SWCNTs, showing distinct radial breathing modes (RBMs) and high G-to-D ratio regardless of the thickness of Fe catalyst, taken from the top of the VA-SWCNTs using a 785 nm laser excitation; Raman spectrum of HiPCO SWCNTs (NanoIntegris Inc.) is shown for comparison.

For all of our samples, the Raman spectrum of the SWCNTs showed a strong G band at ~1592 cm$^{-1}$ (with a clear G$^*$-band shoulder at ~1565 cm$^{-1}$) compared to the D band at 1290 cm$^{-1}$. The resultant G-to-D intensity ratios were all greater than 10, suggesting high crystallinity of as-grown SWCNTs and decreased only marginally with Fe thickness. Also, no hint of amorphous carbon was seen in our extensive TEM observations. Consequently, our experiments covered an accurate control of the SWNT diameter in a previously unexplored regime below 3 nm without sacrificing the high quality of SWCNTs.
2.2.5 Growth kinetics of VA-SWCNTs

The time dependent growths of VA-SWCNTs from the ultrathin Fe catalysts of sub-5 nm in thickness were monitored via stop-and-start (pulsed) growth method and ex-situ SEM analysis of the height of VA-SWCNTs. [134, 135] For the stop-and-start (pulsed) growth, C\textsubscript{2}H\textsubscript{2} was discretely added to a constant Ar flow with a short time interval of 15 s between each growth segment in order to minimize growth disturbance caused by the dead time. Unlike most of the previous studies that have claimed unstable SWCNT growth for too thin catalyst layers, [64, 126] even without any help of water or hydrogen addition the ultrathin Fe catalysts efficiently produced several-hundred-\(\mu\)m tall uniform VA-SWCNTs without significant diameter variation during the growth (Figure 2.9a).

![Figure 2.9](image)

Figure 2.9 Stop-and-start (pulsed) CCVD of VA-SWCNTs for obtaining the time dependent growth height curve; (a) Cross-sectional SEM image of a 380-\(\mu\)m-tall VA-SWNTs grown from 0.15-nm-thick Fe catalyst, showing bright bands marking the start of each new growth segment (inset) and (b) Monomolecular growth kinetics of the VA-SWCNTs grown from Fe catalysts of: 0.1 nm (red), 0.2 nm (orange), 0.3 nm (green) and 0.4 nm (blue) in thickness. All the curves reduce to a master curve (inset, 0.2 division), \(h = A (1 - e^{-t/\tau})\), where \(h\) is the height of VA-SWCNTs, \(A\) is the asymptotic value of \(h\), and \(t\) and \(\tau\) are the time and inverse reaction coefficient, respectively.

Because the activity and lifetime of the catalyst vary with the size and areal density of catalyst particles formed from the different initial thickness of catalytic Fe layers, [136-138] the growth kinetics did not
share the same initial rate and saturation time. Nevertheless, the growth kinetics for these catalyst thicknesses all collapsed to a monomolecular function, or \( h = A (1 - e^{-t/\tau}) \), where \( h \) is the height of VA-SWCNTs, \( A \) is the asymptotic value of \( h \), and \( t \) and \( \tau \) are the time and inverse reaction coefficient, respectively. From the kinetic data of Figure 2.9b, the 0.2 nm-thick Fe catalyst was found optimal in terms of the growth rate and lifetime, resulting in the tallest VA-SWCNTs up to 1 mm after 60 min growth. Growth efficiency, represented by \( \tau \), gradually diminished, as the Fe film took thickness values away from this optimum one.

The Fe thickness dependent growth kinetics could be explained by the relation between carbon supply and catalyst particle size. Vulnerable to high \( \text{C}_2\text{H}_2 \) flux, catalyst particles formed from the Fe film thinner than 0.2 nm did not show any CNT nucleation at the \( P_{\text{C}_2\text{H}_2} \) over 0.035 mbar. Thus, growth for these thinner catalysts could be limited by \( P_{\text{C}_2\text{H}_2} \). Meanwhile, the diminishing trend in the asymptotic growth height (\( A \)) for the catalysts thicker than 0.2 nm should be related to insufficient carbon supply relative to larger catalyst particles that possess higher carbon capacity. The larger the catalyst size, the shorter the VA-SWCNT height at a given low amount of \( \text{C}_2\text{H}_2 \) supply (low \( P_{\text{C}_2\text{H}_2} \)). Note that a further increase of \( P_{\text{C}_2\text{H}_2} \) led to a faster initial growth rate for the Fe catalyst thicker than 0.2 nm while deteriorating the growth efficiency for 0.2-nm-thick Fe catalyst. It seems that carbon influx on/into the catalyst and their conversion rate to nanotube are balanced well for the 0.2-nm-thick Fe catalyst in our growth conditions, leading to optimal growth efficiency without significant loss in the quality and diameter of SWCNTs. Consequently, we choose the 0.2-nm-thick Fe as an optimum catalyst for studying growth characteristics and mechanism of diameter controlled growth of small-diameter VA-SWCNTs hereafter.

### 2.2.6 Diameter increase in millimeter-tall VA-SWCNTs

Figure 2.10 shows evolution in the diameter and alignment of VA-SWCNTs grown at 750 °C for 60 min from the 0.2-nm-thick Fe catalyst. The uniform heights suggest that SWCNTs of a certain range of diameters can grow in a concerted way, overwhelming the diameter-dependent variations in their catalytic activities. The macroscopic
structure emerges as the self-assembled, self-supporting structure of densely packed CNTs caused by their collective vdW interactions, after which well-aligned CNTs extend downward. The gradual loss in CNT alignment (also packing density) coincides with an increase of $d_{\text{CNT}}$. For example, the average diameter gradually increased from 1.43 nm (200-μm-tall CNTs after 10 min growth) to 1.87 nm (1-mm-tall CNTs after 60 min growth) with concomitant broadening of the distribution. Kinetics of the $d_{\text{CNT}}$ increase was of a monomolecular type, or $d_{\text{CNT}}(\text{nm}) = 1.25 + (1 - e^{-t_{\text{min}}/28.2})/1.37$, which indicates that $d_{\text{CNT}}$ began to expand from an initial value of 1.25 nm at a rate of 0.026 nm/min, but the broadening slows down with a characteristic time constant of 28.2 min to reach an asymptote of 1.98 nm. From the $d_{\text{CNT}}$ expansion kinetics, for this 0.2-nm-thick Fe it is likely to tailor the diameters of VA-SWNTs in the sub-2-nm range if growth is cut off earlier than 10 min. Upon nucleation of CNTs the catalysts initially evolve to support vertical growth of CNTs. Simultaneously their size distribution begins to diverge, when small catalyst particles can be quickly deactivated whereas the large particles maintain the CNT growth at lower packing density due to the size effects on catalyst activity, lifetime and stability. As the growth proceeds, the density and alignment of VA-SWCNTs could be reduced and weakened. However, from the monomolecular kinetics of $d_{\text{CNT}}$ (Figure 2.6 inset), such tendencies are likely to slow down with prolonged growth. This deceleration in SWCNT diameter expansion can be attributed to the surface depletion of metal available, possibly via subsurface diffusion of Fe into $\text{Al}_2\text{O}_3$ support. Note that Ostwald ripening could be ruled out in our experiment because no clear bimodality in the SWCNT diameter distribution was observed. In summary, the monomolecular kinetics of $d_{\text{CNT}}$ expansion can be an outcome of the interplay between surface Fe migration-coalescence and subsurface diffusion of Fe into the $\text{Al}_2\text{O}_3$ support. Such structural changes of the individual nanotubes as well as the bulk morphology of VA-SWCNTs can often cause an issue for many practical applications. Interestingly, compared to other works, we have achieved a far better control of SWCNT diameter and their fluctuations in millimeter-tall VA-SWCNTs. For instance, Hasegawa et al. have reported a doubling in the average diameter of SWCNTs from 1.7 to 3.7 nm in a 0.8-mm-tall structure, which is nearly a 2–3 times faster diameter expansion than our results. [131]
Figure 2.10. Optical (a) and (b) SEM images of a 1-mm-tall sub-3 nm diameter VA-SWCNTs grown for 60 min using a 0.2 nm thick Fe catalyst; A five-rappen coin on the right is for size reference. (c) Close-up SEM images of entangled CNTs on the top (violet), well-aligned and dense CNTs near the top (red), well-aligned but less dense CNTs in the middle about 500 µm below from the top (green), and ill-aligned and less dense CNTs at the bottom of the structure (blue). (d) Growth time versus heights of VA-SWCNTs and (e) TEM diameter histograms of the VA-SWCNTs obtained from different growth times; 0.03 mm tall after 3 min (N = 108), 0.26 mm tall after 10 min (N = 73), 0.59 mm tall after 30 min (N = 145) and 1.00 mm tall after 60 min (N = 104) growths, showing gradual increases in the CNT diameters during growth.
2.2.7 Surface analytical studies on catalyst evolution

The origin of improved diameter control in sub-3 nm regime as well as the gradual changes in diameter, density and alignment of VA-SWCNTs during growth (both addressed in section 2.2.4 and 2.2.6) can be attributed to the formation (thin film dewetting) and evolution (migration-coalescence, Ostwald ripening, and subsurface diffusion) of Fe catalyst nanoparticles on electron beam deposited Al₂O₃ support. To elucidate the mechanism behind the catalyst formation and evolution, we carried out microscopic surface morphology and elemental analysis of the Al₂O₃-supported, ultrathin Fe catalysts using AFM and XPS.

First, we compared AFM images of the as-deposited Al₂O₃ support and 0.2-nm-thick Fe on this support (Figure 2.11). The as-deposited Al₂O₃ film as a template for Fe catalysts revealed a granular morphology with a mean roughness height of 1.77 nm (RMS = 0.42 nm). Interestingly, the mean and RMS values of surface roughness decreased to 1.10 nm and 0.15 nm, respectively, after the 0.2-nm-thick Fe was deposited atop the Al₂O₃ film. This indicates that e-beam-evaporated Fe prefers to nucleate in the trenches of the Al₂O₃ surface approximately 2 nm deep.

Figure 2.11. AFM characterized surface morphologies of (a) electron beam deposited Al₂O₃ (20 nm) support showing a granular structure of a mean feature height of 1.77 nm and RMS of 0.42 nm and (b) 0.2nm thick Fe catalyst deposited on Al₂O₃ support. (Scale bar: 200 nm)
Next, thickness-dependent morphology and thermal evolution of the Fe catalysts were studied by characterizing a set of catalysts exposed to the growth environment without C$_2$H$_2$ for 15 and 60 min. Amama et al. previously confirmed that the catalyst ripening trend does not change in the absence of C$_2$H$_2$ as long as other CVD parameters remain constant. [102] The average feature heights of 15 min annealed ultrathin catalysts were measured as 1.29 nm (for 0.2-nm-thick Fe), 2.92 nm (for 0.3-nm-thick Fe), and 5.04 nm (for 0.4-nm-thick Fe). Both these AFM and TEM data from section 2.2.4 well prove that transition in the dimensions of catalyst particles during thermal annealing occurs rather rapidly for the thicker Fe layers, thus producing larger Fe particles (Figure 2.12).

We found an important feature from Figure 2.12a-c that the average heights of catalyst particles derived from this ultrathin Fe catalysts do not show dramatic evolution in the particle size, changing very slowly from 1.10 nm (as-deposited) to 1.29 nm (after 15 min) and 2.20 nm (after 60 min), in contrast to data reported by other studies. [12, 131, 139] Consistent with the observations from previous sections, this result proves that an Al$_2$O$_3$ support having dense surface asperities comparable in size to subsequently deposited Fe catalysts can allow for uniform dispersion, good isolation and longer preservation of catalytic Fe seeds under thermal CVD conditions.

In other words, this particular catalyst configuration could efficiently suppress severe coalescence and/or Oswald ripening of catalyst particles that can nucleate the small-diameter SWCNT growth, corroborating the nanotube diameter distribution shown in section 2.2.4. We attribute this finding to the intrinsic roughness of the Al$_2$O$_3$ support that acts as effective boundaries for the trapped Fe particles. The observation of pronounced expansion of nanotube diameters for thicker Fe could be understood by an overfull trench effect in that an excessive amount of Fe may overfill the Al$_2$O$_3$ trench and form a rather connected, less granular layer to facilitate surface migration and negate the Fe trapping effect of the Al$_2$O$_3$ support.
Figure 2.12. AFM characterized surface morphologies of 15 min annealed Fe catalysts in CVD growth condition without C$_2$H$_2$; (a) 0.2 nm-thick, (b) 0.3 nm-thick, (c) 0.4 nm-thick Fe catalyst film and those of 0.2 nm Fe catalyst samples exposed to growth condition for different durations; (d) as-deposited, (e) 15 min annealed, and (f) 60 min annealed. (Scale bar: 200 nm)

Further, surface elemental analysis by XPS, especially to investigate the inward diffusion phenomena of surface Fe into the supporting Al$_2$O$_3$ layer, were performed on the ultrathin Fe catalysts before and after their 60 min exposure to the CNT growth conditions. Since X-ray penetrates only a few nanometers into the catalyst substrate, XPS can be a suitable tool for probing the subsurface diffusion phenomena in the very thin catalysts. Several studies have reported that severe
subsurface diffusion of Fe in the similar Fe-Al$_2$O$_3$ catalyst system can become a major cause of catalyst deactivation, leading to growth termination. [102, 116] Figure 2.13a is a superposition of the Fe2p spectral curves of 0.2-, 0.3-, and 0.4-nm thick Fe catalysts on the Al$_2$O$_3$ support. It showed nearly the same peak positions in binding energy but strong dependence of the Fe2p signal intensity on the nominal thickness of Fe. Figure 2.13b quantitatively shows the changes in the atomic concentrations of surface elements, Fe and Al, before and after the 60 min annealing in the C$_2$H$_2$-free growth condition. The concentration of surface Fe clearly decreased from 17% to 7 % for 0.2-nm-thick Fe, from 30 % to 10 % for 0.3-nm thick Fe, and from 32 % to 14 % for 0.4-nm-thick Fe.

**Figure 2.13.** XPS analysis of the ultrathin Fe catalyst evolution on and into Al$_2$O$_3$ support; (a) comparison of normalized Fe2p peaks for as-deposited Fe catalysts of different nominal thickness from 0.1 to 0.4 nm and (b) Surface Fe and Al atomic concentrations of these Fe catalysts before and after 60 min annealing in growth condition.

We exclude both possibilities of the surface Fe loss by evaporation and lift-up because the given annealing temperature (750 °C) is not high enough, and all CNTs in this study grew by the bottom growth mechanism as verified by the absence of catalyst particle at the tip of the SWCNTs in TEM images. The significant loss of surface Fe at the uppermost surface after annealing, therefore, evidences the thermally induced diffusion of surface Fe into the underlying Al$_2$O$_3$ support. Based on these AFM and XPS results along with the kinetics of $d_{CNT}$ evolution, we conclude that the effects of surface and subsurface diffusion of Fe co-exist and interplay to cause the kinetic behaviors of
VA-SWCNT growth and the expansion of nanotube diameter, and the deterioration of density and alignment.

2.2.8 Effect of CVD temperature on diameter modulation

![Figure 2.14](image)

**Figure 2.14.** CVD temperature effect on the diameter distribution of VA-SWCNTs obtained by TEM imaging; 0.2 nm-thick Fe catalysts were used and the growths were performed for 10 min at the temperatures of 750 °C (cyan, N=145), 775 °C (yellow, N=188) and 870 °C (magenta, N=145). Log-normal fittings (dashed lines) are added to the histograms.

The actions of surface and subsurface diffusion of Fe should find their balance in producing CNTs, and this balance manifests differently at various temperatures. As a result, the diameter expansion is strongly influenced by CVD temperature. The temperature dependence (750-870 °C) of the diameter distribution of VA-SWCNT samples catalyzed by the 0.2-nm-thick Fe layer (Figure 2.14) showed that the diameter distribution changes from unimodal to bimodal and broadens with an increase in growth temperature. Previously, several studies reported
the bimodal diameter distribution in VA-SWCNTs, attributed to Ostwald ripening through adatom motion. [131, 140] Similarly, our observation of drastic transitions in the SWNT diameter distribution can be understood by thermal acceleration of Ostwald ripening. Activation energy calculated from Figure 2.14 was about 0.1 eV, which hints the Fe surface diffusion to be the rate determining step of the thermal expansion process of $d_{\text{CNT}}$. The size distribution posed by an ensemble of polydisperse catalyst particles, and the evolution of it, is predominantly determined by the growth temperature. These results suggest that lowering the growth temperature could assist the formation of small particles from ultrathin catalysts and their preservation without significant ripening during the entire CVD process.

### 2.2.9 Effect of $P_{\text{C}_2\text{H}_2}$ on diameter modulation

The effect of $P_{\text{C}_2\text{H}_2}$ on the VA-SWCNT growth rate, alignment, and diameter expansion is investigated. We base our analysis on the results of SWCNT growth at 750 °C for 3 min on the 0.2-nm-thick Fe catalysts with $P_{\text{C}_2\text{H}_2}$ varied between 0.035 and 0.280 mbar (Figure 2.15). Note that that all the CNTs obtained were also single-walled. In this $P_{\text{C}_2\text{H}_2}$ range, the growth height and alignment monotonically decreased with $P_{\text{C}_2\text{H}_2}$. In particular the $P_{\text{C}_2\text{H}_2}$ dependence of the growth height, representative of an initial growth rate, shows an exponential decay: $h \propto \exp(-P_{\text{C}_2\text{H}_2}/P^*)$ with a characteristic decay constant, $P^*$, equal to 0.051 mbar (Figure 2.15). Although quantitative characterization of the VA-SWCNT alignment was limited in our study, we could observe a clear change from well-aligned dense VACNTs (at $P_{\text{C}_2\text{H}_2}$ of 0.035 mbar) to ill-aligned VACNTs (0.140 mbar) to a loose network (0.280 mbar). It remains to be further investigated to find out a detailed relation as a function of $P_{\text{C}_2\text{H}_2}$ between growth rate and alignment of VA-SWCNTs.

At $P_{\text{C}_2\text{H}_2}$ values of 0.035 and 0.070 mbar we obtained SWCNTs sharing a similar diameter range of 0.64–2.07 nm despite the reduction in their growth rate and packing density (Figure 2.16a,b). The diameter distribution began to broaden with only a small shift as the $P_{\text{C}_2\text{H}_2}$ increased, e.g., 0.80–2.41 nm at 0.140 mbar (Figure 2.16c), attributed to precursor influxes not high enough to poison all the
small Fe particles, but enough to nucleate CNTs on a bit larger Fe particles. When $P_{\text{C}_2\text{H}_2}$ was further increased, a loose SWCNT network was obtained with reduced diameters of 0.5–1.5 nm (Figure 2.16d). This implies that the majority of the catalyst particles had been deactivated, and so the number of remaining active particles was not sufficient to support the structure of VACNTs. These SWCNTs must have been produced at the very early stage of the growth so-called induction period (the time interval between injection of carbon precursor and initiation of VACNT growth). [141]

**Figure 2.15.** $P_{\text{C}_2\text{H}_2}$ dependence of average heights (growth time: 3 min) of the VA-SWCNTs obtained from 0.2 nm-thick Fe catalysts, with an exponential fitting and TEM diameter histograms of the CNTs grown at different $P_{\text{C}_2\text{H}_2}$ conditions of (a) 0.035, (b) 0.07, (c) 0.14, and (d) 0.28 mbar with log-normal fittings (dashed lines).

Overall, it seems that as the $P_{\text{C}_2\text{H}_2}$ increases, the number of active catalytic particles declines, and the diameter distribution turns broader to favor larger diameter SWCNTs and suppress the formation of SWCNTs with smaller diameters. These findings suggest that ultrathin Fe layers over $\text{Al}_2\text{O}_3$ can generate, upon exposure to the CVD conditions, subsets of particles of various sizes, each of which can catalyze CNTs and become deactivated in a $P_{\text{C}_2\text{H}_2}$ range different from the other subsets due to their size-dependent catalytic activity and poisoning tolerance. These support that smaller particles should have greater catalytic activity so as to nucleate fast-growing, small diameter SWCNTs, but simultaneously they are vulnerable to high
carbon flux by readily losing the activity via catalyst poisoning. Therefore, $P_{C_2H_2}$ should be tailored low enough to allow for an efficient and controlled growth of small-diameter VA-SWCNTs.

**Figure 2.16** Effect of $P_{C_2H_2}$ on the structure of VA-SWCNTs; low and high magnification SEM images of the VA-SWCNTs obtained from 3 min growth at different $P_{C_2H_2}$ conditions of (a) 0.035, (b) 0.07, (c) 0.14, and (d) 0.28 mbar.
2.2.10 Summary

Key to efficient and diameter-controlled growths of VA-SWCNTs is to prepare well-isolated, sufficiently dense and small size catalysts and to suppress their evolution during the CVD process. By employing ultrathin Fe catalysts ($\leq 0.4$ nm), successful growth of long, high quality VA-SWCNTs up to 1 mm with average diameters bracketing 1.25-2.67 nm is demonstrated that are much smaller than previously achieved with the simple catalyst preparation method of PVD. Optimal balance between Fe surface and subsurface diffusion, found as two primary mechanisms for catalyst evolution, can be achieved by control of deposited catalyst thickness, growth time, temperature, and carbon precursor supply, in the direction to minimizing the diameter enlargement and broadening. We also confirmed that the size-matching between Fe seeds and $\text{Al}_2\text{O}_3$ asperities can effectively suppress the SWCNT diameter enlargement during the CVD process, a problem often reported in the mm-scale SWCNT growths. Finally, this study shows the potential in precisely tailoring the diameter distribution of VA-SWCNTs through well-chosen catalyst thickness, growth temperature and $P_{\text{C}_2\text{H}_2}$. The new findings and strategies from this section have been successfully adopted in the growth of small diameter VA-SWCNTs for membrane fabrication.
2.3 Synergistic Effect of Mo Addition on the Fe Catalyst


2.3.1 Brief description of section 2.3

Fe-Mo bimetallic catalyst is a promising candidate for an efficient growth and a structural tailoring of VACNTs. Understanding the surface morphological evolution of bimetallic film and accompanied changes in the resultant CNT structure is a key to modulating the VACNT growth. This section presents the direct correlation between catalyst evolution of Fe-Mo nanofilms and the growth rate, diameter, and areal density of VACNTs. At typical CVD conditions, the layered bimetallic nanofilms evolve into the entirely different ensembles of polydisperse nanoparticles, highly depending on the atomic ratio and stacking order between Fe and Mo. For instance, Fe-on-Mo type catalysts develop to denser and smaller nanoparticles with more pronounced bimodality in diameter than do Mo-on-Fe type catalysts and thus lead to better alignment and unique diameter distribution of CNTs. With microscopic and spectroscopic characterizations, we find the clues to the positive effect of the Mo co-catalyst in a controlled VACNT synthesis and accordingly speculate a mechanism by which catalysts are formed and deactivated in the Fe-Mo bimetallic system. By highlighting the effect of interactions among all the surface components (Fe, Mo, and Al₂O₃) on the formation of actual catalyst particles, this study provides a rational basis of designing bimetallic catalysts for the growth of structurally programmed VACNTs.

2.3.2 Previous studies on Fe-Mo bimetallic catalysts

Besides the monometallic catalysts of transition metals (i.e., Fe, Ni, and Co), multicomponent catalysts have been regarded useful for the CVD synthesis of VACNTs. A number of studies in the past decades have reported about the potential of such binary and ternary catalysts
toward chirality selection [60, 143], size control [144], high quality [145-147], and low temperature growths. [148-150] Mo added to an Fe-catalyzed CVD process has been drawing attention due to its promise of higher growth efficiency, particularly when the Mo-to-Fe ratio is tuned very low. [151-153] It is presumed that pure Mo does not participate in the CNT nucleation for it converts to Mo carbide (Mo\(_2\)C) during the CVD process. Earlier studies, nevertheless, discovered that when used as a co-catalyst, Mo can alter the catalyst-assisted reactions of feedstock gases by forming alloy catalysts. [154, 155] Later, an in situ environmental TEM study has revealed that Fe-Mo catalysts can evolve into not only inactive Mo-rich Fe-Mo oxide (Fe\(_2\)Mo\(_3\)O\(_8\)) but also into active forms such as FeMo carbide ((Fe, Mo)\(_{23}\)C\(_6\)) and Fe carbide (Fe\(_3\)C) depending on the Mo content. [74, 96]

The primary aims of the Fe-Mo catalyst investigations have been so far to find out which case stands out as the best one in improving the catalytic activity and lifetime. Several studies have focused on the complex interactions between surface elements of Fe, Mo, and support materials (i.e., Al\(_2\)O\(_3\) or SiO\(_2\)) in order to understand their catalyst formation and influence on CNT growth. [156-158] On the other hand, Harutyunyan et al. have suggested that a small amount of Mo added to Fe can lower the minimum catalyst size compared to the monometallic Fe catalyst. [63, 148, 159] Despite the previous works, still elusive is a clear relationship of the surface morphological evolution of the bimetallic catalyst system to the collective growth features of the VACNTs.

### 2.3.3 Experimental details: catalyst deposition & CCVD

A series of catalysts of several nanometers thick, Fe-Mo films having various Fe-to-Mo ratios, thicknesses, and stacking orders were prepared by electron beam evaporation (Univex 550, Leybold) at low chamber pressure in the range of \(8.0 \times 10^{-7} - 2.0 \times 10^{-6}\) mbar and slow deposition rate of 0.033 Å/s. In all cases, VACNTs grew from the catalyst supported by a 20 nm thick Al\(_2\)O\(_3\) layer on Si substrate. VACNTs were grown in a vertical cold-wall CVD reactor (Black Magic Pro\(^\text{TM}\), Aixtron). A detailed description of CVD process is in section 2.2.2. Briefly, when the base pressure reached below 0.2 mbar, the CVD chamber was heated to 750 °C at a ramp rate of 300 °C/min and
held there for 5 min in a gas mixture of H₂ (200 sccm) and Ar (800 sccm). A CNT growth began by mixing 5 sccm of C₂H₂ (purity >99.6%) to the gas mixture. Throughout the entire process, chamber pressure was retained in the range of 7-8 mbar. The gas concentrations and flow rates were adjusted to grow tall single-walled VA-CNTs on a 0.4 nm thick Fe catalyst used as a reference.

2.3.4 Catalyst analysis techniques: AFM and XPS

The morphological evolution of the bimetal surface was characterized ex situ by use of AFM (Asylum Research MFP-3D™) having a supersharptip with a tip radius of curvature less than 5 nm (Nanosensors™, SSS-NCHR). Images were obtained in the tapping mode with a scan rate of 1 Hz and a cantilever oscillation frequency of ~279 kHz for a scan size of 1 × 1 µm², later processed using the WSxM 5.0 software. [133] For elemental analysis, a PHI Quantum 2000 microprobe spectrometer with base pressure of 8×10⁻⁷ Pa and monochromatic Al Kα (1486.6 eV) radiation was used to obtain the XPS spectra at two different incident angles of 17° and 45°. Altering the angle of incidence enables to change the sampling depth to a level that includes almost exclusively the surface atoms. [160] Although the bulk contribution to the signal is still present, the surface portion shows a significant boost in signal strength. The increase in surface resolution depth-wise can allow revealing the difference between binding energies of the surface atoms and the bulk atoms as well as atomic compositional change at the surface and subsurface. The surface contribution increases as the incident angle increases. The spectrometer energy scale was calibrated using the Au 4f₇/₂, Ag 3d₅/₂, and Cu 2p₃/₂ photoelectron lines at 83.96 eV, 368.21 eV, and 932.62 eV, respectively. The FWHM of the Ag 3d₅/₂ lines were 1.62 and 0.6 eV at 117.4 and 11.75 eV of pass energy, respectively. The surface elemental composition was determined using the MULTIPAK software package (Physical Electronics), which uses proprietary relative sensitivity factors to calculate element concentrations in atomic percentages.
RESULTS AND DISCUSSION

2.3.5 Catalytic performance of bimetallic catalysts in the growth of VACNTs: Fe-on-Mo versus Mo-on-Fe Types

To understand the role of Mo in the Fe-catalyzed VACNT growth, we prepared two groups of bimetallic nanofilms, namely Fe-on-Mo (Fe over Mo) and Mo-on-Fe (Mo over Fe) of different ratios and thicknesses. As a reference catalyst, we selected a 0.4 nm thick Fe monometallic film. Previously, we observed that temperature and $P_{\text{C}_2\text{H}_2}$ are the critical parameters for diameter modulation of VACNTs. [132] In this study we retained the $P_{\text{C}_2\text{H}_2}$ at 0.025 mbar, above which VA-SWCNTs could not grow selectively from the 0.4 nm thick Fe catalyst, and varied temperature.

The average heights of VACNTs after 10 min growth revealed strong dependence on temperature and catalyst configuration (Figure 2.17a). First, the reference Fe catalyst showed activities between 580 and 870 °C far greater than the bimetallic catalysts whereas a 0.4 nm thick Mo layer show no catalyst activity under the given conditions, corroborating the previous studies. [96, 156] Note that the decreased growth efficiency has also been previously observed when Mo is added to the metal-catalyzed system at high contents (relative to an optimum Mo-to-Fe ratio of 1:16). [63, 153]

Second, the two groups of Fe-Mo catalysts revealed clearly different behaviors in nucleating and growing CNTs. For the Fe-on-Mo type, Mo addition did not change the temperature window for VACNT growth but reduced the catalytic activity and lifetime altogether. For the Mo-on-Fe type, on the other hand, the growth window narrowed down (600-780 °C) with significantly lower growth rates and shorter lifetimes. While the nanotubes nucleated on pure Fe continued to grow over an hour until they reached a terminal height of ca. 520 µm, those nucleated on Fe-on-Mo and Mo-on-Fe catalysts ceased to grow within ca. 20 and 10 min, respectively. Such a degrading tendency in catalytic efficiency became greater with an increase in the Mo content. It is clearly seen that the Mo co-catalyst is responsible for the catalytic performance degradation in this binary system, and the degree of catalyst deactivation strongly depends on the Mo thickness and stacking order.
Figure 2.17 Temperature dependence of (a) the average height and (b) the average growth rate of VACNTs grown from Fe (reference), Fe-on-Mo, and Mo-on-Fe type catalysts after 10 min growth. The stacking orders of Fe and Mo film are noted along with their nominal thicknesses (nm) in the legend. Dashed lines in the Arrhenius plot are drawn for visual guidance.

The temperature dependence of the average growth rates revealed Arrhenius relations (Figure 2.17b). One can observe the general trend of increased growth rate when the synthesis temperature is increased and the surface coverage of Fe is maximized. We attribute the diminishing Arrhenius slope and the temperature shift of maximum
growth rates to surface processes limited by the presence of Mo, which is not as catalytically active as Fe and likely to form stable carbide. We suggest that, as for the Mo-on-Fe type catalysts, surface exposed Mo may impede the hydrocarbon decomposition of the neighboring Fe and thus deplete the carbon adatoms available on the surface. This effect can result in the reduction of effective carbon influx to active catalyst particles and eventually limit the growth rate. This explanation is supported well by the very low growth efficiency along with the very sparse nucleation of VACNTs observed from the Mo-on-Fe type catalysts. For the Fe-on-Mo type catalysts, the overall reduction of growth rate with increased Mo content is attributed to the existence of Mo islands embedded within and lying in between the Fe particles, which can interrupt the carbon diffusion on the catalyst nanoparticle and intercept the available surface carbons, respectively. Several reports claimed that Mo addition to the Fe catalyst can affect the conversion rate of hydrocarbon (i.e., CH\(_4\), C\(_2\)H\(_2\), and C\(_2\)H\(_5\)OH), thereby directly influencing the growth rate and CNT yield. [146-148] Other studies suggested that Mo and Mo carbide could act as a carbon sink whereby they supply carbon intermediates to the neighboring active sites, suppressing otherwise rapid deactivation of catalyst. [62, 155, 159, 161] Our observations are consistent with these previous findings. In particular, the Mo-on-Fe type seems to fit better with the former cases, while the Fe-on-Mo type shows similar tendency to the latter cases.

Interestingly, the curves of VACNT height versus growth temperature share a similar shape with two local maxima, different from the typical bell-shaped. [162] In order to identify the origin, we compared several VA-CNT samples grown on Fe-on-Mo (0.4/0.2 nm) at several temperatures: 750, 775, 810, and 840 °C. There was little difference in the density and alignment of CNTs, while the CNT quality indicated by RBMs and G-to-D ratio was improved at higher temperatures (Figure 2.18). Further TEM analysis provided more details on the difference in CNT quality. The diameter distribution is broad and multimodal at the low temperature height maximum (750 °C) but gradually narrows down and shifts to smaller diameters, converging to a Gaussian distribution until the high-temperature height maximum (810 °C) is obtained (Figure 2.19). Surpassing this temperature, diameter distribution becomes broadening again while decreasing the growth rate until the catalyst system cannot sustain
the VACNT growth any longer. We suspect that the sudden drop in the growth rate could be somehow attributed to the physical polydispersity of various diameters of bundled CNTs. The growth rate mismatch among the CNTs of different diameters and wall numbers could exert mechanical stress on these CNTs bundled together in physical contact, thereby decreasing the collective growth rate. [163]

Indeed, it is quite interesting that we obtain the maximum growth rate when the diameter distribution is narrowed altogether so that the growth rate mismatch is minimized. On the other hand, the sudden drop in the height of VACNTs is observed to take place at 775-790 °C with no dependence on catalyst configuration and Mo content. Hence, thermally induced surface processes of metal catalysts and alteration of dominant gas pyrolysis products at different temperature range could also be the possible common causes. [13, 164, 165]

**Figure 2.** 18. (a) Raman spectra and (b) high magnification cross-sectional SEM images of VACNTs grown from Fe-on-Mo (0.4/0.2 nm) type catalyst at different CVD temperatures, showing the difference in their alignment (indirectly their areal density).
Figure 2.19. TEM diameter and wall number histograms of VACNTs grown from the Fe-on-Mo (0.4/0.2 nm) type catalysts at different CVD temperatures: (a) 750 °C, (b) 775 °C, (c) 810 °C, where the tallest VACNTs grow, and 840 °C. SW-, DW- and TWCNTs are shown in grey, yellow and cyan, respectively. The violet lines are log-normal fittings, and the mean and standard deviation are given in parentheses. VACNT height-growth temperature diagram is shown in the middle for indicating the growth efficiency.

2.3.6 Catalytic evolution of Fe-Mo bimetallic catalysts

Numerous studies have evidenced that not only the structure of CNTs [125, 166] but also their growth rate and terminal height [24, 167] are closely related to the nature of catalyst nanoparticles. We addressed that the growth characteristics of VACNTs drastically vary depending on the catalyst configuration in the section 2.3.5. To elucidate the origin, we studied the formation of catalyst nanoparticles on the Al₂O₃ support at CVD temperatures by ex-situ AFM. Prior to AFM analysis, catalysts underwent the preannealing process, followed by quenching without proceeding to the CNT growth step.

The AFM topography of the bimetallic catalyst was obtained by accounting for the asperity of the underlying granular Al₂O₃ support (1.77 ± 0.42 nm). [132] It is clearly seen that Fe and Mo show very
different wetting-dewetting behaviors on Al₂O₃ support. Much larger and denser nanoparticles formed on the Fe than on the Mo films of the same thickness (Figure 2.20). At the high CVD temperatures, thermodynamically stable catalyst nanoparticles are likely to form to minimize the surface free energy at the catalyst-support interface. Upon annealing, thus, Fe (higher surface energy of 2.939 J/m²) is expected to dewet easier than Mo (lower surface energy of 2.877 J/m²) on Al₂O₃ (negative surface energy) (Figure 2.20). [166, 168-170] This argument is supported by previous findings that the more electropositive a metal species is (e.g., Mo rather than Fe), the more likely the species is to wet the oxide layer, leading to a layer-by-layer configuration. [171, 172]

![Figure 2.20. AFM topography images of Al₂O₃ supported 0.4 nm-thick (a) Mo and (b) Fe films; to monitor their dewetting process, both samples were exposed to the CVD condition but without a supply of carbon source.](image)

The dewetting of the bi-layered film is more complicated due to the influence of interdiffusion and different thermodynamic behaviors of the two metal species. It is known that high temperature annealing of a Fe/Mo bilayer induces Mo diffusion into Fe (e.g., Mo solubility of 3% in α-Fe at 970 K). [173, 174] Hence, the dewetting of the thin bilayer will be accompanied by the production of Fe-Mo alloys at interfaces. In addition, theoretical modeling and experimental characterization have supported that the stacking order of the bilayer can play a crucial role in determining both the structure and composition of the dewetted particles. In particular, for the Fe-Mo bimetallic system Pint et al. have described a competition between metastable formations of
persisting Mo cores within Fe particles and surface segregated Mo clusters on Fe particles, of which resulting catalyst configuration depends on the initial position of Mo (whether it is inside or outside of the Fe cluster) and the Mo concentration with reference to the catalyst size. [158, 175]

Figure 2.21. Comparative AFM topography images of $\text{Al}_2\text{O}_3$ supported Fe, Fe-on-Mo, and Mo-on-Fe type catalysts whose total thicknesses are the same as 0.8 nm while the atomic ratio of Fe to Mo retain at 1:1 except for the monometallic Fe catalyst (left column) and those of Fe-on-Mo type catalyst with different Fe to Mo ratios; to monitor their dewetting process, both samples were exposed to the CVD condition but without a supply of carbon source.
We observed that upon annealing both the Fe-on-Mo and Mo-on-Fe configurations generated nanoparticles in disparate size distribution and number density from each other. The Mo-on-Fe type generated larger particles with lower number density than did the Fe-on-Mo type. When Mo was deposited onto Fe/Al\(_2\)O\(_3\) at 1:1 ratio, the average height of the resultant nanoparticles was three times larger than those resulted from the Fe/Al\(_2\)O\(_3\) whereas their number density dropped by one-fifth. Compared to those resulted from Fe (0.8 nm)/Al\(_2\)O\(_3\), these nanoparticles are still much larger in size and nearly 40% lower in number density (Table 2.1).

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Mean height (nm)</th>
<th>RMS (nm)</th>
<th>Catalyst height profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo (0.4 nm), black line</td>
<td>0.98</td>
<td>0.27</td>
<td><img src="image1.png" alt="Graph" /></td>
</tr>
<tr>
<td>Fe (0.4 nm), red line</td>
<td>2.51</td>
<td>1.23</td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
<tr>
<td>Fe (0.8 nm), green line</td>
<td>2.84</td>
<td>1.32</td>
<td><img src="image3.png" alt="Graph" /></td>
</tr>
<tr>
<td>Mo-on-Fe (0.4/0.4 nm), violet line</td>
<td>7.74</td>
<td>3.91</td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
<tr>
<td>Fe-on-Mo (0.4/0.4 nm), gray line</td>
<td>5.21</td>
<td>2.73</td>
<td><img src="image5.png" alt="Graph" /></td>
</tr>
<tr>
<td>Fe-on-Mo (0.4/0.3 nm), dark yellow line</td>
<td>4.34</td>
<td>1.92</td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td>Fe-on-Mo (0.4/0.2 nm), orange line</td>
<td>1.79</td>
<td>0.85</td>
<td><img src="image7.png" alt="Graph" /></td>
</tr>
</tbody>
</table>

**Table 2.1.** Summary of the Surface Morphological Properties of the Difference Types of Al\(_2\)O\(_3\) Supported Fe, Mo, and Fe-Mo Bimetallic Catalysts Obtained by AFM after 5 min annealing in the Absence of C\(_2\)H\(_2\): Mean Height, RMS, and height profiles.
In the Mo-on-Fe type, Mo atoms seem to reside on the surface of preformed Fe beads and/or exposed Al$_2$O$_3$, resulting in Mo patches bound to Fe beads and/or Mo beads in between them. Indeed, XPS data as shown in Figure 2.22 suggest that the absolute atomic concentration of Mo as well as the Mo-to-Fe ratio drastically drop at the shallow incidence angle, or very near the surface, indicating that the two metal components are not well mixed and rather exist in a segregated fashion.

![Figure 2.22](image.png)

**Figure 2.22.** XPS spectra of annealed (a) Mo-on-Fe (0.2/0.4 nm) and (b) Fe-on-Mo (0.4/0.2 nm) catalysts at two incidence angles of 17° and 45°; intensities obtained from the smaller angle possess larger surface contribution indicating closer to the surface, and the corresponding atomic concentrations of Mo and Fe.

The dominant presence of Mo on the surface also explains the very low growth rate observed from the Mo-on-Fe type catalyst. Because of the nature of Mo that is prone to carbide formation, this morphology will be most likely to cause a decrease in an effective carbon flux to catalytically active nanoparticles such as Fe rich Fe-Mo alloys, lowering the growth rate of CNTs. [74, 96]

From the aforementioned observation of larger nanoparticles and lower number density, we finally recognize that, having easily dewettable Fe components dominantly in contact with the Al$_2$O$_3$ underlayer, the Mo-on-Fe configuration could induce an extensive reconstruction of the entire film leading to the formation of large
alloy nanoparticles upon annealing. The strong tendency of forming large alloy particles could also be partly attributed to the surface segregated Mo atoms capable of impeding the cracking and migration of the surface Fe components.

In the Fe-on-Mo type, on the other hand, the particle size enlarged gradually with an increase of the Mo thickness, but the catalyst number density was maintained similar to that of the Mo/Al₂O₃. The pre-deposited Mo atoms cannot bead up on Al₂O₃ as easily as Fe atoms do (Figure 2.20). As the result, the Fe-on-Mo type produces smaller particles than the Mo-on-Fe type does when annealed. Nearly constant particle number density independent of the Mo underlayer thickness and similar to that of the Mo/Al₂O₃ implies that the presence of Mo at the catalyst-support interface can alleviate the fluctuation of entire film. We further observed bimodality in the size distribution of catalyst particles, which tends to be more pronounced in the Fe-on-Mo type and at the high Mo content (Right column of Figure 2.21). The XPS intensity ratio of Fe to Mo did not vary at different incidence angles (Figure 2.22b), which indicates that the Fe-on-Mo type favors stable alloy configurations between the two metal species, unlike the Mo-on-Fe type catalysts. This finding is consistent with the previous description that Mo can choose a metastable core configuration inside an Fe cluster considering excessive strain energy required for Mo to overcome and surface. [158] These observations consequently suggest that our Fe-on-Mo type catalyst could thermally evolve into either Fe-shelled Mo particles or small Fe particles in between Mo particles.

Deposited catalysts are inevitably exposed to air while stored and transferred to the CVD chamber, and if they are not reduced completely, the effect of oxidation could play a significant role in the final catalytic activity. A thin layer of native oxide will be present on the catalyst surface in the forms of FeO/Fe₂O₃ for the Fe-on-Mo type and MoO₃ for the Mo-on-Fe type and may have a certain impact on the evolution of the thin bimetallic film. [176-178] On the other hand, the bottom layer of the stacked metal film can be relatively better protected against the oxidation; according to a previous report, for example, Mo underneath Fe in an Fe-on-Mo stack has maintained its metallic nature even at a severe oxidizing condition. [179] Since all the catalysts of our study were annealed in a low-pressure Ar/H₂
ambient prior to the CNT growth step, Fe oxides could undergo thermal reduction via H\textsubscript{2} assisted O\textsubscript{2} loss while Mo oxides could sublimate (>600 °C) and/or reduce to low oxidation states (>400 °C). We note that there could be other factors influencing the catalyst oxidation state. For example, reduction of Fe oxides may be promoted by the presence of Mo oxides because the reduction potentials of Fe oxides are higher than those of Mo oxides. [114, 180, 181] Also, substantial interdiffusion of Fe and Mo could occur at the interfaces simultaneously, with an alteration in the composition and the distribution of surface metal oxides. [173, 174, 182] A number of studies on bimetallic catalyst systems of the similar kind, X-Mo (X = Fe, Co, Ni), have reported that even after long annealing in a pressurized H\textsubscript{2} ambient a significant amount of Mo tends to remain oxidized on the substrate in the mixed form of MoO\textsubscript{x} (x < 3) and oxidized metal molybdates (FeMo\textsubscript{x}O\textsubscript{y} or CoMo\textsubscript{x}O\textsubscript{y}). [62, 64, 96, 156, 183] They claimed that such oxidized Mo promotes reduction of the neighboring metal and also physically traps the reduced metal particles. In the analogous sense, it can be hardly true that the metal oxides are fully reduced during the CVD process in our growths as well. Relatively low growth efficiency found in this work may be partly ascribed to the partial or incomplete reduction of oxide phase. [183]

It is likely that the stacking order of Fe and Mo could affect how and where such oxide phases form and how they interact with the other components at the surface. For instance, the presence of stable oxide phase at catalyst-support interface may contribute to the suppression of thermally activated surface phenomena such as particle coarsening, thereby narrowing the diameter and distribution of nanoparticles, as observed in our Fe-on-Mo type catalysts while oxides resided on surface cannot restrict the dewetting at the interface and thus allow extensive reconstruction of catalyst particles. Further studies via atomic-level surface analysis techniques performed in \textit{situ} or in a time-resolved manner are desired for an in-depth understanding.
2.3.7 Influence of catalyst evolution on the diameter control of resultant VACNTs

A close examination of VACNTs was carried out using TEM and SEM to verify the catalytic performance of the evolved bimetallic films in controlling the structure of individual CNTs as well as their alignment. The reference, 0.4 nm thick Fe catalyst selectively grew VA-SWCNTs whose diameters constituted a Gaussian distribution between 1.95 and the minimum diameter achieved from pure Fe catalyst, consistent with our observations on the catalyst evolution.

For the Mo-on-Fe type, the diameter range was broad at a low Mo content but narrow and shifted toward smaller sizes at high Mo contents. In the section 2.3.6, the particle size and bimodality increase with Mo content. It is apparent that the large alloy nanoparticles rich in Mo on the skin did not participate in the CNT growth even though they exist in large population. According to several recent studies, carbon flux can significantly affect the diameter distribution of nanotubes. [12, 167, 184] An excessively high carbon flux can overfeed small particles inhibiting their catalytic activities, while too low a carbon flux may be insufficient to activate large nanoparticles. Here, the large alloy nanoparticles skin-enriched with Mo have not only the low catalytic activity for hydrocarbon decomposition but also high demand of carbon influx for supersaturation. Therefore, it is not likely that they can nucleate large diameter CNTs.

For the Fe-on-Mo type, in contrast, the diameter range continued to broaden as the Mo underlayer became thicker, and much larger nanotubes appeared to nucleate at the high Mo content. This tendency is corroborated by the Raman RBM spectra. The Raman G-to-D ratios show fairly high values larger than 8, indicating high crystallinity of CNTs in all cases (Figure 2.24). As pointed out above, having Mo in the core the alloy catalysts could retain their surface activity by breaking hydrocarbon on their Fe skin, thereby allowing the large alloy nanoparticle to nucleate nanotubes. Unlike the Mo-on-Fe type case, the outcome of the thermally induced morphological evolution of the Fe-on-Mo type catalyst can be well reflected in the diameter distribution of the resultant CNTs. Nevertheless, the reduction in the growth rate described in section 2.3.5 suggests that
the presence of large portion of Mo within the alloy nanoparticle could consume carbon significantly prior to its complete conversion to carbide.

Nanotubes composed of more than a single wall showed up in both bimetallic types at all compositions. Unlike the general tendency for Fe catalysts that the CNT wall number depends on their diameter (i.e., small nanotubes tend to be single-walled whereas large nanotubes to be double- or multiwalled), [185] we found out that a large proportion
of the small-diameter subset of the VACNTs were multiwalled. This result implies that the size effect of catalyst nanoparticles on the CNT wall number could be hardly applied to the Fe-Mo bimetallic system. We speculate that the multiphase crystalline structure of an alloy nanoparticle may provide multiple nucleation sites per nanoparticle, and the local variation of carbon saturation within the particle could lead to asynchronous budding of graphitic shells on a particle. [1, 144, 186]

Figure 2.24 Comparison of Raman RBMs and G-to-D ratios obtained from VACNTs grown from (a) the 0.4 nm thick Fe (reference, (b) Mo-on-Fe type, and (c) Fe-on-Mo type of catalysts.
2.3.8 Influence of catalyst evolution on the alignment of resultant VACNTs

We emphasize that not all the nanoparticles present on the substrate are capable of growing the nanotubes. As described above, the bilayered metallic films generate rather inhomogeneous nanoparticles, not only in terms of the size but also of catalytic nature (e.g., atomic composition, oxidation state, etc.) As the result, observable disparities exist between nanoparticles and nanotubes about size distribution (Figure 2.21 and 2.23) and areal density (Figures 2.21 and 2.25). The CNT alignment has been related to the areal density of active nanoparticles based on the crowding effect that, as more catalysts are packed on the surface, CNTs can interact more with neighboring nanotubes and grow aligned vertically. [187, 188] In addition, Bedewy et al. in their recent work have pointed out that the packing density and alignment of collectively grown VACNTs could be influenced by mechanical coupling among CNTs in contact and variable growth rates per CNT diameters. [163]

All the VACNTs grown from bimetallic catalysts were much less aligned, representing lower density, than those grown from the reference catalyst. Nanotubes grown from the Fe-on-Mo type catalysts showed a gradual transition from uniform and wavy aligned structure to partial alignment containing more laterally traversing nanotubes as the catalyst system incorporates more Mo, explained by more nanoparticles becoming inactive at the given CVD condition. This observation agrees well with the above findings that, even though the Fe-on-Mo type catalysts do not drastically change the nanoparticle number density as the Mo content increases, the population of large nanoparticles rich in Mo and thus incapable of nanotube nucleation increases gradually.

On the contrary, the Mo-on-Fe type catalysts showed very poor alignment even at low Mo content, attributed to both (i) the initially very low number density of annealed nanoparticles (Figure 2.21) and (ii) a drastic reduction in the active catalyst population, quite sensitive to a small change of surface Mo content. The latter is consistent with the observation that even at the low Mo content (i.e., Mo (0.2 nm)/Fe (0.4 nm)) the Mo-on-Fe type shows very low growth rates. As a result, only the small size subset of catalysts that evolves
into the form of thinly populated, Fe-rich beads amid Mo-rich alloy nanoparticles could produce VACNTs in the poor vertical alignment.

Figure 2.25. Comparison of the cross-sectional SEM images, revealing the alignments of VACNTs grown on (a) 0.4 nm-thick Fe (reference), (b-d) Mo-on-Fe type, and (e-g) Fe-on-Mo type of catalysts; the relevant surface morphological property of catalysts obtained from the AFM analysis (the areal density of catalyst nanoparticles on annealed samples) is shown in (h) and (i). (Scale bar: 300 nm)
Finally, structural features of individual CNTs are more diversified for the cases of Fe-on-Mo type catalysts (wider variation in diameter and wall number as shown in Figure 2.23), signifying mismatches in their catalytic performance (i.e., nucleate at different time scale, grow with different rate and lifetime, etc.) and mechanical properties (i.e., stiffer with more nanotube walls). Although they must have affected the formation of entangled network and bundling for collective growth of VACNTs, the influence on the morphology of the VACNTs cannot be unambiguously distinguished from the effect of catalytic nanoparticle density, calling for further investigations geared toward the design of a proper catalyst platform and the detailed understanding of the factors governing the morphology of VACNTs.
2.3.9 Summary

Fe-Mo bimetallic nanofilms with different thickness and stacking order are found to evolve into entirely different ensembles of polydisperse catalyst particles and lead to quite distinct growth results. Correlation between the morphological evolution of Fe-Mo bimetallic catalyst system and resultant VACNT structure provided an explanation on how the bimetallic catalysts function in the growth of VACNTs. The morphological evolution of the catalysts is accompanied by the change in their chemical nature (reactivity, threshold for supersaturation, etc.) These differences can directly affect the growth rate and the diameter range of VACNTs. In addition, it is merely a small amount of Mo in the Fe nanoparticle that affects catalyst particle formation in the early stage prior to CNT growth and contributes to narrowing down the CNT diameters. In the Fe-on-Mo type, for example, Mo at low content is observed to suppress the coarsening of catalytic nanoparticles effectively, producing small catalyst particles. In the Mo-on-Fe type, Mo turns the chemical nature of large alloy particles inactive, so that they cannot nucleate large diameter nanotubes. Although more study is needed to comprehensively understand the surface atomic composition and structure of the individual catalyst particles generated from the bimetallic nanofilm, the new findings of this study will help further improve the catalyst design and preparation method.
2.4 Bimetallic Catalyst Particle Formation from a Layered Fe-Mo-Al$_2$O$_3$ catalyst

Parts of this section have been submitted for publication in: S. K. Youn, J. Buchheim, B. Keller, H. G. Park, “Catalyst formation via metallic interdiffusion for the growth of vertically aligned, small-diameter single-walled carbon nanotubes,” 2014

2.4.1 Brief description of section 2.4

Hinted from the findings on the limited dewetting of Fe on Mo type catalyst (section 2.3), a new type of catalyst is developed and found promising to alleviate current difficulties in the mass production of VA-SWCNTs, often using ultrathin metal catalysts. A trilayer stack of continuous Fe, Mo and Al$_2$O$_3$ films can turn to densely packed, catalytic nano-granules, which subsequently produce VA-SWCNTs having wafer-scale uniformity in height and only a few nanometers in diameter. Based on topographical and compositional surface analyses, we elucidate the origin of catalyst formation, that is, metallic thermal interdiffusion throughout the entire stack, resulting in a uniquely granulated alloy structure. Our results lead to significant, and rather counterintuitive, findings that the actual dimension of catalysts for the nanotube growth does not have to be limited by the initial metal film thickness, unlike the conventional catalyst system, and further that the alloyed granulation method from the thick films can promote height uniformity of the nanotubes grown, thereby enhancing scalability and consistency of CCVD.

2.4.2 Motivation: Is an ultrathin catalyst a must for the growth of small diameter VA-SWCNTs?

To selectively and controllably grow VA-SWCNTs, most of methods currently employ CCVD technique and densely packed catalyst nanoparticles prepared by a thin-film dewetting method. That is to say, at high-temperature CVD conditions, internal stresses and defects within the thin metal film can vigorously dewet at the metal-support interface, producing metal nanoparticles at the surface. [189, 190] Since it is well known that catalyst particle size determines the
diameter and wall number of a nanotube, [1, 125] extensive attempts have been made to modulate catalyst thickness and dewetting process conditions (i.e., temperature, annealing, reducing gas, etc.). [71, 166, 191, 192] In particular, preparation of ultrathin metallic films with angstrom precision is an essential prerequisite for the catalytic CVD of a high-quality small-diameter VA-SWCNTs. In such a thin film regime, however, conventional physical vapor deposition (PVD) methods such as electron beam evaporation and sputtering often suffer from the issues of spatial non-uniformity and difficulty in fine control of the film thickness. [155, 193-196]

Recently, synthetic deposition of a Co-Mo bimetallic catalyst on the substrate has yielded a small-diameter VA-SWCNTs, while the catalytic activity decayed rather rapidly with varying the nanotube alignment (density) significantly even along the very short VACNTs. [64] Several alternative routes have been taken to overcome such issues and mass produce catalyst nanoparticles over a large area, such as coating of a catalyst precursor in the liquid phase followed by convective or dendrimer-assisted assembly of premade nanoparticles. [197-201] Although they are potentially scalable, inexpensive, and capable of tailoring the size dispersion and packing density of catalyst particles to some extent, these approaches are not yet applicable to very tiny particles owing to the technical difficulties in their self-assembly modulation.

In this section, to address this issue, we propose a unique catalyst design based on a Fe-Mo-Al$_2$O$_3$ trilayer having a 10-nm-thick Mo layer in between a 10-nm-thick Fe top layer and a 20-nm-thick Al$_2$O$_3$ underlayer. This new catalyst configuration is developed while tuning the chemical composition of catalyst particles during the dewetting of the Fe-on-Mo type bimetallic film. In section 2.3, Mo-on-Fe type bimetallic films are found to generate much larger and more inhomogeneous alloy particles of a high Mo content and Mo-rich surface than Fe-on-Mo type bimetallic films. Thus, it is beneficial to choose the stacking order of Fe-on-Mo type for narrowing down the CNT diameter. However, issues remain in the loss of catalyst activity and resultant CNT packing density by the effect of Mo. [96, 153] Attempting to lower the Mo-to-Fe ratio of alloy particle, the thickness of each metal layer are varied so as to alter the interdiffusion distance and the degree of intermixing. Despite the large total thickness of the
metal film, dense nano-granules evolve during annealing to activate the single-wall-selective growth of carbon nanotubes having only a few nanometers in diameter. The subsurface diffusion causes a significant loss of metal, thereby reducing the effective catalyst size while the Fe-Mo interdiffusion across the interface drives mixing of the two metals, eventually forming and restructuring the catalytically active surface alloy species. Moreover, the VA-SWCNTs resulted from this new catalyst design achieve great height uniformity over the entire 4-inch wafer scale, demonstrating superiority in the process scalability and consistency.

2.4.3 Experimental details: catalyst deposition & CCVD

A trilayer catalyst stack of 10 nm Fe, 10 nm Mo, and 20 nm Al$_2$O$_3$ is sequentially deposited on a Si wafer by electron beam evaporation without breaking a vacuum. The actual thickness of the deposited film is found close to the nominal value within a ± 5-10% error range over multiple runs based on the AFM characterization in-between the depositions of each Fe, Mo and Al$_2$O$_3$ layers. The CCVD of VACNTs is performed in a cold-wall, vertical CVD reactor (Black Magic™, Aixtron) equipped with 4 inch size sample stage for a wafer scale batch production. First, the prepared catalyst substrate is introduced into a CVD chamber preconditioned to 300 °C and the chamber is evacuated to low vacuum (10$^{-3}$-10$^{-4}$ mbar) level. Then, the chamber temperature is raised to a target value (650-850 °C) at a fast ramp rate of 300 °C/min. During the rise of temperature, the chamber is filled with H$_2$/Ar gas and maintained a constant total pressure in the range of 3-5 mbar. For catalyst formation, catalyst substrate is annealed in the same condition for 10 minutes. For CNT growth, carbon source, which is C$_2$H$_2$ in this study, was supplied in addition to the carrier gases. For the process cessation, carbon supply is stopped after 15 minutes and the chamber is cooled down by flowing massive N$_2$ gas. The process for optimizing the CVD parameters for the growth of VA-SWCNT is described in the section 2.4.4.
2.4.4 Optimization of CVD parameters for the growth of VA-SWCNTs from the newly designed 30-nm-thick Fe-Mo-Al$_2$O$_3$ trilayer catalyst

We first defined a growth window of $P_{C_2H_2}$ and synthesis temperature for VA-SWCNTs growth by varying these major parameters over a wide range. CNT type changes from SW- to DW- and TWCNTs with an increase of $P_{C_2H_2}$ (Figure 2.26), and the maximum height as well as the highest Raman G-to-D ratio was obtained at 730 °C (Figure 2.27). Also, high frequency RBM peaks start to appear at and above this temperature. Thus, we adopt the same condition for the following growth experiments, that is, a $P_{C_2H_2}$ of 0.03 mbar (when the total chamber pressure is in the range of 3-5 mbar) and temperature of 730 °C. More information on the catalytic performance at different CVD condition is available elsewhere. [164]

![Figure 2.26. Optimum $P_{C_2H_2}$ condition for the growth of VA-SWCNTs: TEM images of few-walled and SWCNTs obtained at the same CVD temperature of 730 °C but different $P_{C_2H_2}$ of (a) 5 mbar and (b) 0.3 mbar. (Scale bar: 20 nm)]
Figure 2.27. Optimum CVD temperature condition for the growth of VA-SWCNTs obtained at the same $P_{\text{c2h2}}$: (a) temperature versus average height of VACNTs curve shows the maximum growth at 730 °C and also (b) not only low but high frequency RBMs start to appear around the temperature of 730 °C.

Further we tune the CVD process gas composition during catalyst formation and CNT growth steps separately to modulate CNT structures, mainly diameter and wall number. The variations were made by changing the ratio among the flow rates of individual gas components at the fixed total flow rate and pressure. First, gas composition for annealing, in other words, catalyst formation step, is varied as follows while growth gas composition (C$_2$H$_2$, H$_2$, and Ar) remained unchanged: (i) pure H$_2$, (ii) low vacuum (< 10$^{-2}$ mbar), (iii) Ar, and (iv) H$_2$/Ar atmosphere (Figure 2.28). The mean heights (growth duration: 15 minutes) and TEM histograms of resulting VACNTs are shown below (case i, ii, and iii) and those for case iv: “optimum condition for the growth of small diameter VACNTs” are presented in the following section 2.4.5. The mean heights changes drastically and it marks the maximum when annealed in H$_2$/Ar (2:3 in ratio) and the minimum when annealed in pure H$_2$. On the other hand, CNT diameter range shows a slight dependence on the H$_2$ content in the CVD gas, having average diameters of 2.64 nm at 0 % H$_2$ (iii), 2.45 nm at 40 % H$_2$ (iv), and 2.59 nm at 100 % H$_2$ (i), respectively. When annealed in a low vacuum condition without any gas flow, rather large diameter CNTs grow. Finally, the 100 % selective growth of VA-SWNTs can be achieved only with the pure Ar or the H$_2$/Ar (2:3 in ratio) annealing (case iii and iv).
It is unlikely that the annealing gas composition affects the sub-surface phenomena but it mainly influences the surface phenomena. High temperature annealing of metallic catalyst in H\(_2\) atmosphere can have various impacts on CNT growth because the hydrogen species can reduce surface metal oxides and adsorb on the surface with a high concentration. The former can contribute to improve activity and reduce size of catalysts while the latter can facilitate the surface catalytic reaction. [71, 191, 192, 202] For the Fe-Mo-Al\(_2\)O\(_3\) catalyst, a moderate H\(_2\) exposure up to 40 % is found optimum for obtaining smaller and tallest VA-SWNTs with an effect of adequate metal oxide reduction. When overexposed, however, the nanotube diameters begin to increase and broaden. This can be due to activation of large nanoparticles which was formerly covered with metal oxide layer and the small presence of oxide species with low mobilities which can suppress the surface fluctuation, or the alteration of surface process at high surface coverage of H\(_2\) (case i and iv).

On the other hand, the low vacuum annealing resulted in a rather large and few-walled VA-CNTs with an average diameter of 3.37 nm (case ii). This is about 30 % larger than the Ar annealing case (case iii). Since Ar is an inert gas, the only difference between the two conditions is the total pressure imposed on the catalyst substrate: ~10\(^{-2}\) mbar for low vacuum annealing and ~10\(^{0}\) mbar for Ar annealing. It is known that the evaporation rate of surface metallic species depends highly on the chamber temperature and pressure due to saturated vapor pressure of the metal species and gas-phase diffusion of evaporated metals. [203] Hence, one plausible explanation is that the low pressure and high temperature condition during annealing facilitates the evaporation and surface diffusion of metal species, thereby lowering the stability of small catalytic nanoparticles and/or partly increase the Mo-to-Fe ratio on the surface.
Next, we varied the gas composition during CNT growth step while annealing condition is fixed, pure $H_2$ (Figure 2.29). Unlike the variation of annealing gas composition which affects the initial catalyst evolution, changing the growth gas composition can influence the actual carbon flux colliding on the catalyst surface. Much taller VACNTs could grow when the $H_2$-to-$C_2H_2$ ratio ($vi > i > v, vii$) or the actual carbon flux were increased ($vii > i, v, vi$) without sacrificing the quality as indicated by high Raman G-to-D ratio of ~5 (case $vi$ and $vii$). Also, in these cases, the diameter range shifted to larger values without a noticeable broadening. $H_2$-rich gas mixture for nanotube growth, as in case $vi$, can take part in the gas-phase pyrolysis of $C_2H_2$ precursors and therefore alter the actual amount and composition of carbonaceous precursors on the catalyst surface. [164, 204] On the other hand, a high carbon flux can enhance the CNT growth by reducing the induction time for nucleation and accelerating the $C_2H_2$-to-CNT conversion rate, but an excessive supply may kill or deactivate small catalyst particles as it breaks the balance between carbon uptake rate and precipitation rate necessary for the prolonged CNT growth. [184, 205] In this context, the observed shift of CNT diameter to large values can be attributed to the selective growth of large size
catalyst particles at high C flux condition. In other words, for the new trilayer catalyst system, it is also recommended to limit the carbon supply to below a certain value to retain the activities of small catalyst particles as in other catalyst systems.

**Figure 2.29.** Effect of different growth gas compositions on average height of VACNTs after 15 min growths and corresponding TEM histograms and images of CNT diameter and wall-number: while growth gas composition is varied, annealing gas composition was fixed at pure H₂ atmosphere.
2.4.5 Catalyst analysis techniques: AFM, ToF-SIMS, FIB, and TEM

The morphological evolution of the bimetal surface was characterized ex situ using AFM (Asylum Research MFP-3D™) and a supersharp tip with a tip radius of curvature less than 5 nm (Nanosensors™, SSS-NCHR). Images were obtained in the tapping mode with a scan rate of 1 Hz and a cantilever oscillation frequency of \(~279\) kHz for a scan size of \(1 \times 1 \, \mu\text{m}^2\), later processed using the WSxM 5.0 software. [133]

ToF-SIMS depth profiles were obtained with a ToFSIMS5 (IonTof GmbH) equipped with a \(\text{O}_2^+\) primary ion gun for sputtering (0.5 keV, 30 nA, 500 \(\times\) 500 \(\mu\text{m}^2\)) and a \(\text{Bi}^+\) liquid metal ion gun (25 keV, 1 pA, 100 \(\times\) 100 \(\mu\text{m}^2\)) for analysis in static spectra recording and measured in a dual beam mode with alternating sputter/characterization cycles.

The cross-sectional catalyst lamellae for TEM characterization were prepared using a focused ion beam (FIB) milling. The lamellae were thinned down using a \(\text{Ga}^+\) beam at 30 keV and 0.7 nA to 120 nm thickness followed by gentle cleaning and further thinning to 50 nm at 5 keV and 120 nA to avoid \(\text{Ga}^+\) ion implantation into the catalyst layer.
RESULTS AND DISCUSSION

2.4.6 4-inch wafer scale production of small diameter VA-SWCNTs from Fe-Mo-Al₂O₃ trilayer catalyst

Control experiments using an individual metal film (Fe or Mo) with thickness of 10 nm did not show sufficient catalytic activity and nucleation density at this optimum CVD condition addressed in the section 2.4.4. Many previous studies point out that Mo is virtually lowering the conversion rate of carbon precursors in the Fe-Mo system, especially when its atomic content is high. [96, 142, 153] Our result of no growth on pure Mo catalyst corroborates this expectation. For 10-nm-thick Fe catalyst the given carbon precursor flux is too low to saturate the large Fe particles dewetted, resulting in no CNT growth, either. [139, 167]

Figure 2.30. (a) Cross-section SEM images of uniformly grown VA-SWCNTs on the Fe-Mo-Al₂O₃ trilayer catalyst (inset: close-up images near the top and bottom of the forest, scale bar: 100 nm), (b) An optical image of a 4-inch wafer scale growth, (c) TEM diameter histograms, (d) a Raman spectrum and (e) TEM images of the SWCNT.
In contrast, our 20-nm-thick Fe-on-Mo film on the Al₂O₃ support can successfully grow selective VA-SWCNTs with surprisingly small diameters considering the initial film thickness. The state-of-the-art minimum value of the mean diameter for VA-SWCNTs is around 1-2 nm, for example on the Co-Mo catalyst with a tailored composition or a nanolaminate Fe-Al₂O₃. [64, 126] Our 18-μm-tall SWCNTs uniformly grown (Figure 2.30a) on the 4-inch catalyst substrate (Figure 2.30b) have diameters in the narrow range of 2.45±0.85 nm (Figure 2.30c), comparable to those grown from the ultrathin monometallic catalysts. [132] Unlike the previous works, vertical alignment and areal density of as-grown nanotubes are well maintained throughout the entire height of VA-SWCNTs (Figure 2.30a, inset). A high Raman G-to-D ratio (Figure 2.30d) and clean graphitic walls (Figure 2.30e) indicate high quality SWCNTs. From the above evidence, we believe that our catalyst design poses great potential for the small-diameter VA-SWCNTs production in the large-scale batch process.

2.4.7 Mechanism of catalyst formation on Fe-Mo-Al₂O₃ trilayer catalyst

To understand how the 30 nm-thick in total Fe-Mo-Al₂O₃ trilayer catalyst could nucleate and grow VA-SWCNTs of a few nanometers in diameters, we have analyzed thermally induced changes in the surface morphology, composition, and structure of the trilayered catalytic film using AFM, time-of-flight SIMS and TEM. Figure 2.31 shows the AFM images and topography profiles of as-deposited and annealed catalyst samples. The catalyst surface initially has rather smooth morphology with average feature height of 0.81 nm (RMS = 0.51 nm), however after thermal annealing it turns into sharper and densely packed protrusions, or granules, with average feature height of 2.48 nm (RMS = 0.91 nm).
Figure 2.31. Surface morphological change of Fe-Mo-Al$_2$O$_3$ trilayer catalyst: AFM images and height profiles of (a) as-deposited and (b) annealed Fe-Mo-Al$_2$O$_3$ trilayer catalysts (scale bar: 200 nm), showing the transition of the catalyst surface from a smooth continuous state (RMS=0.51 nm) to a roughened state with discrete nano-granules (<3 nm in the average feature height, RMS=0.91 nm).

Taking into account the initial film thickness and presence of the stable Mo interlayer, these nanometer-scale protrusions cannot be originated from the thin film dewetting at the metal-support interface. In order to understand the granulation process, we carried out ToF-SIMS elemental depth profiling of as-deposited and annealed catalyst samples. The result (Figure 2.32) clearly reveals that substantial interdiffusion is occurring within the stacked layers of the Fe-Mo-Al$_2$O$_3$ system. For an as-deposited catalyst sample (Figure 2.32, dashed line), both the Fe ($^{54}$Fe, orange) and Mo ($^{114}$MoO and $^{130}$MoO$_2$, green) signals get weakened at longer sputter times (farther away from the surface) until they disappear at a sputtering time of 600 sec with a simultaneous rise of Al signals ($^{27}$Al and $^{43}$AlO) originated from the Al$_2$O$_3$ support. Note that the signals are collected from surface- to deep level. Because the relative intensity coefficient between Fe- and Mo oxides remains constant during the ToF-SIMS measurement, the secondary ion count data can be used to analyze the interdiffusion phenomenon quantitatively.
Figure 2.32 Surface composition change of Fe-Mo-Al$_2$O$_3$ trilayer catalyst: ToF-SIMS depth profiles of as-deposited (dashed line) and annealed (solid line) Fe-Mo-Al$_2$O$_3$ trilayer catalysts; (a) secondary ion counts of Fe- and Mo-related elements with prominent intensities, and (b) variations in the Mo-to-Fe ratio plotted as a function of sputter time in the log scale.

Signal intensities of $^{54}$Fe, $^{114}$MoO and $^{43}$AlO reach the maximum at sputter times of 20, 55, and 2200 sec, respectively, reflecting the relative distances of the metal species from the surface. After annealing, the width of the detection depth (or sputter time) broadens for all the elements, indicating vigorous atomic diffusion of the metallic and oxide components across their interfaces. In particular, the observed intensity broadening is far more pronounced for Fe than Mo, so that the Fe secondary ion signal diffuses all the way to the bottom of the Al$_2$O$_3$ layer whereas the Mo diffusion is not so obvious (Figure 2.32a). Another observation is that the intensity maximum of Mo-related elements appears at a much shorter sputter time of 23 sec (Figure 2.32a, red arrow), while that of Fe moves little. This behavior hints clear asymmetry in the diffusion speed between Fe and Mo, with Fe diffusing much faster than Mo as previously reported. [173, 206-208] Such interdiffusion should occur via collective jumps of atomic clusters through extended defects and/or grain boundaries, instead of via interstitial diffusion, because the relative atomic-size difference between Fe and Mo is tiny (<10%). [209, 210] We also note that
thermal annealing can change the Mo-to-Fe compositional ratio at the topmost surface (approximately averaged over sputter time of 15 sec) from nearly zero to unity (Figure 2.32b), which suggests that upon annealing the initially pure Fe top layer turns into Fe-Mo alloys to constitute the catalyst composition.

**Figure 2.33.** The catalyst formation via metallic interdiffusion for SWCNT growth: a schematic diagram of catalyst formation from the trilayer stack of Fe-Mo-Al$_2$O$_3$ and corresponding cross-sectional TEM images of (a) as-deposited and (b) SWCNT grown catalyst samples. The initially layered film is observed to merge into the underlying alumina and leave 2-3 nm-sized particles catalyzing the growth of SWCNTs on the surface.

The cross-sectional TEM images of the lamella-cut catalyst samples before and after the growth of SWCNT forests (Figure 2.33) do not only provide further evidence of the extensive interdiffusion but also
manifest severe subsurface diffusion of both metals into the high porosity Al₂O₃ underlayer, which is partly corroborated by the surface-risen ⁴³AlO secondary ion signal (Figure 2.32a). Clearly, for the catalysts after the SWCNT growth, interfaces between Fe, Mo and Al₂O₃ layers are no longer distinguished, and the entire film thickness is significantly reduced from the initial value of 40 nm to around 25 nm (Figure 2.33b). Figure 2.33b also illustrates the formation of bimetallic Fe-Mo alloy catalysts in the morphology of the alloy surface studded with 2-3 nm-sized particles. Vertically sprouting SWCNTs with tethering the particles to their bases (Figure 2.33b, inset) establish the role of these nanoparticles as the catalyst in the CNT bottom growth mechanism.

Consequently, thermal annealing converts the initially thick Fe-Mo-Al₂O₃ trilayer to a Fe-Mo intermetallic film of which topmost surface is granulated with densely packed few-nanometer-thick nanoparticles. It is these nanoparticles studded on the alloy surface that serve as catalysts for the SWCNT forest growth without suffering much from disappearance via subsurface diffusion into the otherwise porous Al₂O₃ underlayer, to which we attribute the height uniformity of the as-grown SWCNTs. The small and uniform nanotube diameters could be related to the suppression of coarsening and ripening (as the merging and alloying across interface improves the layer integrity) as well as to the sluggish solid-phase interdiffusion (for Fe-Mo, 2.13 × 10⁻²¹ m²/s) [209] in comparison with surface migration of metal adatoms (for Fe, 7.2 × 10⁻⁸ m²/s). [211] If the initially thick Fe film would obviate self-granulation through dewetting, metallic interdiffusion process could overwhelm the former surface processes frequently occurring in the ultrathin-film-based catalytic CVD. Further investigation on the detailed mechanism of granulation of the thermally annealed Fe-Mo alloys will open up the new paths to the facile modulation of catalyst dimension and composition, which is the main bottleneck in catalysis applications.
2.4.8 Summary

We presented a trilayer catalyst stack of 10 nm Fe, 10 nm Mo, and 20 nm Al$_2$O$_3$, which is found unique in that the initial catalyst thickness does not primarily determine the diameter of CNT. Thermally driven metal interdiffusion across the interfaces of the trilayer catalyst stack can surprisingly generate a granulated alloy. Catalyst formation via such an alloyed granulation of the thick films can promote height and diameter uniformities of the CNTs grown, which could potentially be even more improved by further investigation. As being free from the common problems often found in the ultrathin catalysts, this new type of catalyst design can resolve the persistent issues of limited scalability and inconsistency of a large-scale CVD process. This result does not only provide a new concept of catalyst preparation for the controlled mass production of SWCNT forests but also inspire us to apply the principle to other catalytic processes for various 1D and 2D nanomaterial syntheses.
Parameter Optimization of CVD Process for Control over the Growth Dynamics and Structural Properties of VA-SWCNTs
3 Parameter Optimization of CVD Process for Control over the Growth Dynamics and Structural Properties of VA-SWCNTs

3.1 Background Knowledge

In addition to the proper selection of material and configuration for catalyst (as discussed in section 2), a deeper understanding on the nature of the CCVD processes influencing the various structural aspects of resultant VACNTs, in particular diameter distribution in this thesis work and adjusting the process parameters to meet the demands of the target application (i.e., membrane based on VACNTs in this thesis work) are also important. There is a great wealth of knowledge about the factors affecting the CCVD growth of CNTs, including carbon-containing feedstock gas chemistry (thermal or plasma treatment, composition, reaction time, etc.) reactor condition (i.e., total pressure, temperature, heating configuration, reactor wall condition, etc.), catalyst treatment (i.e., reducing or oxidizing ambient, plasma, etc.), sample position, existence of growth enhancers (i.e., moisture content, etc.) and other factors. However, not all the CVD parameters have been identified and understood and therefore it still remains as a major subject of research. Current understanding on the relation between the CVD conditions and structural properties in the growth of VACNTs will be scrutinized hereafter.
3.1.1 CVD process variables; incompletely known

Before proceeding to the most influential parameters, it is noteworthy that most of the previous researches in the field of CVD synthesis of nanomaterials were implemented at the laboratory scale and they have admitted the difficulties in reproducing the published results and the process inconsistency even under typical laboratory conditions. For instance, Liu et al. have observed that the carbon deposits (a type of disorder carbon) on the reactor wall accumulated from previous CVD runs are beneficial for increasing the nucleation density in the growth of VA-MWCNTs. The mechanism is speculated that not the carbon deposits themselves but some activated species adsorbed in them may be released during the temperature ramping step of the following CVD runs and promote the catalyst restructuring for the nucleation. [212, 213] On the other hand, Yamaguchi et al. have observed that the residual reactant gases in gas lines and a CVD chamber have a negative influence, reducing the nucleation density as well as the catalyst activity. However, such effect can be prevented by a careful pre-condition of the CVD reactor because the concentrations of residual gases would exponentially decay with time. [214] Moreover, In et al. have argued that even the nominally ultrahigh purity gases contain a trace amount of gas impurities enough to affect the growth drastically and emphasized the necessity of high performance gas purifiers. [215, 216] Recently, Oliver et al. have presented a statistical analysis on the effects of the perturbations in so far uncontrolled variables, which proves that ambient conditions (humidity level and barometric pressure), catalyst substrate position with respect to the gas inlet or the neighboring catalyst substrate, the moisture level in the reactor (which can vary even by the air intrusion into the CVD reactor during sample loading), and even the surface ageing of a quartz tube wall and the material and quality of gas supply line connected to the reactor (whether they are stainless steel or polytetrafluoroethylene (PTFE)) altogether can significantly alter the dewetting process of thin film catalyst and various aspects of CNT growth. [217] Accordingly, several precaution measures of pre-conditioning the CVD reactor for minimizing the perturbation of the aforementioned variables have been taken while implementing all CVD runs throughout this thesis work. Details are addressed in section 3.2.
3.1.2 Carbon precursors

A large number of carbonaceous molecules have been used in CCVD of CNTs but the most commonly used carbon precursors are gaseous molecules such as $\text{C}_2\text{H}_4$ ($\text{sp}^2$ hybridized ethylene), $\text{C}_2\text{H}_2$ ($\text{sp}$ hybridized acetylene) and $\text{CH}_4$ ($\text{sp}^3$ hybridized methane). [218, 219] As seen in the molecular formulas of the carbon precursors contain not only carbon but also hydrogen (in different C-to-H ratios) and are often supplied along with a carrier gas such as inert Ar and N$_2$ or a reducing gas such as H$_2$ and NH$_3$. Therefore, one should always keep in mind the possibilities that these elemental additives can have impacts on gas phase reaction and/or surface catalysis process. The primary aspect for CCVD of CNTs would be whether the conversion of carbon precursors to $\text{sp}^2$ carbon in nanotubes is thermodynamically favored under the given temperature and pressure conditions. This tendency can be seen from the change in Gibbs free energy ($\Delta G_0$).

![Gibbs free energies of formation for the most frequently used carbon precursors for CCVD of CNTs](image)

**Figure 3.1.** Gibbs free energies of formation for the most frequently used carbon precursors for CCVD of CNTs; acetylene, ethylene and methane. The energies are normalized to the number of carbon atoms in the molecule and corresponds to its self-pyrolysis, adapted from ref. [220].
Figure 3.1 shows the difference in the reactivity of different carbon precursors for their thermal decomposition (pyrolysis). Ethylene and acetylene can undergo exothermic decompositions (as seen in the negative value of $\Delta G_f$ at 200 °C), while methane is found very stable at temperatures up to around 600 °C. It means that unless CVD is performed at relatively high temperature or with assistance of plasma, the self-pyrolysis and further conversion of methane in the gas phase can be all neglected. [221] On the contrary, acetylene and ethylene can self-decompose into carbon and hydrogen and produce a large variety of volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs). [222, 223] Empirically, CCVD using the acetylene or ethylene precursor is carried out in the temperature range of 500-750 °C and 650-850 °C, respectively, while the methane based CCVD requires temperatures above 850 °C. [220, 224]

During the CVD process, carbon precursors happen to experience not only thermal but catalyst-assisted decomposition and the conversion equilibriums and temperature will vary depending on the partial pressures of all the gas species involved in the CVD process. For instance, a series of reactions involved in the CVD of CNTs can be simplified as $C_2H_2$ (gas) $\rightarrow$ $2C$ (CNT) + $H_2$ (gas) under the assumption that nanotubes grow from the carbon supplied by the complete decomposition of $C_2H_2$ into graphitic carbon and hydrogen. For this reaction to be spontaneous, its change in free energy should be a negative value: $\Delta G = \Delta H - T\Delta S < 0$, where $\Delta H$ is the enthalpy of the formation and $\Delta S$ is the entropy. The thermodynamic parameters, $\Delta H^0$ and $\Delta S^0$ in the standard state ($P=10^5$ Pa and $T=298.15$ K) per carbon atom of product are given to be -1.18 eV and -0.305 meV/K, respectively. In the practical system, the two gas species are not in their standard states. Depending on the given pressure of the two gas species, $P_{C_2H_2}$ and $P_{H_2}$, the reaction spontaneity will be altered by the relation of $\Delta G = \Delta G^0 + \Sigma n_i k_B T \ln(P_i/P^0)$, where the $n_i$ is the stoichiometric coefficients (negative for reactants and positive for products). Finally, the overall change in free energy can be described as $\Delta G = (\Delta H^0 - T\Delta S^0) - k_B T \ln(P_{C_2H_2}/P_{H_2})$, and one can roughly judge whether the CNT growth reaction is thermodynamically favored under the given CVD condition. [225]
3.1.3 Precursor gas chemistry

The CVD process, in most cases, inevitably involves a pre-exposure of a gaseous carbon precursor to high temperature environment before its arrival at catalyst surface. Also, taking into account the high reactivity of the carbon precursors, it is reasonable to suspect a vigorous gas phase reactions, occurring along with surface catalytic reactions. Nevertheless, due to the limited information about the high temperature gas-phase reactions and difficulties in implementing direct elemental analysis at the extreme conditions, it has been for long believed that the carbon precursor in its intact form adsorbs onto and then dissociates at the catalyst surface or the carbon precursor undergoes complete pyrolysis prior to arrival at the catalyst.

Since a few years ago, there have been attempts to unveil the influence of thermal treatment on thermal rearrangement of carbon precursors and the resulting CNT growth. Linear hydrocarbons such as methane, ethylene and acetylene thermally decompose into atomic carbons or linear dimers/trimers of carbon and are prone to grow high crystallinity CNTs compared to the cyclic hydrocarbons such as benzene, xylene, cyclohexane and fullerene. Meshot et al. and Plata et al. have shown that thermally treated gas mixture of CH4/H2 in a modified APCVD reactor equipped with a separate gas preheating unit contains a broad range of compounds (Figure 3.2a) and led to completely different growth results compared with the conventional single-zone tube furnace. [11, 223] These works provided a hint that some of these gas pyrolysis products are likely important reactants for CNT production, while others are detrimental for growth efficiency and quality control of CNTs. Plata et al.’s following work identified the alkyne types of pyrolysis products (i.e., acetylene, methyl acetylene, and vinyl acetylene) as important precursors but not the previously suspected molecules such as benzene and methane. Based on the observation that ethylene is required along with the alkynes for enhanced CNT growth, they newly proposed metal mediated polymerization-like mechanism of CNT formation, which is described in Figure 3.2b. [226] The next step would be to develop a practical way of exerting control on the gas phase reactions. Recently, Yasuda et al. have introduced dwell time of feedstock gases as one of CVD parameters and reported the strong correlation between the gas dwell time and various aspects of growth results (Figure 3.2c). [13]
Figure 3.2. (a) Analysis data of the product gas mixture from the thermal treatment of C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} (0.2/0.5 atm), adapted from ref. [11]. (b) A scheme of polymerization-like mechanism proposed based on the advantageous role of C\textsubscript{2}H\textsubscript{4} in C\textsubscript{2}H\textsubscript{2}-based CVD for CNT growth, adapted from ref. [226]. (c) The CVD reactor equipped with a gas shower head with adjustable height to modulate the gas dwell time and the obtained linear relation of carbon efficiency to the dwell time, adapted from ref. [13].

On the other hand, Xiang et al. have provided intriguing observation that the two carbon atoms in ethanol do not contribute equally to the formation of graphitic carbons in nanotubes by the use of isotopically labeled ethanol (\textsuperscript{12}CH\textsubscript{3}\textsuperscript{13}CH\textsubscript{2}-OH) as a carbon source. \textsuperscript{12}C is preferably incorporated into the CNT, and this preference is significantly affected by temperature, presence of surface co-catalyst (i.e., Mo) and even by substrate material. This indicates that the carbon precursors and intermediates actively participated in forming the nanotube formation are not only limited to gas pyrolysis products but also other environmental factors which can possibly change the reaction condition or pathway on the catalyst surface. [227] Also note that gas phase reactions are likely assisted by some reactive compounds produced from surface catalysis, since we observe the preconditioning
of the upstream gas by metal substrate promotes the CNT growth on the downstream catalyst substrate. [217] Lastly, several studies have claimed the experimentally obtained activation energy of around 2.6 eV, a value much larger than typical energies for bulk diffusion (1-1.7 eV) and surface diffusion (0.23-0.4 eV) of carbon, which can be attributed to the production rate of active carbon precursors in the gas-phase reaction (namely, rate-determining step). [13, 216]

3.1.4 Acetylene: a key carbon precursor

The use of different precursor varies the relative abundance of various carbon species, potentially altering nanotube growth, which would dictate how the edge of the growing nanotube is attached, or how the carbon species would travel to reach the edge via surface or bulk diffusion. The latter could even influence the dynamic morphological change of the catalyst nanoparticles. Among the diverse varieties of carbon feedstock, acetylene has been considered as the key carbon precursor and even when other types of carbon precursors are used in CVD their conversion to C\textsubscript{2}H\textsubscript{2} is found crucial for SWCNT growth. For instance, Eres \textit{et al.} have suggested C\textsubscript{2}H\textsubscript{2} as a direct building block for CNT formation based on its growth efficiency remarkably higher than other hydrocarbons when they prevented all the possible gas-phase reactions by use of a molecular beam precursor-injection system. [228] Later on, Zhong \textit{et al.} have reported that CH\textsubscript{4}/H\textsubscript{2} mixture gas could grow nanotubes only with assistance of plasma with direct evidence that plasma generate long-lived active species, such as the methyl monoradical or the C\textsubscript{2}H\textsubscript{2}. [228] Sugime \textit{et al.} have also predicted that C\textsubscript{2}H\textsubscript{2} is the key precursor generated from pyrolyzed ethanol for rapidly growing CNTs. They further reported that pyrolyzed ethanol produces few walled CNTs (FWCNTs), while the unheated, intact C\textsubscript{2}H\textsubscript{2} produces SWCNTs, probably due to the superfluous by-products from ethanol pyrolysis. [229] Okasaki \textit{et al.} have used a mixture of \textsuperscript{13}CH\textsubscript{4} and \textsuperscript{12}C\textsubscript{2}H\textsubscript{2} to determine a higher contribution of \textsuperscript{13}C to the final nanotube structure although details of intermediate processes were not obtained. [230] Hence, it is generally accepted that acetylene is preferred for an efficient CVD growth of high quality SWCNTs, which can be further supported by much higher reactivity and sticking probability of acetylene over other carbon precursors.
On the other hand, in the typical CVD reactor where temperature control for gas-phase reaction and surface catalytic reaction cannot be readily and completely decoupled, acetylene molecules are inevitably exposed to extreme CVD conditions (i.e., high temperature, presence of reducing gas, etc.) and thus expected to undergo further extensive pyrolysis, though its potential effect on the CNT growth is known marginally. Acetylene has two outstanding properties: high unsaturation degree and endothermic character. The former enables it to add to itself or to other compound easily, thereby forming a broad range of gas phase reaction products from simple linear molecules to complex aromatic and polymeric chains. The latter tenders it unstable, in other words, very reactive, so that at the elevated temperatures or pressures will vigorously break, rearrange, and combine with others. Egloff et al. have provided a vast amount of information about the high temperature chemistry of acetylene, [231] as summarized in Table 3.1. At the typical CVD temperatures in the range of 600-800 °C, acetylene is prone to polymerize, producing aromatic hydrocarbons with some olefins and paraffins, and its decomposition is insignificant. Several typical pyrolysis reactions of acetylene and their rate constants are provided in Table 3.2.

When catalyst is involved in the pyrolysis process, catalyst can reduce the temperature at which the acetylene molecules begin to polymerize and decompose. For instance, Ni and Pt promote decomposition and hydrogenation, producing large formation of carbon, hydrogen and small amounts of polymerized products. Co and Fe catalysts function similarly though less pronounced. In other words, they tend to assist the decomposition to carbon and hydrogen, but do not prevent the polymerization. Both polymerization and decomposition of acetylene are exothermic reactions and heat produced in this process can be the additional energy source for surface catalytic sites, growing CNTs.
Temperature | Action of Heat (Non-Catalytic)
--- | ---
300-800 °C | - Largely polymerization; maximum at 600-700 °C and decreasing above this temperature  
- Products are aromatic hydrocarbons in great variety, with some olefins and paraffin hydrocarbons  
- Some decomposition to carbon, hydrogen, and methane occurs at the upper portion of this temperature range
800-1000 °C | - Both decomposition and polymerization occur; the former taking ascendency.  
- Considerable amounts of methane and hydrogen form.
T ≥ 1000 °C | - Almost exclusive decomposition but some acetylene exists in equilibrium with the decomposition products at above 1700 °C

**Table 3.1.** A summary of polymerization and decomposition of acetylene in different temperature ranges, adapted from ref. [231].

<table>
<thead>
<tr>
<th>Gas Phase Reactions</th>
<th>Forward Reaction Rate Constant (cm³/mol·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$C_2H_2 + C_2H_4 = 2C_2H_2$</td>
</tr>
<tr>
<td>2</td>
<td>$C_4H_4 + C_2H_4 = C_6H_6 + C_2H_2$</td>
</tr>
<tr>
<td>3</td>
<td>$C_2H_2 + \cdot H = C_2H_3$</td>
</tr>
<tr>
<td>4</td>
<td>$C_2H_2 + \cdot H = C_2H + H_2$</td>
</tr>
<tr>
<td>5</td>
<td>$C_2H_2 + C_2H = C_4H_2 + \cdot H$</td>
</tr>
<tr>
<td>6</td>
<td>$C_2H_4 + C_2H_2 = C_4H_4$</td>
</tr>
<tr>
<td>7</td>
<td>$C_2H_4 + C_2H_2 = C_4H_6$</td>
</tr>
</tbody>
</table>

**Table 3.2.** Typical gas phase reactions of acetylene and their rate constants at 1000 K, adapted from ref. [165].

Ma et al. have deduced that the main reactions with remarkably large rate constants (i.e., reaction 2, 5, 6, and 7 in table 3.2) lead to the
generation of C4 species with high degree of unsaturation. [165] This is related to the unique growth results of the homemade local-heating (LH) CVD reactor in that only when the C2H2/He (carrier) mixture gas were heated enough at high temperatures CNTs could grow in high density, probably owing to the enhancement of polymerization reactions. Presumably, the unsaturated C4 species can be adsorbed with higher sticking probability and their carbon triple bond can be easily opened and coordinated on catalyst surface, eventually added in the form of C2 species to the chain end of growing nanotube. Accordingly, the conversion rate and efficiency are expected to be higher. Also, the asymmetric temperature distribution of this LHCVD reactor was found beneficial to prevent the unwanted gas preheating at too high temperature where amorphous carbon deposits forms, thus improving the CNT quality and process efficiency.

Recently, Gómez-Gualdrón et al. have reported simulation results comparing the CNT growths under two precursor decomposition products: carbon atoms and dimers. [232] According to their findings, if the dimers are the main pyrolysis products their dissolution and carbon association inside the catalyst will be slowed down. Also, in growth stage the dimers can be incorporated into the nanotube end without previous splitting, thus accelerating the CNT growth rate. It suggests that the kinetics of chain elongation and simultaneous self-healing will be altered by the nature of carbon reactant, affecting favorably the quality and terminal height of CNTs.

### 3.1.5 Catalyst pretreatment

Often, CCVD process of CNTs includes a catalyst pretreatment step prior to the growth step. In particular, a supported thin metallic film used for the growth of VACNTs is known to transform into a number of catalytic nanoparticles during this step. As mentioned in section 2.1, the thickness of the metal film and the interaction of the metal with the substrate are critical factors for this dewetting process. However, it is also strongly dependent on the condition of catalyst pretreatment; whether the thin metal film is heated to high temperature for long time or exposed to a specific environment which can alter the physical or chemical properties of the metallic film (i.e., reducing gas, plasma, acid/base treatment etc.).
For instance, 15 min pretreatment of Fe/Al or Al/Fe/Al film in NH$_3$ or H$_2$ at sub-atmospheric pressure (0.6-20 mbar for NH$_3$, 100 mbar for H$_2$) causes restructuring of the catalyst into small nanoparticles suitable for low temperature growth of VA-SWCNTs when C$_2$H$_2$ is later introduced. [233] An exposure to NH$_3$ or H$_2$ gas is known to act as reducing agent for etching initially oxidized Fe surface away. [234] Then, the mobility of metal atoms on the reduced Fe surface becomes higher and the adsorbed gases (i.e., chemisorbed H) and its sub-surface diffusion into the catalyst can contribute to modify surface energies of metallic nanoparticles, affecting the catalyst properties such as surface morphology, carbon diffusivity, etc. [85, 189, 235, 236] H$_2$ is found to require higher pressures than NH$_3$ for the similar effect and catalyst treated under vacuum annealing shows low catalyst activity and larger catalyst particles. One should always keep in mind that these reducing gases can promote the reduction of the catalyst prior to nucleation (reducing the catalyst size and increasing the catalyst activity) but at the same time can reduce gas phase pyrolysis of carbon precursor or enhance the desorption of surface adsorbed or deposited carbon fragments from the surfaces of catalysts. [237-239]

Nessim et al. have experimentally shown the strong correlations of VACNT diameters, areal densities and growth rates to H$_2$ exposure time, which revealed that reducing oxidic Fe to metallic Fe is required for the minimum catalytic activity however excessive reduction is found to accelerate the catalyst coarsening, which is detrimental for the selective growth of small diameter SWCNTs (Figure 3.3a). [240] The most common Fe oxides are in the forms of Fe$_2$O$_3$ (hematite), Fe$_3$O$_4$ (magnetite), and FeO (wüstite) and reduction from the highest oxidation state to metallic state can occur via a two or three steps depending on the temperature and H$_2$ partial pressure (Figure 3.3b). Keeping this in mind, they further provided in depth information about the catalyst oxidation state-how it changes when pretreated in the inert, reductive or oxidative atmosphere (Ar, H$_2$, and O$_2$) for different durations via ex situ XPS analysis. [192] The importance of oxidation state of catalyst particles for the growth of SWCNTs with narrow diameter distribution was again emphasized in Petit et al.’s recent work. [241] The thermal stability of catalyst nanoparticle is observed to vary significantly depending on their oxidation state. For instance, Fe$_2$O$_3$ nanoparticles (stable up to 900 °C) undergo reduction and can be stable on support in the reduced but partially dewetted
form at 700 °C. Above their reducing temperature of 700 °C, however, the fully dewetted metallic Fe nanoparticles increase and broaden in diameters due to their diffusion and coalescence.

![Figure 3.3](image)

(a) Schematic illustration of the evolution of the thin metallic film with increased H\(_2\) exposure; the film is initially in the oxidized Fe form, and an exposure to H\(_2\) leads to the reduction of Fe oxides, the formation of metallic Fe particles, which coarsen over time; adapted from ref. [240]. (b) reduction steps of Fe\(_2\)O\(_3\) to metallic Fe via Fe\(_3\)O\(_4\) and FeO and Bell’s diagram for the Fe-H-O equilibrium at 1 atm showing which Fe oxide is formed at a given temperature and partial pressure; adapted from ref. [192].

Catalyst pretreatment in the reducing atmosphere can be a useful parameter for the structure controlled growth of VACNTs. However, the high susceptibility of thin film catalyst at such condition is still considered to be an issue. Recently, several works have suggested new approaches that can minimize or avoid this problem. For example, the hot filament CVD can produce atomic hydrogen, a highly efficient reducing agent with a minimal influence on catalyst coarsening because H\(_2\) decomposition occurs remote from catalyst. [242, 243] However, the finite diffusion distance of atomic hydrogen once it is produced limits the uniformity and scalability of catalyst surface treatment. As an alternative, Pint et al. found that short exposure (< 15 s) to a small amount of hydrazine (N\(_2\)H\(_4\)) vapor (10 mTorr) leads to
the rapid reduction even compared to the atomic hydrogen and at the low temperature of 350 °C (Figure 3.4a). [244]

Figure 3.4 (a) Rapid and uniform catalyst reduction by the use of hydrazine vapor in conventional CVD system and plan-view TEM images of the Fe (0.5 nm)/Al₂O₃ catalysts, as deposited and pretreated with hydrazine vapor: the rapid reduction with hydrazine results in a particle size distribution closely correlated to the starting particle size distribution; adapted from ref. [244], (b) Strong influence of acid-base character of the Al₂O₃ support surface on the rearrangement of carbon precursor on surface reactive sites and thus the growth efficiency of VACNTs; adapted from ref. [245].

On the other hand, one can employ a destructive method of physically roughening the catalyst surface by plasma treatment or a chemical method of altering the acid-base properties of catalyst surface. Zhong et al. have shown that O₂ plasma treated catalyst support becomes denser and highly oxidized, thus remarkably enhancing the stability of thin metal film catalyst and the densification of CNT nucleation. [126] Also, they reported that catalyst pretreatment with carbon containing plasma (C₂H₂/H₂) leads to the deposition of a thin carbon layer on catalyst surface, which assist maintaining the size of catalyst nanoparticles by lowering their mobility and improving the catalyst reactivity and areal density of CNT nucleation. [246] Margrez et al. investigated the effect of chemical treatment of catalyst by changing
the surface pH in the range of 4 to 12 sing HCl and NH₄OH solution. They observed growth enhancement for the basic catalyst but growth deterioration for the acid catalyst. They attempted to understand the intriguing phenomena in relation to the possible changes of carbon precursor occurring on the catalyst surface. In other words, basic sites on the surface can catalyze the aromatization of carbon precursors, thereby promoting the CNT growth while acid sites assist to generate large and more branched molecules of unsaturated hydrocarbons (Figure 3.4b). [245]
3.1.6 Temperature and gas pressure

Temperature and pressure are the two key variables in the CCVD synthesis of CNTs. Optimal temperature and pressure would be different with respect to the target of the CNT growth (fast growth rate, small diameter, high crystallinity, vertical alignment, etc.) and also depending on other CVD parameters (carbon precursor, reactor type, catalyst pretreatment, water additive, etc.).

The temperature window for CNT growth shifts to higher value when more thermally stable carbon precursors (i.e., CH$_4$ over C$_2$H$_2$ or C$_2$H$_4$) are used. [224] However, the general growth behavior exists. The CNTs grow faster with an increase of temperature due to the thermal activation of catalyst (accelerating catalytic decomposition of carbon precursor) and the enhanced diffusion process on/inside catalyst particles. [162, 195, 247] Beyond the optimal temperature for the maximum growth rate, growth rate starts to rapidly decrease. The growth deterioration is often related to the catalyst deactivation via subsurface diffusion of surface metal atoms and particle coarsening on the catalyst surface. [116, 117] Or, catalyst poisoning by the carbon deposits generated from excessive gas pyrolysis could also be the origin. Accordingly, the growth rates or the average heights of VACNT structure after short growths (to rule out the temperature effect on catalyst lifetime) show a bell-shaped curve over temperature (Figure 3.5a).

This temperature dependence of VACNT growth rate can be described in an Arrhenius plot, which allows the determination of the activation energy ($E_a$) and the rate limiting step of the overall CNT growth process under a given condition. Here, the CNT growth rate at a given temperature is in general the average steady-state growth rate or the initial growth rate at the very early stage of VACNT growth. It is noteworthy that here the growth rate is not of the individual nanotube but the microscopic structure of the VACNTs whose growth dynamics are inherently different. [248, 249] Earlier studies have shown that CNT growth rate can be limited by the gas phase diffusion of feedstock and pyrolysis products, [250, 251] surface catalytic reaction, [162] bulk or surface diffusion of carbon containing species (Figure 3.5b). [85, 236]
Figure 3.5 (a) A typical bell-shaped curve of the average height of VACNTs and growth temperature; adapted from ref. [247], (b) Schematic of possible rate-limiting reactions in the overall CNT growth process.

Figure 3.6 summarizes the growth rate as a function of reciprocal absolute temperature for various CCVD grown VACNTs reported in the literature. Gas phase diffusion is typically a very rapid process with very lower activation energy. Therefore it is unlikely that the mass transport of gas molecules limits the CNT growth from the fully accessible surface of the catalyst particles at the early stage of growth but can be crucial for the growth deceleration that is sometimes observed in the relatively long and dense VA-SWCNT structure. For so long, the bulk or surface diffusion of carbon has been generally accepted as the rate-limiting step. However, the strong pressure dependence of the growth rate observed in many following studies
support that the growth process cannot be solely dictated by the carbon diffusion processes but also partly limited by the catalytic reaction process involving precursor gas as a reactant. [162]

**Figure 3.6** Arrhenius plots of the various CCVD growths of VACNTs from literature showing a broad range of activation energies; surface diffusion limited growths of carbon nanofibers with Fe, Co, and Ni catalyst ($E_a = 0.25, 0.30, \text{and} 0.36 \text{ eV, gray lines}$) [85], bulk diffusion limited growths (green lines) of SWCNTs ($E_a = 1.48 \text{ eV}$) [252] and MWCNTs ($E_a = 1.10 \text{ or } 1.59 \text{ eV}$) [134, 253], diffusion and reaction limited growths (blue lines) of SWCNTs ($E_a = 0.9 \text{ and } 1.07 \text{ eV}$) [162], gas phase reaction limited growths (pink lines) of SWCNTs ($E_a = 2.42-2.96 \text{ eV}$) [13, 254] and MWCNTs ($E_a = 2.64 \text{ eV and } 1.22-1.85 \text{ eV which varies with the gas preheating temperature}$) [11, 216], and some more data from Puretzky et al. ($E_a = 1.87 \text{ eV}$)[195] and Bronikowski et al.’s reports ($E_a = 2.02 \text{ eV}$). [255]
The typical activation energies for the bulk and surface diffusion of carbon are in the range of 1-1.7 eV and 0.23-0.4 eV, respectively. [85, 162] The activation energy for the surface catalytic reaction varies depending on the reactant types; which carbon precursor and metal catalyst are used. For acetylene and Fe catalyst combination, the heterogeneous decomposition of acetylene is reported to be first order reaction with an activation barrier in the range of 1.13-1.85 eV [134, 256, 257] whereas for ethylene and Fe catalyst combination the activation energy becomes slightly higher around 2.0 eV. [258] In addition, several recent studies proposed the gas phase reaction of feedstock generating carbon precursors of high activities as rate limiting step for the CNT growths show relatively high activation energies in the range of 2.6-2.8 eV although the relevant reaction has been specified clearly yet. [13, 216, 254] For ethanol based CVD, the activation energy calculated for the decomposition of ethanol into ethylene is ~2.7 eV and it is comparable to the experimentally obtained values by Picher et al.; 2.8 eV for Ni and 2.4 eV for Co). [254, 259] Similarly high activation energies are also observed in ethylene based CVD and water-assisted supergrowth that are assumably attributed to the gas phase reaction transforming the ethylene to acetylene via pyrolysis process. [13, 216]

Besides the growth rate, growth temperature influences the nanotube quality or in other words defect density (often, indicated by Raman G-to-D ratio). Note that both defects in the nanotubes and defective carbon byproducts (i.e., a-C) contribute to the D band in the Raman spectra of CNTs. The higher the temperature, the more energy is available to thermally anneal defects and produce fewer defects. On the other hand, slower growth rate at lower temperature can provide more time to heal the defects. [260, 261] Besides, excessive pyrolysis of feedstock at high temperatures can promote the co-deposition of defective carbon impurities. Thus, the highest quality can be achieved at the temperature where all these thermally activated processes are optimally balanced. Several researches have reported experimental results that the G-to-D ratio increases with increasing temperature until an optimal temperature, then saturates and finally decreases at higher temperatures. [262, 263] Further, Picher et al. observed that the G-to-D ratio follows an Arrhenius law with activation energy of 1.2 eV for Co and 0.9 eV for Ni in ethanol based CVD growths. [254] This low activation barrier can be attributed to the catalyst assisted
annealing of the defect at the catalyst-nanotube interfaces whose activation energy is calculated to be around ~1 eV. [264] Yuan et al.’s simulation results support this finding and they also showed that the most often use Fe has lower activation barrier for defect healing compared to Co and Ni. [261] Vinten et al.’s recent work reported the similar experimental data ($E_a = 0.82$ eV) and further proved that the mechanism responsible for the temperature dependence of G-to-D ratio is independent of the source gas, concentration, and catalyst thickness while that of CNT growth rate differs with these parameters. This implies again that defect density is dictated by a single process intrinsic to the formation of nanotubes. [225]

Next, the shift to larger diameter CNTs with broader distributions with an increase of temperature has been reported in various CCVD processes, not being very specific to one particular catalyst or source gas. [127, 265-267] In contrast, Kwok et al. showed that higher temperatures grow CNTs with both large and small diameters, while lower temperatures grow CNTs with intermediate diameters. [263] Taking into account the strong correlation between the diameters of CNT and catalyst nanoparticle (as discussed in section 2.1.5), one potential explanation for the observed diameter dependence is the thermal activation of the morphological evolution of catalyst particles. Many studies including Sakurai et al.’s recent work have revealed that catalyst nanoparticle formation is combinatorial result of vertical diffusion into subsurface and lateral diffusion processes on surface of the metallic atoms. [116] High temperatures increase the diffusivity and surface mobility of metal adatoms. The former makes the particle size smaller and areal density lower while the latter makes the particle size larger and broader (if migration-agglomeration is dominant) or bimodal distributed by the emergence of both smaller and larger particles (if Ostwald-ripening is dominant). Another viewpoint is the thermodynamic stability of the nanotube or nucleation cap at the given temperature. [268] The strain energies of CNT lattice and cap are curvature (diameter) dependent; the smaller the diameter, the higher strain energy needs to be overcome and thus has the higher energy of formation. In other words, small diameter CNTs would grow more at high temperatures.

Another key parameter in the CCVD synthesis of CNTs is pressure of the process gas, in particular the partial pressure of carbon precursor.
The growth rate increases proportionally to the precursor pressure although some reported the linear relations [162, 216] and the others observed the gradual saturation of the growth rate above a certain precursor pressure (Figure 3.7). [254, 269] In the latter case, the transition occurs at higher pressures when the CVD temperature is increased.

![Figure 3.7](image)

**Figure 3.7** The precursor pressure dependence of CNT growth rate; (a) a power law relation ($P^{0.61 \pm 0.03}$) found from the acetylene based CCVDs, adapted from ref. [162] and (b) a saturation behavior at high precursor pressures observed in the ethanol based CCVDs, adapted from ref. [269].

The precursor partial pressure effect should be considered in the gas phase diffusion and reaction processes as well as the surface catalytic decomposition of feedstock (Figure 3.5b). The linear relation at low partial pressures indicates that CNT growth is limited by the mass transport of feedstock and pyrolysis product gases while the saturation behavior at high partial pressure is attributed to the surface catalytic process. The transition between the two regimes may occur because the surface process becomes limited by adsorption processes upon high surface coverage at high precursor pressures. Such explicit pressure dependence strongly support that the growth process cannot be solely limited by the simple surface or bulk diffusion process that are supposed to be gas pressure independent.

Similar to the temperature effect, high precursor pressure which increases the growth rate tends to produce more defective CNTs with larger diameter and even higher wall numbers. CNT growth at low growth temperature and high precursor pressure suffer from the
formation of low crystallinity nanotube and co-deposition of defective carbon byproducts. Also, the smaller catalyst nanoparticles (thus, more catalytically active) can be readily over coated and thus CNT growth from these nanoparticles cannot be achieved. [167] It agrees well with the Hasegawa et al.’s work that the key for efficient growth of VA-SWCNTs is to keep the carbon supply sufficiently high to allow the process to be thermodynamically allowed but limit below a certain level to retain the activity of small catalyst particles. [12] A schematic shown in Figure 3.8 summarizes well the combinatorial effects of temperature and pressure on the diameter distribution of CNT. [265]

Figure 3.8 The combinatorial effect of temperature and precursor pressure on the diameter distribution of resultant VACNTs, adapted from ref. [265].
3.2 Description of Thermal CVD System

All CNT growths throughout this thesis work were performed in cold-wall, vertical-flow CVD reactors with 4 inch or 6 inch sample stage (Black Magic™, Aixtron). The details of the reactor are described in Figure 3.9. The effective volume of this CVD reactor is calculated to be 390 or 930 cm$^3$. (d=110 mm for 4 inch reactor or 170 mm for 6 inch reactor and H=4.1 cm) For heating, there are two thermocouples (graphite disc) equipped underneath the gas showerhead (top heater, TH) and the sample stage (bottom heater, BH). The two heaters communicate with each other to reach the target temperature set by the user and aim to heat the effective volume in between instead of the entire chamber; a cold-wall reactor. Temperature control beyond 550 °C was tuned based on the surface temperature of sample stage, in situ measured by infrared pyrometer with an accuracy of ± 6 °C using the two wavelength ratio method.

The process gases were pre-mixed and released to reactor through a gas showerhead from top to bottom direction (parallel to the growing nanotubes). As shown in Yasuda et al.’s work, a gas shower system can improve the uniformity and efficiency of CNT growth and process consistency. [270]

Figure 3.9 A cold-wall, vertical-flow CVD system (Black Magic™, Aixtron) used throughout this thesis work and a schematic representation of the actual CVD reactor
The major parameters of CVD process (i.e., total chamber pressure ($P_{\text{total}}$), flow rates of process gases and step time of temperature ramping, catalyst pretreatment, CNT growth, etc.) were software controlled and real-time monitored. The allowed operating pressures and temperatures are in the range of $3 \times 10^{-2}$ (limited by the connected vacuum pump capacity)–$0.8 \times 10^{3}$ mbar and up to 1000 °C. For varying only the process gas composition, one can set the ratio between the gas flow rates while maintaining the total gas flow rate and chamber pressure. For varying the only the partial pressure of a certain gas component, one can increase the flow rate of a carrier gas as much as the difference in total gas flow rate before and after lowering the flow rate of interested gas while maintain all the other conditions. These are the simplest approaches to tune the parameter without affecting other conditions such as gas dwell time and partial pressure of other gas component.

Most researchers use the APCVD system composed of a 1 inch quartz tube placed inside a high temperature furnace because they are low-cost, easy to set up and operate, and does not require a clean room environment. However, at the same time, this set-up increases the risk of process variation, unless sources of variation are understood and appropriately controlled. Compared to this APCVD system, our reactor conditions are better isolated from the external environment and can be accurately controlled. Also, several steps of reactor pre-conditioning were performed for improving the process repeatability every time before the new CVD run. First, chamber was heated using both heaters at temperature around 900 °C for 30 min under hydrogen atmosphere. Second, when cooled down to around 300 °C under vacuum, the chamber was vented and catalyst substrates were loaded as quickly as possible to prevent chamber contamination by in particular ambient moisture. Third, the temperature for loading and process starting were strictly controlled to be around 300 °C and 250 °C. We learned that both influence a lot the growth results. Lastly, the first run of the day was considered invalid due to the inconsistency in growth results observed frequently. We assume that the chamber condition may be different in case of the first run by being under vacuum overnight.
3.3 Temperature Gradient CVD (TGCVD)

Significant portions of this section were published in: S. K. Youn, C. E. Frouzakis, B. Pagadala Gopi, J. Robertson, K. B. K. Teo, H. G. Park, “Thermal gradient chemical vapor deposition of vertically aligned carbon nanotubes,” Carbon 2013, 54, 343-352 [164]

3.3.1 Brief description of section 3.3

This section presents the growth results of VACNTs in a TGCVD reactor that is newly designed to control the precursor gas pyrolysis. Two heaters on the gas inlet and catalyst substrate sides of a cold-wall, vertical CVD reactor can independently be operated to modulate the temperature distribution inside the chamber and thereby the thermal histories of feedstock gas. It is found that such a precursor thermal history clearly affects the growth efficiency and structural properties of VACNTs. Speculatively, several gas thermal zones that are particularly important to the VA-CNT growth are recognized while evaluating the precursor dwell time in different zones and correlating it with the growth results. Thermal treatment of acetylene precursor at 600-700 °C is found crucial for the growth of VACNTs. When this thermal zone is conjoined in particular with a zone >700 °C, SW and DWCNTs are grown in more aligned structure and taller. These gas thermal zones can contribute to the VACNT growth by mixing various gas phase reaction products with intact acetylene, corroborated by the results of our reacting flow simulation. These findings emphasize the influence of gas phase reactions on the VACNT growth and suggest that TGCVD approach can be practically utilized to modulate complex gas phase phenomena for the controlled growth of VACNTs.
3.3.2 Motivation: does precursor gas chemistry have an impact on the growth of VACNTs in acetylene based CVD?

Most investigations of CNT synthesis by CCVD have assumed that the reactions involved during the initial stages of the CNT growth occur as simple dissociative adsorption of hydrocarbon on the catalyst surface followed by surface and/or bulk diffusion of the reactants. [162] Gas phase reactions of feedstock gas, however, should also be recognized as an important factor in the CNT synthesis because feedstock gas can produce not only carbon atoms but various secondary pyrolysis products, which can participate in the growth. Indeed, hydrocarbon pyrolysis at high temperatures is known to generate a complex mixture of VOCs and PAHs. As addressed in section 3.1.3, several research groups have proven the positive effect of having gas preheating zone prior to the CNT growth reactor and increasing the dwell time of carbon precursor. [11, 13] However, it was ambiguous whether this finding is directly applicable to typical CVD setup and conditions universally.

Moreover, all these recent studies have focused on ethylene as the precursor [11, 13, 226, 271] and there has been lesser work in the study of such phenomena in the acetylene-based CCVD. [165] Several works have observed that carbon precursors such as ethylene and ethanol are eventually pyrolyzed to acetylene, which seems to function as a key precursor for CNT growth. [228, 229] Acetylene is known to very active and undergoes vigorous pyrolysis process at high temperature and pressure condition. Resultantly, it can supply various decomposition and polymerization products such as hydrogen, ethylene, vinyl acetylene and methane together with the intact acetylene. Of course, the amount and composition of the pyrolysis product gas mixture vary depending on CVD parameters such as temperature, pressure, gas dwell time, and feedstock composition. [272-274] Therefore, an influence of acetylene pyrolysis should be taken into account in understanding the acetylene-based CVD of CNTs.

Recently, Ma et al. have reported that thermal treatment of acetylene at temperature above 600 °C enhances the CNT growth, assumably due to the generation of unsaturated carbon chains in the form of
vinyl acetylene (C$_4$H$_4$). [165] However, a deeper understanding of the effect of acetylene precursor gas chemistry on the CNT synthesis has not been achieved due to the complexities and difficulties in controlling and analyzing the multiple gas-phase reactions. To further investigate this issue, we devised a new CVD system which allows the acetylene precursor to experience different temperature gradients while flowing vertically across the reactor. This TGCVD reactor allows us to tailor gas phase reactions for a controlled and enhanced growth of VACNTs. Temperature profiles in the gas phase inside the CVD reactor were simulated and experimentally checked to accurately verify actual temperature condition by using the segmented thermal zones and the gas dwell time in each of them. Gas phase reaction products of acetylene precursor were simulated on such obtained gas temperature profiles over the temperature window of CNT growth. A comparative analysis of growths under various thermal gradients and its correlation to the simulation result of gas pyrolysis products provide hints about the primary and secondary pyrolysis products and their effects on the growth enhancement and structure control of VACNTs.
RESULTS AND DISCUSSION

3.3.3 Temperature distribution of the gas phase

First, we performed a thermal flow modeling of the TGCVD reactor used in this study using a commercial computational fluid dynamics software (CFD-ACE + v2010) based on finite volume method [275], solving the reactor heat transfer on a two-dimensional axisymmetric reactor configuration, reflecting the cylindrical symmetry of reactor as described in section 3.2. A gas mixture of Ar and H\textsubscript{2} was simulated with temperature dependent material properties, while acetylene was ignored, since its concentration was negligible compared to the other two gases. Note that the feedstock gas was a mixture of Ar (300 sccm), H\textsubscript{2} (200 sccm) and C\textsubscript{2}H\textsubscript{2} (5 sccm). Monte-Carlo ray tracing was used to calculate the thermal radiation, considering the surface to surface radiation heat transfer across various boundaries (transparent, semi-transparent and opaque walls). We did not treat the gas mixture as a participating medium in the thermal radiation modeling, which did not affect the obtained temperature profiles. Onset of free convection is unlikely in our geometry and flow and thermal conditions.

Secondly, such obtained temperature profiles were used to carry out a reacting flow simulation. We employed SPIN program (version 3.83) [276] to numerically study the effect of the heating mode on the gas composition in the TGCVD setup. The CVD chamber was modeled as a one-dimensional system. The comprehensive reaction kinetic model for ethylene involving reactions of acetylene was employed [277] and the oxygen-containing reactions were excluded with an assumption that unwanted reactor contamination by moisture or any other oxygen source from environment were strictly controlled during the experiments. The major gas phase reactions chosen for the modelling were 199 reversible reactions of 45 participating species. Although SPIN program can also account for surface catalytic reaction kinetics, heterogeneous reactions were not considered in this work. The code computes the thermodynamic properties, reaction rates and transport coefficients at the mixture averaged level using the Chemkin package and transport library. [278, 279] The boundary conditions were as follows: at the shower head, the mole fractions of the reactants were fixed (acetylene: 0.0099, hydrogen: 0.3960, argon: 0.5941) and the bulk axial inlet velocity was obtained from the volumetric flow rate of
the incoming mixture at the given growth temperature and chamber pressure (480 mbar) and flow area of the shower head; the substrate is assumed to be non-reactive and zero flux boundary conditions are imposed on the species. Figure 3.10 shows the three heating modes of the TGCVD reactor, which can be made by independently turning on and off the top and bottom heaters.

Figure 3.10 A schematic of three temperature control modes for the gas phase in a TGCVD reactor; the red zone is hotter than the yellow zone and the gradual color gradients indicate continuous temperature change.

As shown in Figure 3.11, the simulated values are found to be more valid representation of actual catalyst temperature than the measured one due to significant measurement error caused by the bottom surface reflection of the top heater thermal irradiation and thus chosen for further discussion.

The simulated temperature gradients of the TGCVD reactor under the three heating modes are provided in Figure 3.12. In the BH mode, precursor gases could gain sufficient thermal energy for gas phase reactions only near catalyst substrate and when the set temperature of bottom heater ($T_{BH}$) is high. In the TH mode, the gases happen to flow through thermal zones hotter than the catalyst substrate, and the substrate is indirectly heated by thermal radiation from the top heater. Given the identical catalyst temperature ($T_{catalyst}$), it is likely that the gas precursors in the TH mode experience much higher temperatures than in the BH mode and therefore vigorous gas phase chemical transformation would occur. Lastly, in the BTH mode ($T_{BH} = T_{TH}$),
reactor temperature shows almost uniform distribution and thus the gas phase reactions would occur as a nearly isothermal process, similar to the case of conventional hot wall reactor.

![Graph showing temperature comparison between measured and simulated data for BH, TH, and BTH heating modes.](image)

**Figure 3.11** Comparison between in situ measured and simulated temperatures on catalyst surface under the different heating modes of BH, TH and BTH; experimental data are well-fitted to the simulated data in BH mode. The discrepancies between the experimental and simulated values in the cases of TH and BTH mode are due to the intrinsic tolerance of the IR pyrometer and the significant error in measured values caused by the bottom surface reflection of the top heater thermal irradiation. In order to avoid confusions arise from the ambiguity of experimental value for substrate temperature, we took our simulation values as valid representations in the further discussion hereafter.
Figure 3.12 Simulation results of gas phase temperature distribution in a TGCVD reactor; (a) BH, (b) TH and (c) BTH mode; the numbers in legends next to the heating mode indicate the temperature of catalyst substrate ($T_{\text{catalyst}}$) where the CNT growths occur.
3.3.4 Growth of VACNTs via TGCVD process

All CNT growths for the following comparative study were performed in the same process condition using the same catalyst prepared at a time; 1.5 x 1.5 cm² size pieces of Fe (10 nm)-Mo (10 nm)-Al₂O₃ (20 nm) trilayer catalyst were used. The details about this catalyst are given in section 2.4. Catalyst samples are loaded at 300 °C and heated from 250 °C to the growth temperatures in the range of 500-800 °C for 5 min (cold wall condition) under H₂ (200 sccm)/Ar (300 sccm) atmosphere at the chamber pressure of 480 mbar. After additional 5 min for catalyst annealing, C₂H₂ (5 sccm) is added. After 15 min growth, the flows of C₂H₂ and H₂ are stopped for growth cessation and the chamber is cooled down in Ar atmosphere.

![Figure 3.13](image)

**Figure 3.13** Plots of the average heights of VACNTs grown for 15 min in BH, TH and BTH modes and Raman G-to-D intensity ratios with respect to catalyst substrate temperature; temperature windows for the growth of VACNTs of the three heating modes lie in different temperature ranges and only overlap in 670-700 °C. Solid and dashed lines in the right plot are guidelines.

Figure 3.13 presents the average height and the Raman G-to-D ratio of VACNTs grown for 15 min in TGCVD reactor under three temperature gradient modes-BH, TH, and BTH. It is observed that temperature window for the growth of VACNTs varies depending on
the heating mode. Whereas the growth window was similarly ranged for BH and BTH modes, which also overlaps with the temperature range found in the conventional thermal CVD, it became wider and shifted to low temperature for TH mode: i.e., 670-775 °C in BH and BTH (ΔT_{catalyst} = 105 °C) versus 535-700 °C in TH modes ((ΔT_{catalyst} = 165 °C). Note that we only accounted for the growth of VACNTs in Figure 3.13, excluding the growth of sparse networks of CNTs occasionally found outside the temperature window. Such differently ranged growth windows indicate that thermal treatment of the precursor gases in a TGCVD chamber influence the growth results, most likely by altering the gas composition via thermally driven gas phase reactions.

The Raman G-to-D ratio of VACNTs representing the crystallinity and the presence of α-C is positively correlated with the height data in cases of BH and BTH modes whereas it increases monotonically with temperature in case of TH mode. Observed disparity in G-to-D ratio at two different laser excitations (532 and 785 nm) can stem from the intrinsic limitation of Raman spectroscopy of a bulk VACNTs in that a Raman spectrum can mainly reflect the features of only those CNTs in resonance with a given laser excitation. [280, 281] In other words, such discrepancy may hint a presence of a considerable variety in the CNT structures in the VACNTs grown as a bulk. In the same manner, relatively little differences seen for CNTs grown in BH and BTH modes indicate rather uniform qualities of those CNTs.

The average height of VACNTs grown in BH mode follows a common trend: viz. the VACNT height increased, peaked and decreased with respect to temperature. [153, 162] At T_{catalyst} of 725 °C in the BH mode, we obtained the tallest VACNTs with the highest G-to-D ratio. This condition is regarded to be an optimum at which the carbon influx to the catalyst from the gas phase is well balanced with their catalytic conversion into CNTs. The clear differences in the growth results of BH and BTH modes evidence the effect of the temperature gradients in the gas phase during CVD process. In detail, BTH mode growth at T_{catalyst} of 720 °C resulted in the VACNTs of far shorter height and lower quality than the BH mode growth at the same T_{catalyst}. We correlate this disparity to the gas heating condition that renders the process gases dwell only in a narrow temperature range above 720 °C in the BTH mode, which possibly leads to different reaction pathways.
for precursors in the gas phase. The growth results of the TH modes showed a very different trend from the other two heating modes. One important observation is the shift of temperature window for VACNTs growth to much lower temperature. The TH mode growth began as low as 535 °C and also the growth window is about a 60 °C wider. Moreover, temperature dependence of average height and G-to-D ratio showed noticeable differences compared to that of BH and BTH mode; viz. three domains with the two local maxima at $T_{\text{catalyst}}$ of 565 °C and 640 °C in the average height-temperature curve and also three domains indicated by discontinuous guideline in the G-to-D ratio-temperature curve. These piecewise curves of the TH-mode growth could refer to the distinct aspects of catalyst evolution at different catalyst temperature, coupled with gas phase reaction products generated at much high temperatures than in other heating mode.

### 3.3.5 Structural properties of TGCVD-grown VACNTs

RBM$s$ ($\nu=300$ cm$^{-1}$) in CNT Raman spectra is inversely proportional to the tube diameter. We observe three different types of RBM peak distributions (Figure 3.14); type I: two primary bands centered around 231 and 136 cm$^{-1}$, type II: one dominant band around 231 cm$^{-1}$, and type III: several bands composed of pair peaks of which intensities weaken at higher frequencies. The TEM images (Figure 3.15) reveal that samples showing the type I RBM distribution consist of mostly SW- and DWCNTs with a bimodal diameter distribution. The type II RBM distribution represents a mixture of SW- and DWCNTs with a negligible amount of TWCNTs. Lastly, samples showing a type III RBM distribution dominantly contains MWCNTs.

Findings from Figure 3.14 and 3.15 are summarized as follows; (i) all growths in BTH mode consistently resulted in the type III RBM peaks and mainly MWCNTs except small changes in the ratio of wall number population, (ii) albeit having similar VACNTs’ growth window as BTH mode, BH mode growth showed a transition in the RBM type from type III (MWCNTs) to type I (a mixture of SW- and DWCNTs) at $T_{\text{catalyst}}$ around 710-725 °C. As $T_{\text{catalyst}}$ was increased, CNT structure turned toward lower wall number and wider, bimodal diameter distribution, which is attributed to catalyst evolution such as surface migration and Ostwald ripening. (iii) TH mode growth
showed double transitions in RBM profiles, one from type III to type II at $T_{\text{catalyst}}$ around 535-565 °C and the other from type II to type I at 610-640 °C. As $T_{\text{catalyst}}$ was elevated beyond 610 °C, nanotube diameters slightly broadened in a bimodal way. Such transitions from MWCNTs to SW- and DWCNTs can be attributed to an action of gas preheating and catalyst evolution at high $T_{\text{catalyst}}$. \[117, 139, 156\] From the above observations, we found an interesting trend that CNT type transitions accompanied by an appearance of local maxima in the growth height curve, which implies the interdependence among the nanotube types and compositions of VACNTs and their growth rates. Mechanistic explanation behind this growth transition behavior may need further investigation.

**Figure 3.14** The enlarged RBM region of the Raman spectra collected from VACNT samples grown in BH, TH, and BTH modes. Three different types of RBM distribution are displayed in different colors. Type I with two RBM bands centered at around 231 and 136 cm$^{-1}$ emerges at high $T_{\text{catalyst}}$, BH and TH growths (green). Type II with one dominant RBM band at around 231 cm$^{-1}$ is exclusively obtained for TH growths at intermediate $T_{\text{catalyst}}$ (red). Type III with several paired bands appears in BTH growths and low $T_{\text{catalyst}}$ BH and TH growths (blue).
**Figure 3.15** TEM histograms (diameter, $d_{\text{CNT}}$ and wall number of CNTs) and images of the three VACNTs samples which have shown type I, II and III distinct RBM profiles; (Type I, $N=100$) a bimodal distribution of small diameter SWCNTs and large diameter SW- and DWCNTs, (Type II, $N=90$) a mixture of SW- and DWCNTs with a negligible portion of TWCNTs, and (Type III, $N=80$) a mixture of DW-, TW- and MWCNTs.

**Figure 3.16** Cross-sectional SEM images of VACNTs, showing macroscopic structure of the VACNTs grown in the TGCVD system with BH, TH, and BTH heating modes. (Scale bar: 200 nm)
It is known that the areal density and the degree of alignment of VACNTs can be interrelated through a crowding effect among adjacent CNTs, where large areal density of CNTs can promote the degree of alignment. Cross-sectional SEM images (Figure 3.16) appear to hint that VACNTs having maximal density and good alignment correspond to the tallest and best quality VACNTs obtained at the optimum \( T_{\text{catalyst}} \) of each heating mode.

### 3.3.6 Segmentation of gas phase temperature

As described in section 3.1.3, earlier studies have reported that the unsaturated nature of acetylene enables it to polymerize into gaseous polymers with peak activity between 600 and 700 °C. Above 800 °C, decomposition of acetylene begins to surpass the polymerization until it becomes the single dominant reaction beyond 1000 °C. In order to understand the action of gas phase reaction of precursor gases in light of the aforementioned growth behavior, we focus on gas dwell time (\( \Delta t \)) in the thermal zones that are segmented based on the transition of dominant gas phase reaction (Figure 3.17) and the precursor pyrolysis products (Figure 3.18).

Gas dwell time (\( \Delta t \)) is defined as \( \Delta y/u \), where \( y \) and \( u \) are the vertical distance measured from the gas shower head manifold and the local average gas velocity in the \( y \) direction, respectively. Since the gas velocity at a location \( y \) depends on local temperature and pressure, the local time variable, \( t \), and the gas dwell time can be obtained by:

\[
\begin{align*}
  t &= \int_{y=0}^{y} \frac{273Ap}{Q} \frac{1}{T} \, dy = \frac{273Ap}{Q} \int_{y=0}^{T(y)} \frac{1}{T} \left( \frac{dT}{dy} \right)^{-1} \, dT \\
  &= \frac{273Ap}{Q} \left( \frac{dT}{dy} \right)^{-1} \int_{y=0}^{T(y)} \frac{1}{T} \, dT = \frac{273Ap}{Q} \left( \frac{dT}{dy} \right)^{-1} \ln \frac{T(Y)}{T(0)}, \\
  \Delta t_{T_1-T_2} &= |t(y_2;T_2) - t(y_1;T_1)| = \frac{273Ap}{Q} \left( \frac{dT}{dy} \right)^{-1} \ln \frac{T_2}{T_1},
\end{align*}
\]

where \( A \) is the cross sectional area of the TGCVD reactor, \( Q \) is the total gas volumetric flow rate at the standard state (273 K, 1 bar), \( p \) is the total chamber pressure, \( dT/dy \) is the gas temperature gradient, \( T_i \).
and $T_2$ are the bounds of a gas thermal zone of interest, and an upper bar indicates an average value. We approximated the gas temperature gradient to be constant from the linear profiles of gas temperatures obtained in Figure 3.12. For the BTH mode where temperature profile is nearly uniform, $dT/dy \sim 0$, and the gas dwell time was obtained from direct reading of the simulation data.

Figure 3.17 Changes of gas dwell time in the individual gas thermal zones in (a) BH, (b) TH, and (c) BTH modes. Temperature gradients in the gas phase are segmented into the following three thermal zones; $<700$ °C (black), 700-800 °C (orange), and $>800$ °C (green). The temperatures at which transition of the CNT type occurs are marked with dotted lines, and the corresponding types of VACNTs (type I, II and III) are noted. In BH and BTH modes, the $<700$ °C gas thermal zone is further divided into two subsets of $<600$ °C (line-dotted) and 600-700 °C (dashed).
3.3.7 Identifying the important temperature zone for gas phase reaction and the pyrolysis products

We selected three primary gas thermal zones of interest as: $<700 \, ^\circ C$, 700-800 $^\circ C$ and $>800 \, ^\circ C$ based on Refs. [282-284]. In Figure 3.17, we mark the temperatures at which the transitions of the CNT type took place in dashed vertical lines. The influence of the thermal treatment of acetylene precursor on the gas phase reaction products of hydrogenation, polymerization and decomposition and therefore on the growth of VACNTs can be understood by comparing VACNTs growth results at similar catalyst temperatures, $T_{\text{catalyst}}$, yet in different gas heating modes of BH, TH, and BTH.

First, comparison between BH and BTH mode growths at $T_{\text{catalyst}}$ of 720-725 $^\circ C$ shows that the BH mode is superior in growth height, quality, and selectivity towards SWCNTs. There is a clear distinction in the constitution of the gas dwell time in that $\Delta t$ in the $<700 \, ^\circ C$ zone and in the 700–800 $^\circ C$ zone is 6.2 s and 0.7 s for the BH mode and 0.1 s and 6.1 s for the BTH mode, respectively. This observation suggests that $\Delta t$ in the $<700 \, ^\circ C$ zone is important in the VACNT growth particularly when $T_{\text{catalyst}}$ or the catalytic activity is sufficiently high: i.e., the growth becomes efficient when high catalytic activity is coupled to the precursor gas species produced in the $<700 \, ^\circ C$ zone. When the $<700 \, ^\circ C$ zone does not exist in the gas phase as in the BTH mode growth, only short MWCNTs could grow, even at the similar catalytic activity to that of the BH mode. This is also supported by the observation that the TH mode growth at high $T_{\text{catalyst}}$ (>700 $^\circ C$) without $\Delta t$ in $<700 \, ^\circ C$ produced no VACNT. Via the gas phase reactions, an excessive thermal rearrangement would generate secondary hydrocarbons too much to maintain the catalysts alive for growing VACNTs, while moderate reactions that produce only minimal concentrations of decomposition products along with polymerization products can be advantageous to the growth (Figure 3.18). Compared with the BH mode counterpart, our simulations predicted that the BTH mode growth ($T_{\text{catalyst}} = 720 \, ^\circ C$) can produce more secondary hydrocarbons, almost equal to the levels of BH mode growth at 760 $^\circ C$. Fed with plenty of pyrolysis products catalysts at 720 $^\circ C$ do not seem to have been evolved enough to yield a mixture of SW- and DWCNTs, instead of which MWCNTs (type III) can be grown (Figure 3.15 and 3.17).
The second comparison is made between BH and BTH mode at $T_{\text{catalyst}}$ of 670 °C, a moderate catalytic activity. Both cases produced MWCNT (type III) with similar G-to-D ratio, although the BTH mode grew longer VACNTs. Since precursor gases flow through the $<700$ °C zone mostly in both cases, we further decoupled the gas thermal zones into $<600$ °C and 600-700 °C zones. $\Delta t$ in the $<600$ °C zone and in the 600-700 °C zone is 5.0 s and 2.2 s for the BH mode and 0 s and 6.5 s for the BTH mode, respectively. Presumably, precursor thermal treatment in the 600-700 °C zone seems to produce reactants more effective to VACNT growth than in the $<600$ °C zone. Indeed, the simulated gas compositions atop the catalysts indicate that polymerization occurs a bit more in the BTH mode. Decompositions in both cases are weaker by four or five orders of magnitude than polymerization.

Third, in the low $T_{\text{catalyst}}$ (<725 °C) regime, TH mode enabled VACNTs to grow even at much lower $T_{\text{catalyst}}$ of 565-640 °C and unexpectedly produced CNTs of smaller wall numbers compared to the BH and BTH mode growths. The major difference in the gas dwell time composition is that TH mode at this $T_{\text{catalyst}}$ incorporates high gas thermal zones (700-800 °C and >800 °C) with the extensive $<700$ °C zone. The presence of high temperature (>700 °C) zones on top of the $<700$ °C zone for precursor thermal rearrangement seems to help CNT nucleation on relatively less active catalysts and play a positive role in the production of SW- and DWCNTs. We emphasize that without any change in the catalyst system structural features of VACNTs can be altered by tailoring gas dwell time in various thermal zones, attributed to the secondary gas precursors generated during thermal rearrangement or pyrolysis.

Lastly, the stacking order between gas thermal zones with similar dwell times per se makes little impact on growth height and nanotube structure. For example, BH mode at $T_{\text{catalyst}}$ of 750 °C and TH mode at 565 °C both contain $\Delta t$ in the $<700$ °C zone of around 5.0-5.3 s and in the 700-800 °C zone of 1.3-1.5 s. Both growths successfully resulted in VACNTs of SW- and DWCNTS with minor differences in height (BH > TH) and CNT type (type I for BH versus type II for TH). The latter discrepancy in the CNT type can be attributed to an accelerated Ostwald ripening at higher $T_{\text{catalyst}}$ (750 °C) in the BH mode growth. The effect of distinct catalytic activities (represented by $\Delta T_{\text{catalyst}}$ of
185 °C) on the resulting VA-CNT structure is surprisingly small when gas dwell time composition is similar.

In general, the growth and resultant structure of VACNTs are not only influenced by gas phase condition but also by catalyst preparation and evolution such as migration-coalescence, Ostwald ripening, and subsurface diffusion. We opted for a rather thick, Fe-Mo catalyst system, as it is expected to evolve little in comparison with such a thin metallic system that often undergoes a significant catalyst loss and transformation. Acquisition of catalytic activity and thermal evolution on the substrate during the CNT growth is presented in section 2.4.

**Figure 3.18.** Simulation results of the composition of the precursor gas pyrolysis products that are expected to present atop the catalyst surface. Production of vinyl acetylene (C₄H₄), methane and ethylene in the gas phase hints that acetylene undergoes polymerization, decomposition and hydrogenation.
3.3.8 Role of thermal treatment of C\textsubscript{2}H\textsubscript{2} precursor gas in TGCVD growth of VACNTs

We now discuss the roles of the identified thermal zones based on the previous findings about the high temperature thermal reactions of acetylene. Under Egloff’s categorization of pure acetylene pyrolysis, weak and vigorous polymerization of acetylene can occur in the <600 °C and 600-700 °C zones, respectively. In the 700-800 °C zone both polymerization and decomposition are significant, and decomposition becomes exclusive in the >800 °C zone. Thus, under the high pressure CVD condition of this study (480 mbar), it is plausible that depending on the thermal constitution of gas dwell time precursors approaching catalyst at a certain T\textsuperscript{catalyst} are different composition mixtures of polymerized building blocks (C\textsubscript{3} and C\textsubscript{4} species), decomposition fragments (C\textsubscript{1} and C\textsubscript{2} species), ethylene, unreacted acetylene and hydrogen, etc. Note that, in the presence of hydrogen, Egloff’s acetylene pyrolysis may need to be adjusted to include thermal hydrogenation of acetylene into ethylene, etc. (Figure 3.18). Our reacting flow simulation based on the Chemkin library supports the above reasoning. Other than the five species shown in Figure 3.18, more secondary hydrocarbons such as benzene, C\textsubscript{4} species (butene, C\textsubscript{4}H\textsubscript{8}; butadiene, C\textsubscript{4}H\textsubscript{6}; butadiene radical, C\textsubscript{4}H\textsubscript{2}), C\textsubscript{3} species (propene, C\textsubscript{3}H\textsubscript{6}; propadiene, C\textsubscript{3}H\textsubscript{4}; propyne, C\textsubscript{3}H\textsubscript{4}), C\textsubscript{2} species (ethane, C\textsubscript{2}H\textsubscript{6}; vinyl radical, C\textsubscript{2}H\textsubscript{3}) and atomic hydrogen (H) were also predicted at the partial pressure ranges between 10\textsuperscript{-10} and 10\textsuperscript{-6} bar (Figure 3.19). The other hydrocarbons and radicals turned out to be much fewer by orders of magnitude. The reacting flow simulation results further points out that acetylene is still the main precursor. Albeit all existing by orders of magnitude smaller in concentration than acetylene, these minor hydrocarbon species can make a drastic contrast in the resultant VACNT heights and nanotube structures, which once again puts an emphasis on the role of gas thermal zones in the VACNT growth modulation.

According to our experimental findings, such secondary gas species allow reaction pathways for the VACNT growth that would otherwise be impossible. Most strikingly, in the low T\textsuperscript{catalyst} TH mode growth it can be inferred that the decomposition species are more reactive than the polymerized species or acetylene itself and thus could initiate the nucleation of VACNTs at such a low catalytic activity. We speculate
that decomposition fragments could function as a direct source of surface catalytic conversion or as a conversion enhancer. On the other hand, the early growth termination occurring in the high $T_{\text{catalyst}}$ TH mode growths, in contrast to the BH mode growths, implies that too much of these highly reactive decomposition fragments may not be always advantageous for the VACNT growth particularly when the catalytic activity cannot catch up the influx of these species, possibly leading to speeded catalyst deactivation.

![Image](image_url)

**Figure 3.19.** (a) Mole fractions of all 45 species considered in the reacting flow modeling, displayed separately for different heating modes of TG CVD: BH (blue), BTH (gray), and TH (red) except hydrogen and argon; Mole fractions of hydrogen and argon were 0.396 and 0.594.

Finally, VACNTs of small wall numbers and high quality can be obtained when a sufficiently high $T_{\text{catalyst}}$ for catalytic activity and heat driven morphological evolution is combined with an optimum gas
phase temperature control in a TGCVD reactor. The best gas thermal condition for supplying an optimal mixture of polymerization chains, decomposed fragments, and untransformed C$_2$H$_2$ for VACNT synthesis is found with BH mode at $T_{\text{catalyst}}$ of about 725 °C when the ratio between the gas dwell time in the 600-700 °C and >700 °C zones is around 6. These various carbon intermediates are considered intact at the catalyst surface during CNT nucleation and elongation, and the difference in their interaction energies with a given catalyst surface, for instance, sticking probabilities, activation energies of adsorption, dissociation and rearrangement, would significantly affect CNT growth as often found in the volcano plots of surface catalysis. [87] We interpret that decomposed products may easily adsorb on the surface but the energy barrier for the formation of the graphitic network would be large, while polymerized products may rather possess an energy barrier for adsorption higher than the decomposed products but instead can be readily added to the carbon chains of growing nanotubes. This interpretation explains the effectiveness of having decomposition products and polymerization products at low $T_{\text{catalyst}}$ (less active catalyst) and high $T_{\text{catalyst}}$ (active catalyst). In addition, we expect that these polymerized and decomposed products may react in concert with intact acetylene molecules on the metal catalyst based on the observation of an enhanced growth of VACNTs when gas thermal zones for polymerization and decomposition are combined. The above hypothesis accounting for the temperature distribution in the gas phase, gas dwell time constitution, and $T_{\text{catalyst}}$ dependent catalytic activity supports the potential of TGCVD process for controlled growth of VACNTs.
3.3.9 Summary

We present a new CVD method of systematically modulating the temperature distribution in the gas phase for the controlled growth of VACNTs. Catalyst activity and morphological evolution is primarily determined by catalyst temperature. However, thermal treatment of precursor gases is also found as important in the growth of VACNTs. We recognize that thermal treatment of C$_2$H$_2$ based precursor at 600-700 °C is crucial. Combination of this gas thermal zone with a small portion of a hotter (>700 °C) zone is found beneficial for growth enhancement of VACNTs with high qualities and low wall numbers. Also, given a constant catalytic activity, the nanotube wall number can be tailored by mixing different thermal zones. At optimum gas preheating, C$_2$H$_2$ based process gases undergo polymerization and decomposition reactions, generating mainly intact C$_2$H$_2$ but also many other pyrolysis products. This study provides new insights on the role of thermal treatment of precursor gas in C$_2$H$_2$ based CVD and suggest a new TGCVD method to control complex gas phase reaction phenomena for the enhanced and controlled growth of VACNTs.
3.4 Key Factors Affecting the Structural Properties and the Growth Dynamics of VA-SWCNTs

3.4.1 Brief description of section 3.4

The key parameters of the acetylene based CCVD process governing the structural properties and the growth dynamics of VACNTs are identified and systemically studied in this section. Acetylene partial pressure ($P_{C_2H_2}$) and growth temperature primarily determines the diameter range of catalyst particles that allows the nucleation of stable CNT caps (nucleation window) and that actually exist at the nucleation stage (catalyst particle size window), respectively. The minimum possible diameter and the narrowest diameter distribution for a given catalyst can be achieved at the lower bound of temperature and $P_{C_2H_2}$ range for growing VACNTs where both nucleation and catalyst particle size windows are maximally downshifted. On the other hand, high temperature is preferred for growing high quality VACNTs by the minimal co-deposition of defective carbon byproducts and the thermally activated healing process for structural defects along the CNT, which is also found to increase the collective growth rate. Most of these characteristics gradually change over time because the chemical and physical properties of catalyst particles that host the conversion of carbon species into CNT are significantly altered by being exposed to the extreme CVD condition. In addition, several strategies in the catalyst pretreatment step to further tune the growth of VACNTs are addressed in this section.

3.4.2 $P_{C_2H_2}$ dependence of the growth of VA-SWCNTs

We performed a systematic study of the evolution of various growth characteristics such as initial growth rate (IGR), Raman G-to-D ratio, wall number selectivity and diameter distribution of VACNTs as a function of acetylene partial pressure, $P_{C_2H_2}$. 0.15 nm and 0.30 nm thick Fe catalysts are used for a comparative analysis because they are proven to grow mainly VA-SWCNTs over a wide range of growth condition. Varying the $P_{C_2H_2}$ mainly influences the carbon supply without affecting the other thermally-activated processes.
Figure 3.20 (a) Initial growth rates (IGRs) and (b) Raman G-to-D ratio of VACNTs versus $P_{C_2H_2}$, revealing an inverse relation between the two growth characteristics; CCVDs of VACNTs were performed in a cold-wall condition at two different temperatures of 640 °C (red circles) and 725 °C (black squares) with uniform temperature gradients using ALD deposited Fe (0.15 nm, solid lines) and Fe (0.30 nm, dashed lines)/Al$_2$O$_3$ (20 nm) catalysts. For all cases, the growth gas was Ar diluted C$_2$H$_2$, and the catalyst was preannealed in H$_2$ for 5 min. The gas dwell time was strictly controlled to be 0.15 sec. The inset shows the two representative G and D band range of the Raman spectra of the VACNTs grown at $P_{C_2H_2}$ of below and above 0.15 mbar.
First, the IGRs, which are captured by an ex-situ analysis of the VACNTs grown for a very short duration (less than 90 sec), increases proportionally to the $P_{\text{C}_2\text{H}_2}$ and becomes independent at high $P_{\text{C}_2\text{H}_2}$ regime (Figure 3.20a). The nearly linear increase of IGRs at low $P_{\text{C}_2\text{H}_2}$ strongly suggest that the growth of VACNTs cannot be solely limited by the diffusion processes on the catalyst that is independent of the $P_{\text{C}_2\text{H}_2}$ in the gas phase. This is instead reasonable to deduce that the growth process is partly limited by the gas phase reaction equilibrium producing active carbon precursor or the surface catalytic reaction converting gaseous carbon precursor into surface carbon species.

The IGRs gradually saturate at high $P_{\text{C}_2\text{H}_2}$ regime ($\geq 0.15$ mbar), where one expect higher collision frequencies between carbon precursors and catalyst surface, thereby higher or complete coverage of the surface active sites (Figure 3.20a). For example, Ma et al.’s simulation showed that the fraction of vacant active sites on the catalyst NP decreases with the increase of $P_{\text{C}_2\text{H}_2}$ at a given $T$. [113] Once the maximum concentration of surface carbon adsorbates is reached, which is primarily limited by the number of surface active sites, the growth of VACNTs seems to become limited by the surface and/or diffusion process, as many previous studies have claimed. The surface carbon species can evolve into not only a tube-shaped, ordered sp$^2$ carbon network, that is, a CNT with an assistance of catalyst nanoparticle but also a two or three dimensional disordered network, often referred as an amorphous carbon (a-C, a mixture of sp$^2$, sp$^3$ and even sp$^2$ types of carbon) and defective carbon. The high surface coverage of catalyst substrate by reactive carbon species would promote the generation of the latter products, which would then permanently block the surface active sites, leading to catalyst deactivation and termination. It is important to keep in mind that the formation of carbon byproducts deteriorates the IGR as well as the structural quality of VACNTs.

The structural qualities of VACNTs, indicated by Raman G-to-D ratios show an opposite $P_{\text{C}_2\text{H}_2}$ dependence that the G-to-D ratio drastically drops from 5-6 to below 1 range even with a minimal increase of $P_{\text{C}_2\text{H}_2}$ at low $P_{\text{C}_2\text{H}_2}$ regime and keep constantly low at high $P_{\text{C}_2\text{H}_2}$ regime (Figure 3.20b). The simultaneous transitions in the $P_{\text{C}_2\text{H}_2}$ dependences of IGRs and G-to-D ratios indicates that the process growing VACNTs and forming defective and amorphous carbons
share a common step that involves gaseous carbon precursor as a reactant. Interestingly, the Raman D bands of VACNTs grown at high $P_{\text{C}_2\text{H}_2}$ ($\geq 0.15$ mbar) have much broader linewidth than those of VACNTs grown at low $P_{\text{C}_2\text{H}_2}$ and need at least two Lorentzian curves to achieve a good fit. At low $P_{\text{C}_2\text{H}_2}$ regime, the D band can be well fitted by a single Lorentzian curve and the linewidths are observed to be constant at around 80-100 cm\(^{-1}\) while their intensity increases with an increase of $P_{\text{C}_2\text{H}_2}$. In general, the D band of a CNT sample is attributed to the sum of the structural defects of CNTs and secondary carbon byproducts. The exact nature of the defective carbon byproducts is not all known yet. However, the D band linewidth tends to broaden for CNT samples with broad diameter distributions and less ordered carbon materials. [285, 286] Hence, we attribute the major cause of the decreasing G-to-D ratio at low $P_{\text{C}_2\text{H}_2}$ to structural defects while it is mainly the accumulation of defective carbon byproducts at high $P_{\text{C}_2\text{H}_2}$, which leads to the strong D bands.

Next, the change of $P_{\text{C}_2\text{H}_2}$ during CCVD process of VACNTs is found to influence the diameter distribution as well as wall number selectivity. As shown in Figure 3.21 (0.15 nm and 0.30 nm thick Fe catalysts), the diameters and wall numbers of CNTs are primarily controlled by the size of its catalyst particles. However, we also observe that low $P_{\text{C}_2\text{H}_2}$ produces smaller diameter SWCNTs than high $P_{\text{C}_2\text{H}_2}$. For each set of experiments, catalysts from the same deposition batch are used and process condition for catalyst pretreatment and CNT growth are kept exactly the same except the $P_{\text{C}_2\text{H}_2}$. The $P_{\text{C}_2\text{H}_2}$ dependence of CNT diameters can be well explained by the so termed catalyst volume to surface area model by Rümmeli et al. [287] In this model, a stable hemispherical cap formation is required for nucleation and the amount of carbon precipitating from catalyst particle at nucleation stage depends on the catalyst volume for a given catalyst (differences in eutectic point, carbon solubility, and diffusivity). If the catalyst particle is too small then insufficient carbon is available at the nucleation stage and no stable cap forms, or if the catalyst particle is too large then too much carbon is available and the precipitating carbon will simply encapsulate the entire Fe catalyst. Due to the above stated catalyst volume (carbon supply) to surface area (cap stability) restrictions, a catalyst particle size window for CNT nucleation (nucleation window) exists, which upshifts to with an increase of $P_{\text{C}_2\text{H}_2}$. CNTs can only grow when the nucleation window
for a given catalyst at a given set of CVD process parameters and the size distribution of actual catalyst nanoparticles overlap. Because the latter is controlled to be fixed for each set of experiments but the former is $P_{\text{C}_2\text{H}_2}$ dependent, catalyst particles in a relatively large diameter range within the ensemble of polydispersed nanoparticles formed from the same catalyst can form stable caps and grow CNTs.

**Figure 3.21** Variations of the diameter and wall number distribution of VACNTs grown from Fe (0.15 nm) and Fe (0.30 nm)/ Al$_2$O$_3$ (20 nm) catalysts at the temperature of 725 $^\circ$C with the $P_{\text{C}_2\text{H}_2}$ of ~0.04, 0.1, and 1 mbar; the yellow lines are log-normal fittings and the mean and standard deviation are given in parentheses. Gray and cyan columns indicate SW- and DWCNTs, respectively.
Figure 3.22 Normalized IGRs (derived from Figure 2.15), Raman G-to-D ratios, TEM histograms and cross-sectional SEM images of VA-SWCNTs grown for 3 min from electron beam evaporated Fe (0.1 nm)/ Al₂O₃ (20 nm) catalyst as a function of \( P_{\text{C}_2\text{H}_2} \); CCVDs were performed at temperature of 750 °C in cold-wall and BH temperature gradient conditions. In all cases, catalyst was preannealed in Ar for 5 min and growth gas was pure or Ar diluted \( \text{C}_2\text{H}_2 \) at the constant chamber pressure and total gas flow rate. Therefore, gas dwell time was constant at 0.15 sec. The red lines in TEM histograms are log-normal fittings and the mean and standard deviation are given in parentheses.

Interestingly, the 0.10 nm thick Fe catalyst exhibits an opposite trend in the \( P_{\text{C}_2\text{H}_2} \) dependences of IGR, Raman G-to-D ratio and diameters of VACNTs. As shown in Figure 3.22, the IGR of VA-SWCNTs exponentially decreases with increasing \( P_{\text{C}_2\text{H}_2} \) while the Raman G-to-D ratio rises to a quite high value of ~17 as the \( P_{\text{C}_2\text{H}_2} \) increases. The CNT diameter range upshifts to slightly larger values but eventually downshifts to the very small values at high \( P_{\text{C}_2\text{H}_2} \). Also, a noticeable deterioration of the CNT alignment at higher \( P_{\text{C}_2\text{H}_2} \) conditions is observed for the VA-SWCNTs grown from 0.10 nm thick Fe catalyst,
but not for those grown from thicker Fe catalysts. The nucleation window for thinner Fe catalyst (smaller catalyst particles) is expected to be in relatively smaller diameter range owing to the high surface to volume ratio. Applying the same principle of CNT cap nucleation dynamics, the nucleation window for a 0.10 nm thick Fe catalyst at the tested $P_{\text{C}_2\text{H}_2}$ range overlaps with the diameter range of catalyst particles at the large diameter region of the distribution and then as the nucleation window upshifts to larger diameters by the increase of $P_{\text{C}_2\text{H}_2}$ the two windows becomes non-overlappable, meaning that the number of active catalyst particles drops near zero (Figure 3.23).

![Diagram showing nucleation window and catalyst particle size](image)

**Figure 3.23** Schematic of the CNT nucleation window (green dashed lines) that upshifts with an increase of $P_{\text{C}_2\text{H}_2}$, with respect to the catalyst particle size distribution (brown and red solid lines, obtained from AFM analysis) determined by catalyst thickness and catalyst pretreatment for 0.10 and 0.30 nm thick Fe catalysts; CNTs can grow when the nucleation window and the size distribution of actual catalyst particles overlap because particles that are too large are encapsulated by graphite, and particles that are too small are unlikely to form a stable cap. The degree of the overlap determines the diameter distribution and areal density of CNTs and further influences the CNT growth rate and quality.

Indeed, VACNTs could not be grown at the high $P_{\text{C}_2\text{H}_2}$ of ~ 0.4 mbar. Since the growth rate is based on the average height of VACNTs, not the average length of individual CNTs, observed gradual loss in CNT
straightness with an increase of $P_{C_2H_2}$ can be related to the decrease of the areal density of active catalyst particles. On the other hand, higher Raman G-to-D ratio is obtained at high $P_{C_2H_2}$ condition, which we attribute to the narrower diameter distribution of the grown VA-SWCNTs and the suppressed reaction pathway of producing defective carbon byproducts as nucleation window upshifts to larger diameters.

3.4.3 CCVD temperature dependence of the growth of VA-SWCNTs

The evolution of the major growth characteristics of VACNTs as a function of $P_{C_2H_2}$ has shown two distinct regimes by the threshold $P_{C_2H_2}$ above which the growths of VACNTs reveal saturation behaviors. For a comparative study, we investigate the temperature dependence of the growth characteristics at the two $P_{C_2H_2}$ conditions of 0.1 mbar and 1 mbar (below and above the threshold $P_{C_2H_2}$ found for 0.15 nm thick Fe catalysts).

Figure 3.24 shows the temperature dependence of IGR and Raman G-to-D ratio of VACNTs grown from 0.15 nm thick Fe catalyst at $P_{C_2H_2}$ of 0.1 mbar and 1 mbar in the form of an Arrhenius plot, the natural logarithm of reaction rate coefficient versus the reciprocal of absolute temperature (K). Overall, both IGR and Raman G-to-D ratio increase with increasing growth temperature, which agrees well with the general trend but the slopes of Arrhenius plots (activation energy, $E_a$) change, indicating the rate determining step is different at high and low temperature regimes. The transition temperature is found $P_{C_2H_2}$ dependent; 650 °C at $P_{C_2H_2}=0.1$ mbar and 750 °C at $P_{C_2H_2}=1$ mbar. When $P_{C_2H_2} < P_{\text{Threshold}}$, $E_a$ of IGR changes from 1.82 to 0.35 eV while that of Raman G-to-D ratio changes from 0.48 to 1.57 eV. On the other hand, when $P_{C_2H_2} > P_{\text{Threshold}}$, $E_a$ of IGR changes from 1.58 to 0.10 eV while that of Raman G-to-D ratio changes from 0.27 to 1.89 eV. In both cases, a steep rise of the IGR and Raman G-to-D ratio by the temperature increase occurs at low and high temperature regime, respectively.
Figure 3.24 Arrhenius plots for IGRs and Raman G-to-D ratios of VACNTs grown from 0.15 nm thick Fe catalyst at two different $P_{\text{C}_2\text{H}_2}$ conditions of 0.1 mbar and 1 mbar, lower and higher than the threshold $P_{\text{C}_2\text{H}_2}$ above which the growths of VACNTs reveal saturation behaviors; the activation energies are calculated from the slope of the linear fit to the data.

First, the $E_a$ values of IGRs at low temperature regime are comparable to the previously reported values in the range of 1.1-1.8 eV that are considered to indicate that the bulk diffusion of carbon is the rate
limiting step of CNT growth. [134, 253, 288] Similarly, we proposed that CNT growth rate is dominantly limited by the slow bulk (and surface) diffusion of carbon species at low temperatures but by the catalytic surface reactions of lower $E_a$ values at high temperature where nearly zero resistance for diffusion exits. Next, the observed $E_a$ values of Raman G-to-D ratios (the conversion of defective carbon into sp² CNT carbon) are somewhat deviated from the reported values in literatures around 1.0 eV, which is attributed to the thermally activated catalytic healing of a single type of simple defect; higher growth temperatures make this healing process more effective, thus leading to a lower defect densities. [225, 254, 261] In general, defect healing can have much higher $E_a$ values; i.e., a simple low energy pentagon-heptagon (5-7) pair defect can have formation energy of up to 4.4 eV but can be significantly lowered by the presence of edges, catalytic adatoms, or metal catalyst to values on the order of 1 eV. [289, 290] Hence, defect healing mechanism and the relevant $E_a$ would strongly depend on the physical and chemical properties of catalyst particles as well as the type of defect.

Another thing to consider is that the Raman D band of the VACNTs grown at low temperature regime shows a large contribution of defective carbon byproducts with its wide linewidth and lower peak frequency, different from the sharp D peak (mainly originated from a certain type of structural defect along CNT) at high temperature regime. At low temperatures, defect healing process may not be activated and unwanted deposition of defective carbon byproducts is expected to be severe. Because the transitions in the Arrhenius curves of the Raman G-to-D ratio coincide with the disappearance of the contribution of defective carbon byproducts in Raman D band, we deduce that the defect density of VACNTs at low temperature regime is governed by the formation of defective carbon byproducts (Figure 3.25). On the other hand, at high temperatures the defect density is limited by the healing process of structural defects, which might be in part enabled by the absence of defective carbon byproducts that are very likely to hamper the various processes on catalyst surface. We observe that the transition occurs at higher temperature (750 °C) when CCVD is performed at $P_{C_2H_2} > P_{Threshold}$. This can be understood by the increase of the minimum temperature for matching the carbon supply rate ($P_{C_2H_2}$ dependent) and the conversion rate of surface carbon into sp² CNT carbon. The different $E_a$ values of Raman G-to-D
ratio depending on $P_{\text{C}_2\text{H}_2}$ could be related to the different types of defects formed in the CNT lattice and the difference in the chemical and physical properties of the active catalyst nanoparticles at the given $P_{\text{C}_2\text{H}_2}$ condition.

![Figure 3.25](image.png)

**Figure 3.25** Evolution of the G and D band range of the Raman spectra ($\lambda=785$ nm) as a function of growth temperature at two different $P_{\text{C}_2\text{H}_2}$ conditions of 0.1 mbar and 1 mbar; the D band feature changes at the transition temperature (650 °C at $P_{\text{C}_2\text{H}_2}=0.1$ mbar and 750 °C at $P_{\text{C}_2\text{H}_2}=1$ mbar) where the slope of Arrhenius curves of the Raman G-to-D ratio changes.

Figure 3.26 and 3.27 show the temperature dependent evolution of the diameter distribution of VACNTs grown at the two different $P_{\text{C}_2\text{H}_2}$ of 0.1 mbar and 1 mbar. Not being very specific to the $P_{\text{C}_2\text{H}_2}$ value, CNTs of a larger average diameter and a broader distribution are obtained at higher growth temperatures, primarily attributed to the thermally driven morphological evolution of catalyst nanoparticle. Upon an exposure to high temperature and reducing atmosphere during CCVD process, surface Fe atoms and/or clusters gain high thermal energies so that they can freely diffuse laterally on the surface and vertically into the support. The surface diffusion of Fe species is known to trigger particle migration-agglomeration and/or Ostwald...
ripening process. Since for both sets of experiments the entire CNT diameter range shifts and broadens to larger values without any noticeable emergence of small diameter CNT at high temperatures, we conclude that here the dominant mechanism of catalyst evolution is the particle migration-agglomeration and the subsurface diffusion. However, because the $P_{\text{C}_2\text{H}_2}$ influences the rate of carbon supply and therefore the nucleation window for stable hemispherical cap (as discussed in section 3.4.2), detailed CNT diameter range and wall number type differ at the two $P_{\text{C}_2\text{H}_2}$ conditions. For example, while only SWCNTs grows over the whole range of CVD temperatures at low $P_{\text{C}_2\text{H}_2}$, a mixture of SW and DWCNTs grow at low temperature and high $P_{\text{C}_2\text{H}_2}$. Also, often slightly narrower diameter distribution is achieved at high $P_{\text{C}_2\text{H}_2}$ due to the increase of wall number and the upshifted nucleation window.

The cross-sectional SEM images of the VACNTs in Figure 3.28 showing the variation in the CNT alignment provide a hint on the areal density of active catalyst particles due to the collective growth mechanism of VACNTs based on crowding effect. [9, 163] As clearly seen by the Herman’s Orientation Factor (HOF) values calculated from these images [187], high growth temperatures result in much less aligned and sparse VACNTs. Catalyst treatment at high temperatures makes a broad size range of catalyst nanoparticles available for CNT growth. Intuitively thinking, this will increase the ratio of the number of catalytically active particles to that of all existing particles. However, at the same time the catalyst coarsening process lowers the absolute number of catalyst particles and thus the areal density of active catalyst particles. In addition, the large mismatch in the growth rate and mechanical properties between the simultaneously growing CNTs having a broad range of diameters can allow slips between the CNTs in contact (overcoming the van der Waals interactions) and the stress imposed to the fast growing CNTs to balance with the slow growing CNTs can result in more defective and entangled structure. Lastly, the VACNTs grown at the higher $P_{\text{C}_2\text{H}_2}$ of 1 mbar are observed to be denser, suggesting that the nucleation window for a stable CNT cap formation overlaps with the size distribution of catalyst particles in a broader diameter range.
Figure 3.26 Variations of the diameter distribution of VA-SWCNTs grown from 0.15 nm thick Fe catalysts at $P_{C_2H_2}=0.1$ mbar and different temperatures, showing the gradual upshift and broadening of CNT diameters with temperature increase; the solid lines are log-normal fittings and the mean and standard deviation are given in parentheses.
Figure 3.27 Variations of the diameter and wall number distribution of VA-SWCNTs grown from 0.15 nm thick Fe catalysts at $P_{\text{C}_2\text{H}_2}=1$ mbar and different temperatures, showing the similar trend of a diameter increase and broadening with temperature increase; the solid lines are log-normal fittings and the mean and standard deviation are given in parentheses. The blue and pink in bars in TEM histograms indicate SW and DWCNTs, respectively.
Figure 3.28 Cross-sectional SEM images and the calculated HOF values of VACNTs grown at the two different $P_{C_2H_2}$ conditions of 0.1 mbar and 1 mbar showing the gradual loss in CNT alignment thus the density of active catalyst particles. (Scale bar: 200 nm)
3.4.4 Growth (Annealing) Time dependence of the growth rate and diameter distribution of VA-SWCNTs

We performed a systematic study on the time evolution of the growth of VA-SWCNTs via ex situ quantitative measurements of growth rates and TEM analysis of CNT diameter distributions. The growth rates were monitored as a function of time using a stop-and-start (pulsed) growth method, [134, 135] which forms discernible breaks in the cross-section of VA-SWCNTs. The distance between the breaks is used to determine the growth rate over a well-defined time in the growth process, which is in general composed of 1-3 min of growth durations with 15 sec of intervals in between. The two plots of the growth rate as a function of growth (annealing) time at temperatures of 640 °C and 750 °C are shown in Figure 3.29. Both exhibit two slope transitions in the decay curve of the growth rate. The growth kinetic curve of VACNTs is often fitted by the exponential decay model. [291] This model provides seemingly adequate fits to the curves of the average height of VACNTs versus growth time, however, cannot reflect the three distinct regimes and the abrupt termination.

At the early stage of growth, both the absolute growth rate and its decay rate are high. The high degree of CNT alignment is maintained or even improved while the diameter range of growing VACNTs becomes noticeably broader by the appearance of slightly larger diameter CNTs (Figure 3.30). Based on these observations, we attribute this time dependence to the widening of the diameter distribution of active catalyst particles and their morphological stabilization, occurring via surface mediated coarsening process. Such a surface process in general has a lower energy barrier and a rapid reaction rate compared to bulk diffusion and evaporation process. The increase of the total number of active catalytic sites at the fixed level of C_2H_2 supply contributes to the decreasing growth rate. The decay rate and duration of the first regime are lower and shorter for the growth at high temperature. It indicates that high thermal energy accelerate catalyst morphological evolution to reach the intermediate state fast.
Figure 3.29 Time evolutions of (a) the average height and (b) the sectional growth rate of VA-SWCNTs at growth temperatures of 640 °C and 750 °C, obtained from a series of stop-and-start (pulsed) growths; the height profiles are fitted by the exponential decay model and the three distinct regimes in the decay curves of growth rate are designated by the vertical solid lines. All CVD runs were performed using 0.15 nm thick Fe catalysts and C$_2$H$_2$ as carbon source. The catalyst was preannealed in low vacuum and the CNT growth starts with the C$_2$H$_2$ supply ($P_{C_2H_2}=0.1$ mbar).

In the following regime, the decay rate is slightly slower than in the previous regime and shows different temperature dependence; a faster decay rate for a shorter duration at higher temperature. The CNT alignment gradually deteriorates and the diameter distribution
upshifts during prolonged growth. However, these changes are not as
dramatic as those observed at the early stage of growth (Figure 3.30).
This can be understood by the effect of the inward diffusion of surface
Fe into the alumina support on the diameter evolution of catalyst
particles, discussed in section 2.2.7. [132] In this intermediate regime,
the rapid catalyst particle coarsening process at the catalyst-support
interface is offset by subsurface diffusion of surface Fe atoms. The
subsurface diffusion, which is also a thermally activated process, well
explains the faster decay rate and short duration of this decay regime
for high temperature growths.

![Figure 3.30](image.png)

**Figure 3.30** Cross-sectional SEM images of VACNTs grown for 5 min
(regime I), 15 min, 30 min (regime II) and 40 min (regime III) at 750 °C
showing the variation in CNT alignment thus the density of active
catalyst particles. (Scale bar: 500 nm)

Finally, the third regime where the significant loss of CNT alignment,
followed by an abrupt growth termination occurs is explained by the
subsurface diffusion of surface Fe atoms, the only catalyst evolution
mechanism remaining after a long time growth (Figure 3.30). From
the small angle XPS analysis of the CVD processed catalysts, we found
that nearly one thirds of initially deposited Fe atoms have diffused
away from the surface after being exposed to the given CVD condition
for about 30 min. Because it strongly depends on particle size and
inter-particle distance, the surface process of catalyst particle
coarsening is unlikely to occur as before on the surface of low Fe
concentration. This is consistent with the recent works by Kim *et al.*
and Bedewy *et al.* that reported the rapid growth termination
occurring when CNT density becomes too low. [9, 117]
Figure 3.31 Time evolutions of the sectional growth rate of VA-SWCNTs from 0.15 nm thick Fe catalysts at growth temperature of 640 °C and $P_{C_2H_2}=0.1$ mbar with different catalyst preannealing durations of 5 min, 10 min, and 30 min. TEM diameter histograms of VA-SWCNTs grown for 5 min (regime I) at the three conditions are shown. The solid lines are log-normal fittings and the mean and standard deviation are given in parentheses.

Further, we compared the decay trends of the growth rate for a given catalyst when thermally annealed for different durations (5 min, 15 min, and 30 min) prior to the growth (Figure 3.31). In other words, thermally induced catalyst evolution can be enhanced at the growth with a long preannealing step. Interestingly, for all cases, initial growth rates are nearly the same and growth termination timing match at around 70 min after being exposed to growth temperature. It indicates that catalyst lifetime for a given catalyst is the catalyst annealing duration at growth temperature, regardless of the timing of $C_2H_2$ supply. VACNTs growing from the 5 min annealed catalyst show slower decay rate and continue to grow for longer lifetime, thereby
terminate at the same time with those start growing at a much later time. It hints that the CNT nucleation on catalyst surface at early stage helps to delay and slower the catalyst particle coarsening process. Inspired by the finding, protective coatings of catalyst particles, otherwise highly mobile, with a thin layer of carbon can be beneficial for the diameter controlled growth of VACNTs. Nearly the same initial growth rates of the three cases is somewhat expected. Because all the key parameters such as temperature and $P_{C_2H_2}$ are fixed and thus the particle size windows for CNT nucleation are the same in all three cases. Also, there seem to be no significant change in the distribution of catalyst particles at nucleation stage according the resultant CNT diameter distributions, all in the range of 1-3 nm but with slight shift of the average diameter. We emphasize that a longer annealing without any reducing gas component does not have a drastic impact on catalyst evolution.

### 3.4.5 Catalyst pretreatment with H$_2$

The introduction of reducing gases such as H$_2$ and NH$_3$ during CCVD process is known to influence the chemical and physical properties of metallic catalysts. Investigations on the reduction behavior of Fe suggested that intermediate metastable Fe-alumina compounds form at the interface during the reduction process and thus it influence further catalyst evolution. [292-294] Depending on experimental conditions and the nature of catalyst and support material, different compound can be formed at different rates. The oxidation state of metal catalyst during CNT growth is still a subject of interest. Not only the metallic but also certain oxidation states of transition metals have been found catalytic active for growing CNTs. For instance, Fe, the most commonly used catalyst in combination with an alumina support has 16 oxidation states. [192] Most reports claim that the best oxidation state of Fe is metallic [4, 240, 244] and only a few studies suggest the Fe oxides is preferred than metallic Fe for the nucleation or carbide formation process. [295, 296]

We performed a series of experiments to investigate the effect of catalyst preannealing in H$_2$ on the growth of VACNTs, in particular for the ultrathin Fe catalyst (0.3 nm thick) supported on alumina. In all CVD runs, the catalyst was preannealed at 800 °C for 5 min at
different hydrogen partial pressure ($P_{H_2}$) conditions. Immediately after the annealing, the $H_2$ gas flow is cut off and pure $C_2H_2$ gas is supplied for 5 min at $P_{C_2H_2}$ of 0.4 mbar for CNT growth. Unlike many previous studies, we varied the $P_{H_2}$ instead of the preannealing duration in $H_2$ to avoid the severe coarsening of catalyst particles, negative for small diameter CNTs.

![Figure 3.32](image)

**Figure 3.32** The influence of the $P_{H_2}$ level during catalyst preannealing step on the initial growth rate, diameter distribution and vertical alignment of VACNTs; 0.30 nm thick Fe catalysts are preannealed at temperature of 800 °C for 5 min and CNT growth is performed at $P_{C_2H_2}$=0.4 mbar. The solid lines are log-normal fittings and the mean and standard deviation are given in parentheses. (Scale bar: 500 nm)

A plot of initial growth rate of VACNTs as a function of $P_{H_2}$ at temperatures of 800 °C is shown in Figure 3.32. We find that the most reductive environments at $P_{H_2}$ = 600 mbar yield the most efficient growth although the effect is not substantial. On the other hand, the vertical alignment and the diameter distribution of VACNTs
changed significantly. Much smaller diameter (by about 2 nm) VA-
SWCNTs with narrower distribution were grown from the catalyst
annealed at high $P_{H_2}$. Since the deposited ultrathin Fe catalyst cannot
avoid being exposed to ambient condition during handling, it is
expected to be covered with native oxides when loaded to CVD
chamber for CNT growth. These native oxides can contribute to the
size of catalyst particle if not sufficiently removed by reduction
process. This could be the main reason why we observe a significant
decrease of CNT diameters. By reducing the surface Fe oxides to
metallic Fe, the remaining metallic particle sizes decrease and may
also have higher catalytic activities. The vertical alignment of VACNTs
is improved with the preannealing at high $P_{H_2}$ condition. It indicates
that a larger number of Fe particles on support become catalytically
active. It could be due to the revival of previously inactive particles via
their size reduction or electron enrichment.

This result can be compared with Nessim et al.’s work, which showed
that the particle sizes continued to increase with a prolonged
annealing in the presence of $H_2$. [240] The reduced metallic Fe is
known to have higher reactivity and mobility than the oxidic Fe.
Therefore, once the metallic catalysts are fully reduced and sufficient
thermal energy is available from the surroundings, a longer duration
of preannealing will accelerate surface-mediated catalyst coarsening
process, which in most cases unwanted. We emphasize that catalyst
pretreatment at high $P_{H_2}$ for a short duration is a better approach for
achieving the smallest possible CNT diameters and the maximum
growth rate simultaneously.
3.4.6 Summary

We have investigated the physiochemical mechanisms underlying the nucleation and growth dynamics of VACNTs in the C$_2$H$_2$ based CCVD process, providing insights necessary for engineering the synthesis of VACNTs, mainly in terms of the CNT diameter distribution and defect density. The smaller CNT diameter and narrow distribution can be approached at the low bounds of the temperature and $P_{C_2H_2}$ windows for growing VACNTs at the expense of growth rate and defect density. Two distinct domains with different temperature dependence of IGRs and Raman G-to-D ratio (defect density) are evidenced, indicating the transition of the relevant rate determining step of the CCVD process. Size distribution and chemical reactivity of catalyst particles existing on the surface at nucleation stage can be tuned by controlling the duration and the $P_{H_2}$ of preannealing step. We also suggest that pre-coatings of catalyst particles, otherwise highly mobile, with a thin layer of carbon can be useful for suppressing catalyst coarsening process. The growth characteristics primarily determined by the two key parameters ($P_{C_2H_2}$ and temperature) change over time due to the time evolution of the chemical and physical properties of catalyst particles that host the conversion of surface carbon species into CNT. Accordingly, the VACNTs grown for a short duration is preferred particularly for the applications requiring a strict control of structural properties of individual CNTs.
3.5 CVD parameter window of the average diameter controlled growth of VA-SWCNTs for membrane applications

Figure 3.33 summarizes a wide range of average diameter control in sub-5-nm regime achieved at a given CVD condition with the variations in the catalyst configuration such as Fe thickness, surface roughness of alumina support, deposition thickness ratio and order of bilayered catalyst and a thick Fe (10 nm)-Mo (10 nm)-Al$_2$O$_3$ (20 nm) trilayered catalyst, which has been discussed in chapter 2. Briefly mentioning, average CNT diameter can be reduced by decreasing the nominal deposition thickness of transition metal catalyst, using optimal support whose asperities’ sizes match with those of the metal deposits or Mo co-catalyst which limit the thin film dewetting by being between Fe and alumina or realizing multilayered configuration which can suppress agglomeration and ripening of nanoparticles on surface thanks to the delayed film dewetting.

Figure 3.33 Average diameter control of VA-SWCNTs in sub 5 nm regime achieved by varying catalyst configuration such as Fe thickness (dark gray), type of alumina support (right gray), Mo co-catalyst with different stacking orders (orange and green) and a thick layered structure (blue); VA-SWCNTs are grown at a fixed acetylene partial pressure of 0.033 mbar and growth temperature of 730 °C.
Figure 3.34. Average diameter control of VA-SWCNTs by adjusting various CVD process parameters such as temperature, C\textsubscript{2}H\textsubscript{2} partial pressure, duration and H\textsubscript{2} pressure of catalyst annealing step and temperature gradients in the gas phase.

In addition, this chapter has shown that the diameter range could be further tuned by adjusting the CVD process parameters such as growth temperature, C\textsubscript{2}H\textsubscript{2} partial pressure, H\textsubscript{2} pressure during catalyst preannealing, catalyst exposure time at high temperature prior to growth step, temperature gradient in the gas phase (Figure 3.34). Consistent with previous reports, we see that high growth temperatures produce larger diameter SWCNTs than low growth temperatures, primarily due to the high temperature driven catalyst coarsening. Especially at temperatures above 730 °C, most catalysts resulted in the broadening of diameter distribution and in some cases began showing bimodalities. This is also accompanied by the severe
loss in CNT density (alignment). As described in section 3.4.3, growth temperature also affects the defect density and co-deposition of a-C. Higher the growth temperature is, the lower will be the structural defects on the CNT surface and a-C. Considering the potential effects of various CNT structural properties on mass transport inside nanotubes, we performed the growth of VA-SWCNTs for membrane application at intermediate temperatures of 700-730 °C (Figure 3.34a). Increasing the C_2H_2 partial pressure is observed to increase the average CNT diameter. It is attributed to the shift of CNT formation window to larger size range in a way that the high carbon flux deactivates the more reactive small particles by covering them with defect carbons at a fast rate but activate the less active large particles. Unlike the growth temperature, C_2H_2 partial pressure does not influence the size distribution of dewetted particles but alter the size range of effective catalyst particles at a given CVD condition. Unfortunately, high C_2H_2 flux is found at the same time to significantly deteriorate the CNT quality, as addressed in section 3.4.2. For this reason, the lowest possible C_2H_2 partial pressure close to the threshold for the given particles to thermodynamically and kinetically allow the CNT nucleation and growth is used in growing CNTs for membrane applications (Figure 3.34b). A longer exposure of catalyst to high temperature promotes the catalyst particle coarsening process, thereby leading to the larger average CNT diameter. Instead, catalyst annealing in high pressure H_2 atmosphere prior to CNT growth step is found beneficial for reducing particle sizes and increasing number density of effective catalyst particles because H_2 removes the surface oxide via reduction and the resulting particles that are more metallic and smaller tend to be more reactive (Figure 3.34c). These factors of preannealing duration and H_2 concentration are observed not to influence the CNT quality so much and therefore primarily used to tune the diameter distributions of VA-SWCNTs in making membrane. Lastly, temperature gradient in the gas phase between gas shower head and catalyst substrate inside a vertical CVD reactor used through the studies in this thesis work is found to influence the wall number and diameter distribution of VACNTs. The details are shown in section 3.3 and we remark that TH heating mode (temperature control using only top heater) is in particular beneficial for combining the low substrate temperature to suppress the coarsening and growth enhancers produced from high temperature pyrolysis of acetylene.
Investigation of Mass Transport in SWCNT Membranes
4 Investigation of Mass Transport in SWCNT Membranes

4.1 Brief description of section 4

This section presents new membrane design and a universal fabrication method, which allows for the integration of VA-SWCNTs having a variety of diameter ranges into a robust membrane platform for investigation of mass transport under graphitic nanoconfinement. Along with the strategic selection of VA-SWCNTs with fine-controlled structures, our membrane manufacturing process employs a characteristic step in which individual or locally bundled SWCNTs of the VACNTs is mechanically reinforced by conformal coating via atomic layer deposition (ALD). The conformally coated structure of VACNTs no longer suffers from the common problems in polymer infiltration (i.e., collapse of the nanoforest structure and detachment of VACNTs from the substrate). Since each CNT or CNT bundle becomes sturdier by this step, the conformal coating can basically be followed by any existing polymer-based infiltration methods to complete inter-nanotube gap filling, without damaging the original alignment.

Here, we select a polyethylene (PE) as a gap-filler matrix material whose low viscosity and thermoplastic properties facilitate the infiltration process. Besides, PE is by far the most popular packaging material with properties of flexible, translucent, good low temperature toughness, low cost, and chemical resistance. These features along with the availability of various types of PEs in the market can be particularly beneficial for practical and scaled-up applications of this membrane. Using this new method, we for the first time succeeded in fabrication of a manifold-type SWCNT membrane and used it for the experimental demonstration of mass transport characteristics of a unique pore size ranging from 2 to 5 nm. The measured transport rates of various gases and water are compared with classical models, simulations and experimental data previously reported. These data will be used to complete the map of enhancement over the different degrees of graphitic nanoconfinement and to identify a match between a series of experiments and a set of simulations.
4.2 Requirements for VACNTs in CNT Nanofluidics

In a continuum system, the behavior of a liquid can be described in terms of infinitesimal volumetric elements that are small compared to the flow domain but have well defined thermophysical properties without showing fluctuation. Applying Newton’s second law to a system of continua gives rise to the Cauchy’s Law of Motion (Balance of Linear Momentum) from which Navier-Stokes equations are derived by use of Stokes’ stress tensor. The linearized Navier-Stokes equations in the laminar viscous flow regime of an internal flow result in the Hagen-Poiseuille formalism valid at the continuum level. This representation of the fluid as a continuum, however, begins to break down if one considers a system whose characteristic dimension is commensurable with the size of a transporting molecule. In such a sub-continuum system, many macroscopic properties lose their meaning and thus the prediction of mass and momentum has to incorporate knowledge of the motion of individual molecules. [297, 298] The onset of continuum break-down has not been exactly defined yet, but it is widely accepted that flow through CNTs with lateral dimensions of a few nanometers (e.g., ~6 nm) could fall well into the domain of nanofluidics. [299, 300]

Recent advances in CNT based membrane technology have enabled to realize an artificial nanochannel of only a few nanometers in width. Atomically smooth and hydrophobic properties of graphitic surface and strong nanofinement of the transported molecules inside the CNT channel are found to result in a remarkable slip at the wall, thereby enhancing the mass transport rate far beyond the continuum predictions. [20, 301] Apart from the water flow enhancement, there are many intriguing nanofluidic phenomena expected to occur in the extreme confinement regime, which could not be understood in the framework of the classical continuum flow theories. For example, high proton mobility along one dimensional water chains inside a CNT is predicted, [302, 303] later explained by the transition in proton transport from Eigen (H$_5$O$_4^+$)-Zundel (H$_5$O$_2^+$)-Eigen (H$_5$O$_4^+$) to Zundel (H$_5$O$_2^+$)-Zundel (H$_5$O$_2^+$) mechanism. [304] A controllable molecular sieving of ions can be realized based on the hydrated structure of ions confined inside the CNT channels tunable by tube diameter and surface functional groups. [305] Also, Takaiwa et al. have demonstrated in the MD simulations that water molecules in a
CNT can transform into various ice phases with different number and configuration of hydrogen bonds upon freezing and thus the freezing point of water varies significantly depending on CNT diameter. [306]

Figure 4.1. Water flow enhancement over the Hagen-Poiseuille predictions as a function of the CNT diameter [307]; the red line with solid circles and the black dashed line with empty squares are Falk et al.’s simulation data with and without curvature effect. Schematics of interaction energy landscapes of flat graphene and curved CNT surfaces describe a structural change and a smoothed potential wells by the curvature effect, [22] and the red line with empty circles are Thomas et al.’s data. [308] Also, experimental data from ref. [20, 30, 301, 309] are marked.

In particular, nanoconfinement have great impacts on the structure and configuration of fluid molecules and their interaction with carbon atoms of the CNT. In a large diameter CNT, it is expected that the flow enhancement and other nanofluidic phenomena diminishes drastically. Hence, the use of small diameter CNTs in membrane is particularly intriguing and ultimately desired. As an example, Figure 4.1 shows experimental data and MD predictions to date on the water flow enhancement over the Hagen-Poiseuille formalism with respect to the CNT diameter. Note that the absence of sufficient experimental demonstrations and the large disagreement in the flow enhancement factors among models and experiments have been questioning which
model or result needs to be taken as a standard and how the enhancement factor is related to the nanotube diameter.

For the aforementioned reasons, CNTs used for the nanofluidic investigations are required to have diameters as narrowly distributed as possible and desirably close to the dimension that can be considered in simulations. The narrow diameter distribution of CNTs is particularly desirable because experimentally measured flow rates out of membrane platforms would be an ensemble average value and thus CNTs with the narrower diameter range will produce more representative data for the given mean diameter. Growing the CNTs in a vertically aligned manner and preserving the alignment throughout the fabrication processes are also crucial for uniform spatial density and lengths of CNT channels, whereby the uncertainties associated with the ensemble averaging procedure can be minimized. The homogeneities in membrane pore and thickness are highly desirable for an accurate estimation of the flow rate per CNT from the ensemble averaged experimental value. The CNT quality related to the straightness and structural defects of the CNT channel should also be controlled because the actual CNT channel length could be different from the membrane thickness and also because tortuosity and defect densities could influence the interactions between fluid and nanotube.
4.3 Motivation: Previous reports on CNT membrane fabrication and relevant technical issues

As briefly mentioned in section 1.1.2, the most important challenge remaining for the fabrication of CNT membrane is to integrate high density, aligned CNTs to a membrane matrix in a crack-free and void-free manner. Direct measurement is limitedly applicable to mass transport through individual CNTs because the flow rates are far below the measurement range of the current experimental apparatus. Experimental quantification of the mass transport rate through a CNT can be enabled by the use of membrane configuration which allows the simultaneous measurement of the flow rate through many CNTs in an ensemble-averaged fashion. This method may smooth out the effect of the diameter distribution of CNTs on the distribution of flow rates, and therefore the precise control of diameter distribution of VACNTs is very crucial in determining the diameter-dependent transport. This membrane approach is highly desired not only for adopting the conventional measurement techniques but also for bridging to practical applications.

Qin et al. have recently presented the direct electrical measurement of the water translocation rate through a CNT based on the current change in response to water (a weak electron donor to CNTs). [310] However, this method is found only applicable for CNTs having small bandgaps and has a significant uncertainty in the determination of the potential gradient across a CNT channel. They reported a flow rate enhancement of 51 to 882 for CNTs with diameters of 1.59 to 0.81 nm that are orders of magnitude smaller and thus contradict with previous experimental studies conducted using CNT membranes of similar pore sizes. The bottleneck for the experimental determination of the water flow enhancement arises from the fabrication of CNTs membrane with well-defined structure of CNTs and the rational estimation of the effective pore density and pore area. Previously reported methods in fabrication and characterization of CNT membranes are summarized in Table 4.1.
## Table 4.1. State of the art of CNT membrane fabrication

<table>
<thead>
<tr>
<th><strong>Hinds et al. (2004) [28]</strong></th>
<th>VA-MWCNTs (average $d_{\text{CNT}}$ of 6-7 nm) Freestanding membrane of 5-10 µm in thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Majumder et al. (2005) [301]</strong></td>
<td>Matrix material: polystyrene (PS) Infiltration method: spin-coating of PS (50 wt% in toluene) on VACNTs on a Si support CNT tip opening: H$_2$O plasma-enhanced oxidation which etches PS faster than CNTs, HCl treatment for catalyst removal Characterization: SEM of the membrane surface (pore density), TEM of as-grown CNTs and N$_2$ porosimeter (pore size)</td>
</tr>
<tr>
<td><strong>Holt et al. (2004) [32]</strong></td>
<td>VA-MWCNTs ($d_{\text{CNT}}$ in the range of 20-50 nm): bamboo-like structure Si-supported membrane of 5-10 µm in thickness</td>
</tr>
<tr>
<td></td>
<td>Matrix material: silicon nitride (SiN$_x$) Infiltration method: low pressure CVD (LPCVD) at 800 °C with SiH$_2$Cl$_2$ and NH$_3$ CNT tip opening: RIE (CF$_4$/O$_2$) and Ar ion beam milling, HCl treatment for catalyst removal Characterization: SEM of the membrane surface (pore density), TEM of as-grown CNTs (pore size)</td>
</tr>
<tr>
<td>Figure 4.3. SEM images of the CNTs encapsulated by a SiNₓ and cross-sectioned MWCNTs grown from 5-10 nm Fe catalyst/SiNₓ membrane; a continuous, void-free region extending ~100 nm from the membrane-support interface is denoted by dashed line and the white lines in the image corresponds to individual MWCNTs [20]</td>
<td></td>
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<tr>
<td><strong>Holt and Park et al. (2006) [20, 300]</strong></td>
<td></td>
</tr>
</tbody>
</table>
| VA-DWCNTs (d_{CNT} in the range of 1.3-2.0 nm)  
VA-MWCNTs (average d_{CNT} of ~6.5 nm)  
Patterned-Si-supported membrane of < 5 µm in thickness |
| Matrix material: silicon nitride (SiNₓ)  
Infiltration method: low pressure CVD (LPCVD)  
CNT tip opening: RIE and Ar ion milling  
Characterization: TEM of the sliced membrane (pore density), TEM and size exclusion experiment (pore size) |
| Figure 4.4. SEM and TEM images of the cross-sectioned DWCNTs grown from Fe/Mo/Al catalyst/SiNₓ membrane showing excellent gap filling and CNT channel dimension [20] |
| **Kim et al. (2007) [29]** |
| SWCNTs (average d_{CNT} of ~1.2 nm): acid treated and post-aligned via filtration process  
PTFE-filter-supported membrane of < 1 µm in thickness |
| Matrix material: polysulfone (PSf)  
Infiltration method: spin-coating of a diluted PSf solution onto the filtered CNTs  
Characterization: TEM of the sliced membrane (pore density), N₂ porosimeter (pore size) |
| Figure 4.5. SEM images of the CNTs vertically standing on a PTFE support after filtration and the SWCNTs-PSf membrane after PSf spin-coating [29] |
| **Yu et al. (2008) [27]** | VA-SWCNTs ($d_{\text{CNT}}$ in the range of 2.2-4.7 nm): densified by soaking in n-hexane and drying  
Silver-plated, microporous-filter-supported membrane of ~750 µm in thickness  
No additional filling of inter-nanotube gaps; instead, the inter-nanotube gaps were shrunk to 1.4-7 nm, comparable to the CNT pore size.  
CNT tip opening: *in situ* water etching during CVD [311]  
Characterization: N$_2$ adsorption-desorption measurement (pore density), TEM of as-grown CNTs and N$_2$ porosimeter of as-grown and densified CNTs (pore size) |
|---|---|
| **Du et al. (2011) [30]** | Superlong VA-DWCNTs ($d_{\text{CNT}}$ in the range of 7-14 nm)  
Freestanding membrane of ~4 mm thickness  
Matrix material: epoxy resin  
Infiltration method: dipping the VACNTs on Si substrate in a solvent-free, low viscosity epoxy mixture under vacuum and curing  
CNT tip opening: hand-cutting with a knife  
Characterization: TEM of the as-grown CNTs (pore size), SEM and AFM of the membrane surface (pore density) |

**Figure 4.6.** Photos of densified VACNTs (the original size before shrinkage is indicated by the white lines) and the porous filter supported membrane with an SEM image of its top surface [27]

**Figure 4.7** A photo of DWCNTs/epoxy membrane and AFM and SEM images of the membrane surface [30]
| **Wu et al. (2012) [312]** | SWCNTs (average $d_{\text{CNT}}$ of ~0.9 nm); uniformly dispersed  
Freestanding membrane of ~5 µm thickness  
Matrix material: epoxy resin  
Infiltration method: centrifugal shear mixer  
CNT tip opening: microtoming with a glass blade and water plasma oxidation  
Characterization: TEM of the as-grown CNTs (pore size) and KCl diffusion (pore density) |
| **Ge et al. (2012) [313]** | VA-MWCNTs (average $d_{\text{CNT}}$ of ~7.7 nm and ~5.1 nm)  
Stainless steel microporous mesh supported membrane of ~100 µm thickness  
Matrix material: epoxy resin  
Infiltration method: dipping the VA-CNTs on Si substrate in a solvent-free, low viscosity epoxy mixture under vacuum and curing  
CNT tip opening: mechanical polisher, sand paper and HF treatment for catalyst removal  
Characterization: TEM of the as-grown CNTs (pore size), SEM of the membrane surface (pore density) |

**Figure 4.8** A cross-sectional SEM image of a membrane containing uniformly dispersed SWCNTs in an epoxy resin matrix [312]

**Figure 4.9** SEM images of the cross-sectioned and top surface of MWCNTs/epoxy membrane after mechanical polishing [313]
| **Zhang et al. (2014) [31]** | VA-FWCNTs (average $d_{\text{CNT}}$ of ~7 nm)  
Freestanding membrane of ~10 µm thickness  
Matrix material: poly-para-xylene (parylene-C)  
Infiltration method: room temperature CVD and planarization at 375 °C  
CNT tip opening: Ar/O$_2$ plasma [314] and HF treatment for catalyst removal  
Characterization: TEM of the as-grown CNTs (pore size), KCl diffusion (pore density) |
| --- | --- |
| **Kim et al. (2014) [315]** | A mixture of VA-SW/DWCNTs (average $d_{\text{CNT}}$ of ~3.3 nm)  
Freestanding membrane of 20-50 µm thickness  
Matrix material: polystyrene  
Infiltration method: *in-situ* polymerization at 80 °C  
CNT tip opening: CF$_4$/O$_2$ RIE and HF treatment for catalyst removal  
Characterization: TEM of the as-grown CNTs (pore size), Weight-gain method (pore density) |

**Figure 4.10** SEM images of the cross-sectioned and top surface of FWCNTs/parylene-C membrane after Ar/O$_2$ plasma etching and TEM images of the sliced membrane using an ultra-microtome [31]

**Figure 4.11** SEM images of the cross-sectioned and top surface of SW,DWCNTs/PS membrane after RIE etching [315]
Initial attempts for fabricating VACNT-polymer matrix membrane using the existing methods have revealed severe problems during the gap filling processes, mainly a structural collapse of the VACNTs. This structural disintegration either left a large portion of spaces unfilled (microvoid) or CNT channels blocked, preventing permeation (Figure 4.12).

**Figure 4.12.** (a) A schematic of capillary force driven collapse and agglomeration of VACNTs during polymer infiltration process, SEM images of (b, c) the failed SWCNT-epoxy membrane showing structural collapse and detachment from substrate, (d, e) the failed SWCNT-PS membrane showing incomplete gap filling and mushroom-like structure with kinks, (f) the FIB- cut cross-section (parallel to the CNT axis) of a failed MWCNT-PS membrane showing severe bending of CNT channels and kink formation. (Permission of use obtained by [316].)
In order to investigate the infiltration of viscous polymer into the high-aspect-ratio VACNTs, Buchheim and Park have conducted a detailed forensic study on the failed membrane sliced using a FIB technique. [316] The cross sectional cuts revealed that the initially aligned CNTs were strongly distorted and become discontinuous, forming kinks at the region close to catalyst substrate even though they were well-embedded in the polymer matrix. This finding is attributed to the surface tension effect on the densely grown SWCNTs having low bending stiffness and high aspect ratio. [36-38] In our trials, all existing methods employing polymer as a matrix material have been found inapplicable for VA-SWCNTs. New approaches and advances in membrane fabrication is highly desired.
RESULTS AND DISCUSSION

4.4 Fabrication of VA-SWCNT Membrane

Parts of this section have been submitted for publication in: S. K. Youn, J. Buchheim, H. G. Park, “Fabrication of the first vertically aligned single walled carbon nanotube membrane and the diameter dependent mass flow enhancement”, 2014 (in preparation).

Through collaboration, we have developed a new fabrication process for CNT membrane, which is even applicable to small diameter SWCNTs and thus has universal usability in manufacturing carbon nanofluidics platforms. To the best of our knowledge, this research realizes for the first time the membrane based on VA-SWCNTs. Key to this membrane fabrication method is to mechanically reinforce the individual (or initially bundled) CNTs by conformal coating of a thin oxide layer via ALD prior to gap filling process.

This new approach can be advantageous to the other existing methods in light of (i) lowering membrane fabrication barrier for various types of VACNTs from single- to multiwalled and from sparse to ultra-dense, (ii) literally preserving the initial structure, not only the individual tube straightness but also the inter-nanotube distances, and (iii) broadening the scope of matrix formation.

Another method that can manage to produce a CNT membrane is to prolong the ALD process until most of the gaps are more or less filled by the atomic layer deposited material. Owing to the hindered diffusion of ALD precursor through VA-SWCNTs and the original tortuosity of individual or bundled VA-SWCNTs, a complete gap filling can hardly be achieved. However, the void-free region of ~20 nm thickness near membrane-support interface is found sufficient to block leakage and withstand a pressure drop up to 1.5 bar, surprisingly. Still, application of this approach is limited to VACNTs with relatively low areal densities and low aspect ratios.
4.4.1 New fabrication procedure

The fabrication process for the two types (A and B) of membranes is illustrated in Figure 4.12 and can be summarized as follows.

(1) Micro pit formation on the backside of Si support with the top side being protected for catalyst deposition

(2) Catalyst deposition on the HF-cleaned, top side of the Si support

(3) CCVD of VACNTs

(4) ALD for the conformal coating of VACNTs with a 20–30 nm-thick oxide layer: mechanical reinforcement

(5-A) Filling the remaining gaps with a PE melt; by placing a microtomed PE film at the top of the VACNT structure and thermally annealing at temperature higher than the softening point of PE in a vacuum oven for overnight

(5-B) Additional ALD until the bottom region of VACNT structure is completely buried in an oxide matrix and becomes void-free.

(6) Further etching from the micro pits to define active membrane areas, removal of excessive PE, atomic layer deposited oxide and catalyst layers, and uncapping the both ends of VACNTs.
Figure 4.13. Schematic of the CNT membrane fabrication process. Step 1: formation of micro pits on Si substrate by KOH anisotropic etching. Step 2: catalyst deposition. Step 3: CCVD of VACNTs. Step 4: conformal ALD coating of CNT bundles with 20–30 nm-thick oxide. Step 5-A: Gap filling with low viscosity polyethylene (PE) melts for type A membrane. Step 5-B: additional ALD process with a target layer thickness between 50 and 80 nm for type B membrane. Step 6: backside sequential etching of AlOx, Si, and catalyst layer by XeF2 isotropic etching and Ar ion beam milling, along with top side etching of excessive PE (for type A membrane) and ALD-coated oxide layer by O2 and Ar ion beam millings, often followed by the CNT uncapping by RIE etching, from which the membrane begins to show gas permeance.
4.4.2 Step 1-3: Preparation of VACNTs on a patterned membrane support

The membrane fabrication begins with the preparation of a patterned support on top of which VACNTs will be grown via CCVD. Starting material for a membrane support is a 4-inch diameter <100> Si wafer (510-550 µm in thickness) coated on both sides with low stress SiNₓ (100-250 nm in thickness). One side of the SiNₓ/Si/SiNₓ wafer is patterned by flood-exposure photolithography using the mask shown in Figure 4.14a. Each wafer produces ten membrane chips of 2 cm x 2 cm and each membrane chip contains an array of 89 micro pits of 800 µm x 800 µm. The photoresist pattern is transferred to the SiNₓ layer by reactive ion etching (RIE), which becomes an etch mask for Si etching process.

Figure 4.14. (a) A 4-inch photomask pattern used for the preparation of the membrane supports. (b) Each 2 cm x 2 cm chip contains (c) 89 micro pits of 800 µm x 800 µm lateral dimension. (d) A cross-sectional SEM image of VACNTs grown on the catalyst deposited on remaining Si on the other side of the pyramid shaped micro pits.
The SiNx (patterned)/Si/SiNx wafer is anisotropically etched in a continuously sonicated 44 % KOH (aq.) solution at 80 °C. Each 800 µm x 800 µm square shaped exposed Si area is etched down, resulting in a pyramid shaped micro pits with an angle to the wafer surface of 54.7 ° due to the preferential Si etching in the ⟨100⟩ plane (Figure 4.14b). The etch rate of Si with 44 % KOH (aq.) at 80 °C is about 1 µm/min. The etch depth (z) of micro pit can be approximated by the relation of $z = W_m/\sqrt{2}$ where $W_m$ is a lateral dimension. For the given case of $W_m$=800 µm, the tip of micro pit will be located about 565 mm down the wafer surface. Considering the initial thickness of Si layer that is about 525 µm, this etching process is stopped before the self-termination, leaving around 10–50 µm-thick Si layer on the opposite side of wafer. The etch selectivity of Si and SiNx in a KOH (aq.) solution is very high. Therefore, the SiNx layer on the opposite side of the micro pits is not damaged during this wet etching process and can be protected till further etched by HF (aq.) solution prior to catalyst deposition.

The wet etching of SiNx with HF has very fast etching rate of 20 nm per min and it also removes native oxide layer that could potentially exist at interface. With a fresh 40 % HF (aq.) solution, 25-30 minutes were enough to remove the remaining SiNx layer. The use of freshly made HF solution every time is preferred to minimize unnecessary exposure of Si surface to HF (aq.) solution which could also etch Si (10:1 HF etch selectivity of SiNx and Si) and make the surface rough. Uncontrolled variation of the Si surface roughness can hinder the fine control of catalyst for CCVD of VACNTs. Various types of catalysts are then deposited by electron beam evaporation or ALD. Details about catalyst and CCVD parameters taken for growing VA-SWCNTs of a certain diameter range are addressed in previous sections. Figure 4.14d shows an example of VA-SWCNTs grown from the catalyst deposited on the other side of micro pits.

In step 3, the number density of nanoparticles on the catalyst substrate that are exposed to CCVD condition is characterized using AFM (Figure 4.15) and later on compared with that of the grown CNTs and also used as an upper bound of CNT density in the characterization of membrane properties. Individual CNT structure is probed by Raman spectroscopy and TEM image analysis and the bulk properties of VACNTs, mainly the vertical alignment and CNT density
are checked by high magnification SEM images of cross sectioned sample of VACNTs. Note that the most reliable estimation method of CNT density is the averaged number density of CNTs counted from the FIB lamellar of the CNT membrane at the last stage of fabrication, which will be further discussed in section 4.5. In most cases, surface nanoparticle density is somewhat or quite higher than actual CNT density because not all the nanoparticles are catalytically active for growing CNTs in a given condition.

**Figure 4.15.** The number densities of surface nanoparticles (NPs) evolved from the catalysts with various thickness and compositions under different CCVD conditions; catalyst type and CCVD parameters used for membrane fabrication resulted in surface NP densities in the range of $\sim 10^{11}$ per cm$^2$. 
4.4.3 Step 4: Mechanical reinforcement of VACNTs by a conformal ALD coating

In order to prevent the disruption of vertical alignment and uniform CNT distribution during gap filling, we propose to coat intertwined VACNTs with a rigid material using a gas phase deposition technique and make contacts in between them to mechanically support each other from any kinds of stresses in the following steps. One applicable technique is ALD, which deposits materials conformally based on the automated cycling of precursor gases (Figure 4.16).

![ALD coating process](image)

**Figure 4.16.** Schematic of an ALD coating process of alumina on VACNTs composed of two self-limiting surface reactions of TMA and water precursor. A single ALD cycle produces about a monolayer of alumina.

ALD process is composed of two self-limiting reactions, thereby leading to a linear increase of deposition thickness depending on the number of ALD cycles. [317] However, the unique geometry of VACNTs may retard and limit precursor diffusion in gas phase for ALD. Also, achieving a conformal coating on inert surface of non-functionalized CNTs or CNTs with low defect density has been one of the major challenges for ALD on VACNTs. [318, 319] Without functional groups or seed layer on the surface, coating will start with a nodule formation and become smooth merely after relatively thick (approximately 25 nm) film would have been deposited. [320] In this
sense, thinner conformal deposition could be achieved when the CNT surface has defects, created by covalent chemical bonding, or broken graphitic lattice. However, these approaches cannot be considered because they destroy the unique surface and mechanical properties of a CNT channel. [321, 322] Instead, less destructive methods using the strong physisorption of NO\textsubscript{2} gas or ozone on CNT surface are preferred but there could be a so-called “macaroni effect” in these cases, allowing the deposited layer to easily slip off the CNT surface. [323]

![SEM images of alumina-coated VA-SWCNTs after 140 cycles of ALD, showing a decreasing gradient of deposited alumina thickness deeper inside VACNTs; ALD deposition of alumina was performed at temperature of 250 °C using TMA (0.2 s pulse width, 5 s purge) and water (0.5 s pulse width, 5 s purge) as precursors.](image)

**Figure 4.17.** SEM images of alumina-coated VA-SWCNTs after 140 cycles of ALD, showing a decreasing gradient of deposited alumina thickness deeper inside VACNTs; ALD deposition of alumina was performed at temperature of 250 °C using TMA (0.2 s pulse width, 5 s purge) and water (0.5 s pulse width, 5 s purge) as precursors.

A conformal ALD coating of alumina has been attempted on as-grown VA-SWCNTs. When the typical ALD condition for thin film electronic applications using trimethylaluminum (TMA) and water as precursor were adopted for coating ~55 µm thick VACNTs, coating thickness was found to vary depending on the distance from the growth front of VACNTs (Figure 4.17). CNTs in upper section were coated with a continuous alumina layer while those in lower section were decorated with discontinuous nodules. CNTs are a rolled up graphite sheets and their conjugated surfaces tend not to accumulate charges under beam irradiation for SEM imaging. Therefore, the charging induced bright contrast in the upper section of VACNTs must be originated from the insulating property, most likely from the alumina coating.
Such a thickness gradient can be attributed to the hindered diffusion of precursor gases and higher concentration and longer transport time of precursor gases required for chemisorption saturation of the high surface area of VACNTs in every deposition cycle. The former can be partly suppressed for VACNTs of low areal density, less intertwining and shorter height, but cannot be avoided because the transport paths for precursor gas, *that is*, inter-CNT spaces become narrowed and eventually blocked as the number of ALD cycle increases. The latter can be compensated by increasing deposition temperature or pulse width and pulse number of precursor gases per cycle.

![Time diagram of control signals to TMA, water, ballast N₂, and purge N₂ valves; process optimization with higher number of pulse per cycle, longer pulse width and purge duration is needed for a conformal coating of alumina on relatively tall VACNTs.](image)

**Figure 4.18.** Time diagram of control signals to TMA, water, ballast N₂, and purge N₂ valves; process optimization with higher number of pulse per cycle, longer pulse width and purge duration is needed for a conformal coating of alumina on relatively tall VACNTs.

To ensure a conformal coating for further studies, the height of VACNTs grown for membrane fabrication was limited below 20 µm unless the length of CNT channel is a subject of interest. For coating tall VACNTs (< 150 µm), both pulse width and pulse number per cycle of TMA and water were increased from 0.2 s to 0.5 s (TMA), from 0.5 s to 1.0 s (water) and from 1 pulse per cycle to 3 pulses per cycle while the deposition temperature was kept constant at 250 °C. The nitrogen
purge width between the precursor pulses was also increased from 5 s to 10 s (Figure 4.18). Note that increasing pulse width can make the pulse (the actual flow rate of precursor) unstable.

It is noteworthy that other materials including metal oxides (i.e., HfO$_2$, TiO$_2$), metal nitrides (i.e., TiN, TaN) and metals (i.e., Ru, Ir, Pd, Pt, Cu, and W) can be also used in this ALD process. Since Rafiee et al.’s reports on the wetting transparency of monolayer graphene, the question about how atomic or molecular interactions transmit across the thin graphitic lattice plane has been attracting great attentions. For SWCNT membrane, nanotube channels are separated by similarly a single but curve graphene layer from the surrounding coating material. The interaction between water and matrix material and its effect on flow enhancement is also very intriguing question which has been answered yet. Varying the coating material during ALD step can be very simple way to study this subject and will be pursued in the future.

We characterized the morphology of the alumina coated VA-SWCNTs using SEM and TEM and observed a transition of coating mechanism with an increase of the number of ALD cycle (Figure 4.19). After a low number of ALD cycles, all SWCNTs were coated uniformly from top to root but the coating is quite discontinuous because of the lack of nucleation sites on non-functionalized high quality SWCNTs. Only after about 100-150 ALD cycles, the majority of VA-SWCNTs were conformally coated with alumina, exhibiting the core-shell structure. According to TEM image analysis, the conformal coatings were made for a unit of bundled SWCNTs, instead of individual SWCNTs. It is because of that VA-SWCNTs are initially comprised of small bundles, containing 10 or fewer SWCNTs per bundle and the inter-CNT spaces inside the bundle is narrower than inter-bundle spaces. ALD precursors can pre-adsorb and promote the layer growth from the interstitial spaces between individual SWCNTs constituting a bundle. The narrow spaces between the CNTs in a bundle will be filled up much faster than the inter-bundle spaces and at the same time make contacts between adjacent CNTs, merging them into a large CNT-alumina composite rod structure of tens or hundreds of nanometers in diameters.
Figure 4.19. SEM images of (a) as-grown and alumina-coated VA-SWCNTs after (b) 50, (c) 100, and (d) 450 ALD cycles, the coating morphology changes from discontinuous nodules on individual CNTs to conformal coating layers on bundled CNTs.
Figure 4.20. TEM images of the alumina (700 ALD cycles)-coated, bundled VA-SWCNTs; the cross-sectional lamellar was cut parallel to catalyst substrate using a FIB technique and an inset image is obtained from the detached and solution-dispersed fragments of alumina-coated, bundled SWCNTs by scratching the sample with a sharp tip of a tweezer.

Figure 4.20 shows the cross-section of alumina-coated, VA-SWCNT bundles after 700 ALD cycles, prepared using a FIB technique. Based on TEM image analysis, we approximate that each alumina coated bundle contains about 3 to 8 SWCNTs. As seen by the presence of voids between the SWCNT bundles excessively coated with alumina, the void-free gap filling of VA-SWCNTs cannot be achieved by this ALD process alone because of the gradual blockage of precursor transport path and the inherent tortuosity and entanglement of VA-SWCNTs.
Figure 4.21. The measured diameters of alumina coated VA-SWCNT bundles from the cross-sectional SEM images with respect to the number of ALD cycles; 150-300 ALD cycles which generates alumina coated bundles of 30-50 nm in diameter (highlighted by green color) are found to be optimum for membrane fabrication. An inset show a representative SEM image of the conformal coated SWCNT bundles with alumina layer.

Here, our primary goal for ALD process is to protect the fragile small diameter SWCNT channels from mechanical deformation during subsequent polymer infiltration process. For membrane fabrication, therefore, deposition of not too thick and continuous alumina layer is desired to fully encapsulate all the CNTs, strengthening the structure to be highly resistant to lateral and vertical compressive stresses and still leaving sufficient vacant spaces that can be used as infiltration paths for matrix material. Figure 4.21 shows the relation between the diameters of alumina coated VA-SWCNT bundles and the number of ALD cycles. 150-300 ALD cycles are found to be optimal for the conformal coating of as-grown VA-SWCNTs with density in the range of ~10^{11}/cm^2. SEM images in Figure 4.22 show the coating uniformity from top to bottom and the void spaces of several tens of nanometers in diameters parallel to the alumina coated VA-SWCNT bundles.
Figure 4.22. (a) Cross-sectional and (b) top-view SEM images of the bundled VA-SWCNTs coated with 10–15 nm-thick alumina layers after the optimal number of ALD cycles.

To understand the interaction between alumina and SWCNTs, we characterized the VA-SWCNTs subjected to various number of ALD cycles using Raman spectroscopy. The absolute peak intensities were reduced as well with an increasing number of ALD cycles because alumina-coated CNTs cannot resonate with the same magnitude as before. The Raman peak shifts of the G band and the 2D (G’) peaks reflects doping and stress induced effects on CNTs by the dielectric coating. According to the literature, peak shifts in the G band can be attributed to the circumferential and axial stress induced by ALD coatings on CNTs [327, 328] or the doping effects that occur due to precursor molecules bonding with CNT and charge transfer at defect site. [329] ALD deposited alumina were reported to have an n-doping effect on CNTs, resulting in a red shift from the original peaks. [330] We observed a blue-shift (increase in frequency) with an increase of number of ALD cycles, indicating that the stress effect is dominant in this case (Figure 4.23a). On the other hand, G-to-D ratio as a measure of CNT quality decreases with a thicker ALD coating. This can be seen that ALD layer growth on CNTs generates defects, degrading the C-C bonding of graphitic network. However, we found that the G-to-D ratio can be recovered when the deposited alumina layer is dissolved in water (Figure 4.23b). This indicates that ALD process does not alter the surface chemical properties of CNT channels and therefore is a good method not only for mechanical reinforcement but also chemical protection of VA-SWCNTs in a heterogeneous matrix material.
Figure 4.23. (a) Variations in the Raman G-to-D ratios of VA-SWCNTs with respect to the number of ALD cycles (the coating thickness of alumina layer) and (b) Raman spectra of as-grown, alumina-coated (700 ALD cycles) and alumina-removed VA-SWCNTs. All spectra were recorded using 785 nm laser excitation.
4.4.4 Step 5-A: Gap filling with polyethylene

The next critical step for the membrane fabrication is to fill up the remaining inter-bundle spaces with a matrix material, which is the low viscosity PE (Aldrich, $M_w \sim 35,000$, density 0.906 g/mL, melting point ($T_m$) 90 °C, and softening point ($T_s$) 104 °C determined by ring and ball method). Note that softening point is the temperature at which a material softens beyond some arbitrary softness, reflecting not only the melting point but also molten polymer viscosity (the resistance of a polymer melt to flow). The ring and ball method measures the temperature at which the polymer becomes soft enough to allow the ball enveloped in it to fall a certain distance.

![Figure 4.24. Gap filling of the VA-SWCNTs with polyethylene: (a) the ~10 µm thick microtomed PE film is placed on top of VA-SWCNTs and heated up to the temperature above softening point in a vacuum oven; (b) the gaps between alumina coated VA-SWCNT bundles are perfectly filled with PE.](image)

A PE film with the thickness higher than the forest height is microtomed from PE block (prepared by solidification of molten PE granules in a mold) and placed on top of the structure covering the surface evenly (Figure 4.24a). When heated above the softening point inside a vacuum oven, the solvent-free molten PE penetrates into the alumina-coated VA-SWCNTs, completely filling up the rest of the spaces within 5-6 hours. Figure 4.24b shows an example of complete gap filling without any voids or cracks visible in the cross-section of membrane. A few micrometers thick pure PE and pure alumina membranes showed no gas and water permeabilities. Therefore, the
CNT channels can be considered as the only transverse fluid paths in this alumina-coated VA-SWCNTs/PE membrane.

Thanks to the low viscosity and thermoplastic property of PE, the infiltration became much simpler and easier to control compared to the existing method of using polymeric solutions or vapors. During the infiltration, the polymer chains with enhanced fluidity above $T_m$ melt down gradually along the topography of the bundles from the contact points between thin PE film and the tips of alumina-coated SWCNT bundles without forming a meniscus and fill up the void from bottom to top direction. Initially, infiltration process is optimized by varying temperature and time. Melt viscosity of a polymer melt varies with shear rate, temperature, pressure and molecular properties of polymer (i.e., viscosity increases for more rigid monomer units, with molecular weight). When the shear rate reaches a critical value, the polymer chains begin to align in the direction of flow and the melt viscosity starts to decrease with increasing shear rate, showing a power law relation. The shear rate, however, was not considered as a process parameter since we do not prefer to impose any kind of shear stresses to the VA-SWCNTs. Instead, increasing temperature and decreasing pressure during infiltration process are more practical approaches to lower melt viscosity.

![Image](image_url)

**Figure 4.25.** An incomplete gap filling of alumina-coated bundled VA-SWCNTs when PE infiltration is performed at temperature of 90 °C ($T_m$) for overnight in a vacuum oven.

Infiltration at temperature at 90 °C ($T_m$) resulted in an incomplete gap filling that only the bottom part of the structure was filled without
voids and the rest part was circumferentially coated with thin PE layer (Figure 4.25). PE film placed on top of the structure maintained its integrity throughout the process and could be easily stripped off from the membrane surface. This is due to the high melt viscosity of PE at the given condition which holds the polymer chains together and the slow and localized flow of a molten PE at the contact points (Figure 4.26). Accordingly, the infiltration needs to be performed at temperatures higher than $T_m$.

![Figure 4.26](image)

**Figure 4.26.** Comparison of PE infiltration through alumina-coated bundled VA-SWCNTs at different temperature ranges: (a) temperatures higher than melting point but lower than softening point and (b) temperatures higher than both melting and softening point of PE; other parameters such as pressure, infiltration time and initial PE film thickness were kept the same in these experiments.

We observed a noticeable difference in the gap filling process of a molten PE at different temperature conditions (Figure 4.26). At temperatures higher than melting point but lower than softening point of PE, the inter-bundle gaps were perfectly filled while at temperatures higher than both melting and softening point of PE a number of nanosized voids were found in the PE matrix. Since these voids were observed to be discontinuous and formed locally, it may not have a great impact for making the membrane. Still, the former
temperature range is preferred for the better membrane integrity and the ideal integration of VA-SWCNTs into a perfectly impermeable matrix. The upper images in Figure 4.26 provide hints on how the thin PE film melts and infuses into the structure at the interface. The two planes of PE film and alumina-coated VA-SWCNTs were not in complete contact with each other during infiltration at $T<T_s$, while at $T>T_s$ there was no clear boundary interface between the two media. Also, for former case, it was possible to peel off the remaining film after infiltration.

![Figure 4.27](image_url)

**Figure 4.27.** Two distinct mechanisms for the infiltration of a molten PE into the alumina coated bundled VA-SWCNTs at different temperature condition that is higher or lower than the softening point ($T_s$) of PE.

Based on these observations, we claim that gap filling mechanisms are intrinsically different at the two temperature regimes as described in Figure 4.27. At lower temperatures than $T_s$, the molten polymer with still quite a high viscosity can flow down along the bundles at a slow rate and gradually fill the gaps in a layer-by-layer mode parallel to the bundles. In other words, a massive displacement of the bulk PE can be avoided thanks to the strong entanglement among PE chains in the film. In this case, when the infiltration is completed, embedded bundles can be seen through the thinned PE top layer whose surface morphology remains almost the same, indicating that the bulk PE film maintain the integrity below $T_s$ and the melts flow locally occurs at the interface of PE film and $\text{Al}_2\text{O}_3$-coated SWCNT bundles. At higher temperatures than $T_s$, on the other hand, the overall infiltration requires much shorter time due to the low viscosity of the polymer melts, however, has high probabilities of trapping the air in polymer matrix (void formation) and imposing high stress on the
bundles. The lower image of the Figure 4.26b showed a broken alumina coated VA-SWCNT bundle after the infiltration at $T>T_s$.

Note that in both cases the molten PE, which has lower surface energy than alumina, is prone to wet and well-spread over ALD coated alumina surfaces of the VA-SWCNT bundles. [331-333] But the temperature driven changes in the interactions between polymer chains (thus, the surface tension of a molten polymer) alters their infiltration behavior into the nanochannels. The unique thermo-viscosity of the PE chosen for gap filling (softening point higher than melting point) enables to finely control the flow behaviors of polymer melts and aids the void-free gap filling of the nanochannels in between the alumina-coated VA-SWCNTs bundles. Lastly, we emphasize that optimal ALD coating of VA-SWCNTs in step 4 is a prerequisite for a successful gap filling. Figure 4.28 clearly shows that insufficient ALD coating results in the structure deformation and excessive ALD coating does not provide paths for a molten polymer.

**Figure 4.28.** Cross-sectional SEM images of PE infiltrated, alumina-coated VA-SWCNTs; (a) initial CNT alignment was disturbed and membrane film was locally detached when the mechanical reinforcement of VA-SWCNTs is insufficient by a discontinuous alumina coating, (b) the molten PE even at the temperatures higher than $T_s$ could not penetrate into the structure due to the blocked top surface after excessive number of ALD cycles.
4.4.5 Step 5-B: Void-free region of VACNTs excessively coated with alumina layers using ALD

As mentioned in section 4.4.3, a complete void-free gap filling of VA-SWCNTs can hardly be achieved by the ALD process. The diffusion paths for ALD precursors continue to shrink with an increase of the number of ALD cycles and the intrinsic tortuosity and entanglements of VA-SWCNTs promote the progress to pore blockage. However, we found that about 20-250 nm thick region extending from membrane-support interface were void-free, as denoted by the dashed line in Figure 4.29.

A control experiment with a 20 nm thick ALD deposited freestanding alumina film showed no gas permeance. Also, the membrane having ~20 nm thick void-free region showed no gas permeance till the CNT tips on the top side of membrane were opened, indicating that the large voids in the top region of structure does not propagate through the membrane. Accordingly, we report that a few tens or hundreds of nanometers thick void-free region of the VACNTs embedded in an alumina matrix is sufficient to block any leakage flows and can withstand a pressure drop of up to 1.5 bar. Thickness of the void-free region could not be increased more than a few hundreds of nanometers. Because even at the very low deposition rate of ALD process the gap filling (the penetration depth of precursor gases) is strongly limited by the density and height of VACNTs. Additional deposition beyond 500 ALD cycles had no influence on the thickness of void-free region. Compared to the alumina-reinforced SWCNTs/PE membrane, this platform requires simple and low number of steps in fabrication process. Therefore, we chose this method to fabricate the membranes for studies on gas transport through SWCNT membranes. However, this platform is not suitable for other studies in an aqueous, acid or basic environment due to the amphoteric property of an alumina.
Figure 4.29. SEM and TEM images of the cross-section of alumina coated VA-SWCNTs; the void-free region (about 80 µm in thickness) of the membrane is indicated by the black dashed line and the bundled VA-SWCNTs embedded in an alumina matrix are also distinguished. Here, the lamellar was cut perpendicular to the substrate using a FIB technique.
4.4.6 Step 6: Etching processes for membrane opening

Once the fixation of VA-SWCNTs within the PE or alumina matrix is completed, multiple steps of etching process for excessive PE layer, ALD deposited alumina coatings, underetched Si substrate, catalyst film and both ends of CNT channels should be followed to activate the CNT membrane. Figure 4.30 describes the overall etching process for opening the two types of CNT membranes and also summarizes the etching techniques used in each step.

**Figure 4.30.** Schematic of the overall etching process and the description of the used etching techniques to open the two types of CNT membranes (Al$_2$O$_3$-coated SWCNTs/PE and SWCNTs/Al$_2$O$_3$); the numbers and dashed lines denotes the etching process order and the target material to be etched away.


**Ar or O₂ ion beam millings and reactive ion etching**

Considering that none of the gap-filling materials, alumina and PE, is a good thermal conductor, we first proceed the top side etching of the CNT membrane prior to the etching of the bottom Si substrate that can function as heat dissipater during the energy intensive etching processes. The excessive PE layer, ALD deposited alumina coatings and later on the exposed catalyst film and both ends of CNT channels can be etched away using ion millings with Ar or O₂ gas and reactive ion etching in oxygen-containing plasma.

Ion beam milling is, conceptually speaking, an atomic sand blaster. In place of fine sand grains, sub-micron ion particles physically bombard the surface of the substrate mounted on a rotating sample holder (maximum 20 rpm). The ionized species of Ar or O₂ source contained within plasma formed by an electrical discharge are accelerated by a pair of optically aligned grids. The highly collimated ion beam is focused on target substrate with tunable angles during the milling operation. A neutralization filament prevents the charge buildup that would repel the ion beam (so as to allow the milling of both insulators and conductors) on the sample holder whose temperature is at the same time maintained at room temperature by a dedicated chiller system. It also minimizes space-charge spreading of the positively charged ions that can generate image charges after the acceleration grids and retard the ion beam.

The ion energy and beam current density which determines etch rate and uniformity of the milling process depend on acceleration voltage and source plasma density. The ion energy determines the sputtering yield, defined as the average number of atoms ejected from the target surface per incident ion, while the beam current density determines the total number of sputtered atoms and thus the etch rate. [334, 335] For the ion beam milling system (ionfab 300, Oxford) used in this study, a monitored ion beam current of 100-250 mA corresponds to the current density of 0.51-0.85 mA/cm², resulting in the etch rates of 2-4 nm/min for ALD-deposited alumina with Ar ion source and 20-25 nm/min for PE with O₂ ion source. It is known that the etch rate of ion milling linearly proportional to the ion beam current and quasi-linearly proportional to the ion energy. We chose to use a moderate beam current and ion energy to minimize the substrate heating (damage) during the milling process and spatial non-uniformity of
etching. Another crucial parameter affecting etch rate and uniformity is the incident angle at which the ion beam hits the substrate surface. As shown in Figure 4.31, etch rate increases with an increase of the ion beam incidence angle at first (because a collision occurs near the sample surface) and reaches a maximum at around 30-60°. [300] At this oblique incidence, due to the reduced momentum of ions normal to the surface, surface scattering becomes dominant and ions cannot penetrate deep into substrate. At large angles beyond the maximum etch rate point, the etch rate decreases because the incoming ion beam spreads over a much larger surface area. [336]

**Figure 4.31.** Etch rates of Al, Si, SiO₂ and photoresist with respect to the ion beam angle of incidence for a 600 eV Ar ion beam [300] and a schematic of the ion beam milling system used in this study (ionfab 300,Oxford). [337]

The ion beam milling system (ionfab 300, Oxford) used in this study is made to load the substrate holder at an angle of -90° with the ion beam source and allows to tilt between -90° and up to about + 65° (Figure 4.32). In all cases, for etching excess PE and alumina coatings of VACNT bundles from the top side or catalyst (metal and alumina support) from the bottom side, the rotating surface was tilted by -5° or -20° to minimize the redeposition effect. [338] Ion beam milling is known to be non-selective and thus suitable for our purpose to etch different materials constituting the CNT membrane at the same time. Only when O₂ was used as an ion source, we observed a faster etch rate for PE than for alumina, which is beneficial for the removal of excess PE.
In case that excess PE layer is too thick to be etched in reasonable process time by ion beam milling method of a relatively low etch rate, we used RIE process with O\textsubscript{2} containing plasma, which gives higher etch rates in the range of 250-400 nm/min at a power density of 0.25 W/cm\textsuperscript{2}. Different from ion beam milling, RIE involves not only physical bombardment but also chemical reaction mechanism and the etch rate can be controlled by varying bias voltage, O\textsubscript{2} flow rate and composition of gas mixture. In Ar/O\textsubscript{2} plasmas, as the Ar-to-O\textsubscript{2} ratio increases, dominant etching process changes from an ion-enhanced chemical process with high etch rate to a physical sputtering process with low etch rate. RIE with O\textsubscript{2} containing plasma is also used for CNT cap opening and membrane surface cleaning at the last stage of fabrication.

**Isotropic vapor phase etching of Si with XeF\textsubscript{2} vapor**

Isotropic dry Si etching method with Xenon difluoride (XeF\textsubscript{2}) vapor is used to remove the remaining 10–50 µm-thick Si layer beneath the gap-filled VA-SWCNTs. XeF\textsubscript{2} sublimates at its vapor pressure (~3.8 Torr at 25 °C) in a separate chamber and when reaching its vapor pressure it is released to the process chamber to etch the Si; 2XeF\textsubscript{2} + Si → 2Xe (g) + SiF\textsubscript{4} (g). Figure 4.33 shows the exposed catalyst layer underneath CNT membrane (mainly, alumina support deposited for metallic catalyst showing a granular surface morphology) on a micro pit after 60-80 etching cycles. We analyzed the surface with an EDS (Energy-dispersive X-ray spectroscopy) detector and the appearance of alumina elements is evident in the inset of the Figure 4.33b. The
dimension of the square shaped exposed membrane area was characterized using SEM at the last stage of fabrication to estimate an effective membrane area, which is required to evaluate the membrane performance.

**Figure 4.33.** SEM images of the exposed membrane area after the XeF$_2$ etching of the remaining Si on the tip of the 89 micro pits. Along with the granular surface, an EDX spectrum on the exposed surface indicates that the electron beam deposited alumina layer as metallic catalyst support are exposed on the surface.

Compared to other Si etchants, XeF$_2$ etching is highly selective to Si with respect to SiO$_2$, Si$_3$N$_4$, aluminum and photoresist. [341] Also, being gas phase process, it does not suffer from the stiction between the structure being freed and the substrate, which is different from the typical liquid etchants. Lastly, XeF$_2$ etching shows quite fast etching rate (i.e., ~1 µm/cycle in our case although it significantly drops as the number of samples processed at a time increases). [342] These features of XeF$_2$ etching of Si are advantageous for our purpose.

Nevertheless, XeF$_2$ etching method can result in the etching non-uniformity (especially, when a large sample is subjected to the etching) and the granular morphology of the etched surface. For example, when we attempt to etch the remaining Si layer deep inside the micro pit, we observed that the micro pits near the edge of membrane chip were opened faster than those in the middle. Roughening the surface of Si support should be concerned because we need to place an O-ring on the top surface and make a gas tight seal for precise measurements. To avoid this problem, the rest of the Si surface except the middle
area with 89 micro pits were completely sealed with Kapton (a polyimide film (DuPont), stable over a wide range of temperatures from −269 to 400 °C) tape for XeF$_2$ etching. At the same time, the top side with CNT membrane was covered by a glass microscope slide to be protected from being etched by XeF$_2$. Note that membrane sample needs to be dehydrated prior to the etching to prevent the formation of a silicon fluoride polymer via the reaction between the residual water and XeF$_2$ gas. Also, it is recommended to treat the XeF$_2$ etched surface with a short RIE or ion milling process in order to ensure complete desorption of the product molecule (SiF$_4$ and Xe) or residual XeF$_2$.

**Changes in surface morphology of VA-SWCNT membrane during etching process**

The Figures 4.34, 4.35 and 4.36 show how the surface morphology of top and bottom sides of the two types of VA-SWCNT membranes during etching process. As etching process proceeds, structure of dense alumina-coated SWCNT bundles appear on both sides of the membrane and with a further etching we could observe core-shell structure of the bundles and bright contrast CNTs exposed on the surface in the top view SEM images (Figure 4.34). It is a good indication for the complete removal of matrix materials and an exposure of CNT tips. Once the top side etching is completed, bottom side etching is performed. For type A membrane, surface morphology of the bottom side eventually looks quite similar to that of the top side, which makes sense. However, for type B membrane having a few tens to hundreds nanometers-thick void free region at the interface of membrane and substrate, the etched surface of bottom side shows rather smooth and continuous morphology because all gaps between the bundles are filled up with the same material, which is alumina (Figure 4.35). Once gas permeance reaches a maximum where we consider most CNT channels are opened, we made a membrane lamellar using FIB and confirmed that the membrane is free of cracks and voids. Also, VACNTs maintained initial alignment and their tips were found at the surface of both sides (Figure 4.36).
Figure 4.34. SEM images of the top side of VA-SWCNT membranes before and after etching processes: (a) alumina-reinforced VA-SWCNTs/PE membrane and (b) VA-SWCNTs/alumina membrane.
Figure 4.35. SEM images of the bottom side of VA-SWCNT membranes before and after etching processes: (a) alumina-reinforced VA-SWCNTs/PE membrane and (b) VA-SWCNTs/alumina membrane.
Figure 4.36. SEM images of the cross-section of VA-SWCNT membrane that is cut perpendicular to the substrate: (a) alumina-reinforced VA-SWCNTs/PE membrane before and after etching processes and (b) VA-SWCNTs/alumina membrane after etching processes.
### 4.4.7 Run sheet: CNT membrane fabrication

<table>
<thead>
<tr>
<th>Process</th>
<th>Stage</th>
<th>Parameter</th>
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<tbody>
<tr>
<td><strong>1. Preparation of a patterned membrane support</strong></td>
<td>Photo-lithography</td>
<td>Spin-coating: - 4&quot; &lt;100&gt; Si wafer (525 µm thick) with low stress SiNx layers on both sides - AZ4515 (photoresist) - 4000 rpm 40 s (3.3 µm) Soft bake: - 110 °C (on hotplate), 1 min Exposure: - 90 mJ/cm² (6 s at 15 mW/cm²) Develop: - AZ400K, 1.3-25 s</td>
</tr>
<tr>
<td><strong>2. Catalyst deposition for CCVD of VACNTs</strong></td>
<td>Removal of SiNx and native oxide</td>
<td>HF: -40 % HF (aq.) -temperature: 25-30 °C -time: 20-25 min -Rinse in running DI-water for 10 min Catalyst deposition Ebeam evaporator (Univex 500, Leybold): -deposition rate and thickness 0.2 Å/s (alumina); 20 nm 0.033 Å/s (metals); &lt; 1 nm - base and deposition pressure: ~10⁻⁷, ~10⁻⁶ mbar</td>
</tr>
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### Details of catalyst type & configuration will be given in table 4.2.

| 3. Growth of VACNTs support | CCVD of VACNTs | 6 inch scale Black Magic (Aixtron) | -deposition rate 0.1-0.12 Å/s (alumina)  
- number of cycles: 200-220  
- temperature: 250 °C  
- TMA (0.1 s pulse width, 5 s purge) and water (0.5 s pulse width, 5 s purge) |
|-----------------------------|----------------|----------------------------------|-------------------------------------------------|
| 4. Mechanical reinforcement of VA-SWCNTs | Definition of the area for ALD | A razor blade | - base pressure: $10^{-2}$-$10^{-4}$ mbar  
- Preconditioning: heating chamber at 850 °C in H₂ ambient for 30 min  
- temperature: 650-800 °C  
- carbon source: C₂H₂  
- catalyst pretreatment: 5 min  
- growth time: 10-90 sec |
| 5-A. Gap-filling with PE | PE film | Microtome | - PE block: PE granules were melted and re-solidified in a mold and mounted on a flat aluminum bar.  
- target thickness: 10-20 µm  
- thermal treatment: 250°C  
- infiltration time: 8-12 hrs  
- fast cooling by taking out from the oven |
| | ALD (Picosun) | ALD (Picosun) | - number of cycles: 150-300  
- temperature: 250 °C  
- TMA (0.2 s pulse width, 5 s purge) and water (0.5 s pulse width, 10 s purge); 1 pulses per cycle |
| | | | |
| 5-B. Gap-filling with alumina | ALD | ALD (Picosun) | -number of cycles: 500  
-temperature: 250 °C  
-TMA (0.5 s pulse width, 10 s purge) and water (1.0 s pulse width, 10 s purge); 3 pulses per cycle |
|-------------------------------|-----|---------------|--------------------------------------------------|
| 6. Etching for membrane opening | -Excess PE  
-CNT cap  
-Surface cleaning | Ion beam milling  
(Ionfab 300, Oxford) | - etch rate  
20-25 nm /min for PE  
-sample stage: -5 °, 20 rpm  
-pressure: ~1.5 × 10⁻⁴ Torr  
-beam: I=100 mA, V=700 V  
-accel.: I=12 mA, V=200 V  
O₂ flow rate: 20 sccm
| | O₂(Ar) RIE  
(NPG 80, Oxford) | - etch rate  
250-400 nm/min for PE  
-pressure: 100 mTorr  
-RF power: 300 W  
-O₂ flow rate: 10 sccm |
| | Ion beam milling  
(Ionfab 300, Oxford) | - etch rate  
2-4 nm/min for alumina  
-Pressure: ~1.5 × 10⁻⁴ Torr  
-I=250 or 150 mA, V=600  
Accel.: I=24 mA, V=390 V  
Ar flow rate: 10 sccm  
Sample stage: -20 °, 20 rpm |
| | XeF₂ | - etch rate  
~1 μm/cycle for Si  
-number of cycles: 60-80  
-60 sec/cycle in 2 Torr pure vaporized XeF₂ |
4.5 Characterization of membrane properties

4.5.1 How to confirm the membrane opening

The membrane begins to exhibit gas permeability once the core-shell structure of alumina-coated, bundled VA-SWCNTs appears on the surface of the both sides of membrane (Figures 4.34 and 4.35). The permeability monotonically increases with further etchings until it reaches a maximum where we consider most CNT channels in the exposed membrane area are activated. Details about the gas transport measurement will be given in section 4.6.2. The etching methods at the last stage of membrane opening are ion beam milling (alternately with Ar and O\textsubscript{2}) and O\textsubscript{2} RIE (if the saturated gas permeability is considered low). It is hard to accurately characterize the etch rate for membrane surface. Thus, the etching process was performed for a short interval usually for 2-3 min and the gas permeability was checked after every etching step. Since we choose to do an excessive top side etching prior to bottom side etching in order to minimize the unwanted membrane heating, the pore opening seems to be more limited by the number of open pores on the bottom side. A careful handling for the membrane is needed during etching process. We sometimes observe a breakage of the exposed membrane freestanding on a micro pit, which is at first indicated by the abnormally high gas permeance and/or the non-linear pressure dependence of the gas flow rate and further confirmed by a thorough surface analysis using backside illumination optical microscope and/or SEM. Once the remaining Si on the micro pits after XeF\textsubscript{2} etching step is removed, the freestanding membrane can penetrate the light and once can detect the cracks or punctures by the phase contrast. All broken windows were sealed with epoxy glue (Permatex® PermaPoxy\textsuperscript{TM} 5 Minute General Purpose Epoxy) and the membrane was repeatedly checked for gas permeance until the gas flow rate was brought back to the reasonable range. Also, the membrane windows of inhomogeneous surface morphology and thickness were sealed to reduce errors in the estimation of effective membrane area and areal density of the CNT channel (Figure 4.37).
Figure 4.37. SEM images of the bottom side of the VA-SWCNT membranes showing abnormally high gas permeance and/or the non-linear pressure dependence of the gas flow rate; membrane windows with (a-c) broken membrane films indicated by the solid arrows with yellow color, (d) showing a inhomogeneous phase contrast on the surface indicated by the solid arrow with green color, (e) contaminated with a microscale dust indicated by the solid arrow with blue color, and (f) sealed with an epoxy glue for the membrane repair.
4.5.2 CNT membrane or nanoporous membrane?

The main purpose of fabricating CNT membranes for nanofluidics studies is to provide a platform to measure the mass transport properties through the graphitic pores restricted to the CNT interior of a size regime commensurable with the permeating molecules’ own sizes. In order to prove that an as-fabricated membrane fulfills this requirement, we scrutinize the gap-filling and the distribution of CNT channels by TEM imaging of the FIB cross-sectioned lamellae at open pore area of the membrane. Also, size exclusion tests with gold nanoparticles of relevant diameters were carried out to indirectly show the pore size range of the membrane. This filtration test also can confirm the absence of micro-cracks and voids whose dimensions would be much larger than the travelling gold nanoparticles. The TEM images of the as-fabricated membranes and the results of size exclusion experiments with 5 nm gold colloids are shown in Figures 4.38, 4.39 and 4.40.

![Cross-sectional TEM images](image_url)

**Figure 4.38.** Cross-sectional TEM images (parallel and perpendicular to the CNT axis) of the SWCNTs/PE membrane, showing a void-free gap filling and preservation of initial CNT alignment and areal density.
The TEM lamellae of as-fabricated CNT membrane are prepared using a FIB technique. In the dual beam FIB (FEI Helios 450), a 12×3×5 mm slice is cut from the membrane surface in the region of interest using Ga ions at 30 kV and 9.4 nA current. The slice is glued on a TEM grid and further thinned down to 120nm using a Ga beam at 30 kV and 0.77 pA. After a gentle cleaning, we further thin the sample to 50nm using 5 kV and 120 nA current to reduce the implantation of Ga ions into the TEM sample. The TEM imaging is performed using a FEI CM12 microscope at the acceleration voltage of 120 keV. In Figure 4.38, the SWCNT membrane shows void-free gap filling and preservation of initial CNT alignment and areal density. The bright white aligned tubes (top) and spots (bottom) in the images are CNT channels that are surrounded by the round shaped coating of alumina and the PE in between. The pore density and diameter range of the SWCNT membrane were accurately counted from these images.

Size exclusion experiments are performed using gold nanoparticles (Ted Pella) of diameters larger than the CNT diameters characterized by TEM and the water flow measurement set up, which will be described in detail in section 4.6.3. For example, to characterize SWCNTs/PE membrane with the pore diameters in the range of 2.4-4.9 nm, we carried out the tests with gold nanoparticles of 2 and 5 nm and observed that the membrane flowed 2-nm gold particles yet blocked the passage of 5-nm gold particles completely. Note that pore clogging by particles smaller than the average pore size is unlikely for the solution concentrations used in these experiments. These size exclusion measurements agree well with evidence obtained from the diameter analysis of the as-grown VA-SWCNTs as well as the FIB-cut membrane lamellar using TEM.

For the test, generally about 3-5 mL, or sufficient amount to completely wet the membrane surface of gold nanoparticle solution is injected into the feed side of the membrane while the permeate side is kept dry and open to the air. And, the feed side is pressured to 500 mbar by dry N₂ flow and the permeation of feed solution is monitored as the solution level within the feed side tubing drops. The permeate emerging from the opposite side of the membrane is collected into a vial for UV-Vis characterization. As direct evidence for a successful CNT membrane, we observe the filtered gold nanoparticles on the feed side surface of the membrane after the size exclusion experiment,
which is further confirmed by the appearance of Au elemental peak in the EDX spectrum. The gold colloids were mostly found on the regions of alumina-coated bundled VA-SWCNTs, not on the PE matrix. It may support that there are no transport path on the inter-bundle gaps filled with PE (Figure 4.39).

**Figure 4.39.** SEM images and EDX spectra of the feed side of a SWCNT/PE membrane (a) before and (b) after size exclusion tests with 5 nm gold colloids; after the filtration experiment, membrane surface is covered with a large number of nanosized particles (bright contrast) at the opened pores populated on the membrane surface. Also, EDX spectrum confirms the filtered gold nanoparticles, residing on the feed side surface of the membrane.

Further, we carried out the UV-vis absorption characterizations of the solutions collected from feed and permeate sides of membrane. As shown in Figure 4.40, the collected permeate liquid was colorless and show no characteristic plasmon resonance band around 519 nm of the gold nanoparticles in the UV-vis spectrum. Finally, the conclusion can be drawn that mass transport through the as-fabricated membrane exclusively occurs through the interior of the CNT channels spanning the entire thickness of the membrane.
Figure 4.40. Optical images and UV-vis spectra of the gold nanoparticle solution on the feed and permeate sides of a SWCNT/PE membrane after the size exclusion experiment; feed and permeate solution have clearly different color contrast, indicating that 5 nm gold nanoparticles did not pass while water solvent flow through the membrane.
4.5.3 Properties of as-fabricated SWCNT membranes

The major structure properties of as-fabricated SWCNT membranes made to have a great number of single-walled graphitic nanochannels with different diameters are described hereafter and summarized in the Table 4.2.

The initial alignment and quality of VA-SWCNTs are characterized prior to membrane fabrication process using SEM and Raman spectroscopy. The VA-SWCNTs diameter selectively grown by the optimization of catalyst and CVD process often showed a complex bundled structure of intertwined nanotubes despite their overall vertical alignment. This tendency is stronger for small diameter VA-SWCNTs in sub 5nm diameter regime. Taking into account that the CNT densities change marginally with the shift of CNT diameters within the range of $0.5-1.2 \times 10^{11}$ cm$^{-2}$, the strong bundling and entanglement (CNT tortuosity) among the CNTs is more likely due to the low mechanical strength of individual SWCNTs. Accordingly, the collective height of VACNTs is not equal to the average length of the individual CNT channels; for high tortuosity VACNTs, the measured height of VACNTs underestimates the actual length of individual CNTs. We consider its effect on membrane performance by using the Herman’s Orientation Factor (HOF, $f$), a measure of a degree of alignment, calculated from the Fast Fourier transform (FFT) of the cross-sectional SEM image, adopting the method reported by Xu et al. [187, 343, 344] $f=0$ and $f=1$ represents random and perfect alignment.

One can deduce the actual CNT channel length from the measured membrane thickness based on the relation of $f = (3<\cos^2\phi>-1)/2$, where $\phi$ is the angel between structural unit vector of a CNT and reference direction (perpendicular to the catalyst substrate). The vertical alignments (HOF) of the VA-SWCNTs used for membrane fabrication were found to be in the similar range of 0.44-0.66. This can be understood that they are all SWCNTs and the diameter and areal density deviations among different samples are not severe. As mentioned in previous sections, when the VACNTs grow long, it is likely that the tube diameter diverges and/or increases while the areal density decreases. In order to avoid the structural variation within the VACNT structure, we limit the growth duration to less than 15 sec, avoiding the transition and self-termination in the CNT growth.
The effective thickness and open pore area of the membrane are measured using SEM at the very last stage of fabrication after all etching processes are completed (Figure 4.41). The thickness of open membrane is, in most cases, 2-3 µm shorter than the initial height of VA-SWCNTs.

For the pore size analysis of CNT membranes, we characterize the diameters of as-grown VACNTs using TEM. All the CNTs used for membrane fabrication are confirmed to be single-walled, having the catalyst nanoparticles at base. Bamboo-like CNT structure has never been observed to the best of our knowledge. We emphasize that avoiding the tip-growth of CNTs is crucial for reducing the uncertainty in accurate quantification of the flux through CNT membrane. [28, 313] The CNT diameter histogram gains validity from the observations that no other permeation paths such as cracks or voids exist other than the interior channel of the opened CNTs and the channels span through the entire thickness of membrane, keeping the initial CNT width and alignment, as discussed in section 4.5.2.

The pore densities are derived from TEM images of sliced membrane lamellae (perpendicular to the catalyst substrate) at 8-10 different locations by counting and averaging the CNT number per unit volume of ~0.15-0.18 cm³. The pore densities of the SWCNT membrane were in the range of 0.5-1.2 × 10¹¹ cm⁻², about a factor of 2-5 smaller than the densities of catalyst nanoparticles and consistent with the pore density counted from top-view SEM images of a permeable CNT membrane.
Finally, the effective number of CNT channels for each membrane is calculated by multiplying the open pore area and the averaged value of CNT area density. An assumption was made in this pore density estimation that every SWCNT spanning the 100 nm sliced sections also spans the entire membrane thickness. Most previous works had uncertainties in quantifying the effective pore density because membranes contained the MWCNTs which might have catalyst particles clogged inside CNT channel at arbitrary locations or a bamboo structure. In this case, an overestimation of the pore density can, in turn, result in an underestimation of membrane permeability.

Also, there has not been enough discussion on the structural changes of CNT channels during the membrane fabrication process, which can deactivate some portion of CNT channels in a final CNT membrane. As noted in section 4.3, for example, we observed that the majority of SWCNT channels embedded in PS matrix (Hinds’ method, [28]) were discontinuous by being bent and broken, meaning that they could not function as penetration paths. In this context, our approach of using SWCNTs, protecting them with additional rigid coatings during the entire processes and analyzing the pore density of the final membrane can provide high accuracy data than any other existing approaches.

Table 4.2 summarizes the major structure properties (CNT alignment, Raman G-to-D ratio, membrane thickness, effective membrane area, CNT pore density, average CNT diameter and TEM diameter histogram) of as-fabricated SWCNT membranes.
Table 4.2 Structural Properties of SWCNT membranes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Structural properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Fe (0.3 nm, e-beam) on Alumina (20 nm, ALD)</td>
</tr>
<tr>
<td>CVD condition</td>
<td>T=720 °C, P_{C_2H_2}=0.1 mbar, t(annealing)=5 min, t(growth)=30 sec</td>
</tr>
<tr>
<td>Alignment (HOF)</td>
<td>0.56</td>
</tr>
<tr>
<td>Raman G-to-D ratio</td>
<td>3.70</td>
</tr>
<tr>
<td>Membrane Thickness</td>
<td>3.143 μm</td>
</tr>
<tr>
<td>Membrane area</td>
<td>1.30 ×10⁻² cm²</td>
</tr>
<tr>
<td>Pore density; TEM</td>
<td>0.65-1.45 x 10¹¹/cm²</td>
</tr>
<tr>
<td>Pore diameter (average)</td>
<td>3.62 nm</td>
</tr>
<tr>
<td>Diameter distribution: standard deviation = 0.15 nm</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Fe (0.4 nm, e-beam) on Alumina (20 nm, ALD)</td>
</tr>
<tr>
<td>CVD condition</td>
<td>T=750 °C, P_{C_2H_2}=0.1 mbar, t(annealing)=5 min, t(growth)=30 sec</td>
</tr>
<tr>
<td>Alignment (HOF)</td>
<td>0.44</td>
</tr>
<tr>
<td>Raman G-to-D ratio</td>
<td>2.38</td>
</tr>
<tr>
<td>Membrane Thickness</td>
<td>8.49 μm</td>
</tr>
<tr>
<td>Membrane area</td>
<td>8.15 ×10⁻³ cm²</td>
</tr>
<tr>
<td>Pore density; TEM</td>
<td>0.56-1.13 x 10¹¹/cm²</td>
</tr>
<tr>
<td>Pore diameter (average)</td>
<td>4.15 nm</td>
</tr>
<tr>
<td>Diameter distribution: standard deviation = 0.11 nm</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Catalyst</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------</td>
</tr>
<tr>
<td></td>
<td>CVD condition</td>
</tr>
<tr>
<td></td>
<td>Alignment (HOF)</td>
</tr>
<tr>
<td></td>
<td>Raman G-to-D ratio</td>
</tr>
<tr>
<td></td>
<td>Membrane Thickness</td>
</tr>
<tr>
<td></td>
<td>Membrane area</td>
</tr>
<tr>
<td></td>
<td>Pore density; TEM</td>
</tr>
<tr>
<td></td>
<td>Pore diameter (average)</td>
</tr>
<tr>
<td></td>
<td>Diameter distribution: standard deviation = 0.18 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4</th>
<th>Catalyst</th>
<th>Fe (0.1 nm, e-beam) on Alumina (20 nm, e-beam)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CVD condition</td>
<td>T=700 °C, PCH2=0.03 mbar, t(anneling)=30 sec, t(growth)=20 sec</td>
</tr>
<tr>
<td></td>
<td>Alignment (HOF)</td>
<td>0.62</td>
</tr>
<tr>
<td></td>
<td>Raman G-to-D ratio</td>
<td>6.65</td>
</tr>
<tr>
<td></td>
<td>Membrane Thickness</td>
<td>2.74 µm</td>
</tr>
<tr>
<td></td>
<td>Membrane area</td>
<td>1.25 \times 10^{-2} cm²</td>
</tr>
<tr>
<td></td>
<td>Pore density; TEM</td>
<td>0.96-1.11 × 10^{11}/cm²</td>
</tr>
<tr>
<td></td>
<td>Pore diameter (average)</td>
<td>1.93 nm</td>
</tr>
<tr>
<td></td>
<td>Diameter distribution: standard deviation = 0.19 nm</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Catalyst</td>
<td>Fe (0.15 nm, e-beam) on Alumina (20 nm, e-beam)</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>CVD condition</td>
<td>T=700 °C, P_C2H2=0.03 mbar, t(anneling)=1 min, t(growth)=30 sec</td>
<td></td>
</tr>
<tr>
<td>Alignment (HOF)</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>Raman G-to-D ratio</td>
<td>6.52</td>
<td></td>
</tr>
<tr>
<td>Membrane Thickness</td>
<td>6.28 µm</td>
<td></td>
</tr>
<tr>
<td>Membrane area</td>
<td>4.1 ×10^{-3} cm²</td>
<td></td>
</tr>
<tr>
<td>Pore density; TEM</td>
<td>0.81-1.01 x 10^{11}/cm²</td>
<td></td>
</tr>
<tr>
<td>Pore diameter (average)</td>
<td>2.15 nm</td>
<td></td>
</tr>
</tbody>
</table>

Diameter distribution: standard deviation = 0.27 nm
4.6 Mass transport through the VA-SWCNT membrane

4.6.1 Background Knowledge


4.6.1.1 Gas Transport

The transport of the permeating species depends strongly on the membrane pore diameter ($d$) and the interaction (surface properties) of that species with the membrane structure (dimension). The flow regime or gas transport mechanism is in general categorized based on Knudsen number (Kn), which is defined as the ratio of the molecular mean free path length (MFP, $\lambda$) to a representative physical length scale ($d$), for example, tube diameter ($d_{CNT}$) for the CNT membranes (Figure 4.42).

![Figure 4.42](image)

**Figure 4.42.** Flow regimes categorized by Knudsen number the highlighted regime with blue color indicates the free molecular flow regime where the molecule-membrane wall collisions dominate over molecule-molecule collisions. [346]

For gas that is highly dilute medium, the momentum and energy transfers mostly occur via random collisions between the two gas
molecules possessing distinct thermal velocities. Therefore, not the average gas spacing but MFP will determine the momentum and energy transfers in gas phase collisions and thereby the fluid property. MFP of air at 1 atm and 300 K is estimated to be around 70 nm:

\[ \text{MFP} = \frac{RT}{\sqrt{2\pi d^2 N_A P}} \]  

(1)

where \( R, T, d, N_A, \) and \( P \) are the universal gas constant, absolute temperature (K), the diameter of the gas molecules, the Avogadro’s number \((6.02 \times 10^{23} \text{ mol}^{-1})\) and pressure, respectively. The MFPs of most gases are significantly larger than the typical diameter range of the SWCNT, producing the Kn number in the range of 10-70. Hence, one would expect the gas transport through the SWCNT membrane enters free molecular flow regime.

Before moving on to the gas transport in free molecular flow regime, the dominant transport mechanism in large pores is viscous flow and the permeation flux \( (J_{\text{viscous}}) \) is described by the Poiseuille equation;

\[ J_{\text{viscous}} \left( \text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \right) = \frac{\varepsilon r^2 \Delta P}{8RT\eta\tau L} \]  

(2)

where \( \varepsilon, r, \Delta P, \eta, \tau \) and \( L \) are the porosity, the pore radius, the applied pressure drop, the gas viscosity, the tortuosity and the thickness of the membrane. Here, the viscous gas permeation scales inversely with viscosity \( (\tau) \) and this relation is practically useful to identify the flow regime.

When the mean free path \( (\lambda) \) of gas molecules is much larger than the pore diameter, Knudsen diffusion is prominent, meaning that the molecules collide with the pore wall before they collide with each other. Each collision occurs with complete thermalization so that the angle of reflection is fully randomized with respect to the angle of incidence. The permeation flux \( (J_{\text{Kn}}) \) is expressed by the following equation;

\[ J_{\text{Kn}} \left( \text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1} \right) = \frac{2\varepsilon_p V r^2}{\tau R T L} \]  

(3)

where \( V \) and \( M \) are the average molecular velocity \( (\text{m/s}) \) and the molecular mass \( (\text{kg/mol}) \) of the gas molecule. This gas transport by
Knudsen diffusion scales inversely with the square root of the molecular weight of the gases ($M$) and thus a separation of a gas mixture can be achieved based on the difference between the molecular masses of different gas components with a separation factor of $\sim (M_1 / M_2)^{-1/2}$.

**Figure 4.43.** Experimental demonstrations of the enhanced gas transport through (a) DWCNTs/SiNx ($d=1.6$ nm) and (b) SWCNTs-PSf mixed matrix ($d=1.2$ nm) membranes that are dependent on the molecular weight of gases: adapted from (a) ref. [20] and (b) ref. [29]
However, the Knudsen mechanism has been found inapplicable to explain the gas transport properties experimental measured from CNT membranes. Figure 4.43 shows the two characteristic features of the gas flow through CNT membrane; (a) gas fluxes scaled inversely with their molecular weight by an exponent of 0.49, close to expected kinetic theory velocity expectations and (b) the magnitude of the gas fluxes were one to two orders higher than Knudsen predictions. Also, note that the $M^{-1/2}$ scaling of gas selectivity deviates from Knudsen predication for hydrocarbon gases whose interaction with CNT wall is considered to be higher. [20]

It is important to recognize that the $M^{-1/2}$ scaling of the gas flows through CNT membrane may not mean they are Knudsen flow. MD simulations have suggested that the main reasons for the gas flow enhancement are the atomic smoothness of CNT walls and the very weak interaction between gas and tube wall, which alters the nature of gas-wall collisions from purely diffusive (as in the Knudsen model) to specular. [44, 347] Note that the nature of gas-wall collisions would not affect the mass scaling. The difference in a specular collision is that a reflecting gas molecule conserves its tangential momentum along a colliding surface and thus it is expected that the gas residence time inside a channel decreases relative to a molecule undergoing a diffusive collisions.

In reality, the gas collisions inside CNTs are considered to have both diffusive and specular components. The contribution of the specular collisions to gas transport can be assessed by a tangential momentum accommodation coefficient (TMAC, $\sigma_v$), a measure of a portion of molecules that are reflected diffusively (Figure 4.44). [347-349]

![Figure 4.44](image-url)  

**Figure 4.44.** Schematic of tangential momentum of gas flow in a channel with a slip velocity near the wall of $u_w$; $\lambda$, $u_r$ and $u_\lambda$ are the mean free path of a gas molecule, the reflected tangential velocity of molecules and the tangential velocity of incident molecule. [300]
For example, Cooper et al. have observed that modification of the nanotubule surface properties drove the transition in gas transport mechanism from diffusive to diffusive and specular reflections and determined a TMAC to be 0.52, which indicates the significant contribution of specular reflection to the flow enhancement over Knudsen prediction.

Or, the unified flow model considering wall slip and rarefaction effect can be applied for the transitional and free molecular flow regimes with high Kn in association with the nanochannels. In this model, the velocity profile is given as follows;

\[
U^*(r, Kn) = \frac{U(z, r)}{U(z)} = \frac{-\left(\frac{r}{d/2}\right)^2 + 2\frac{Kn}{1+Kn} + 1}{1 + 2\frac{Kn}{1+Kn}}
\]  

where \(r\) and \(z\) are the radial and axial coordinates, respectively. [350, 351] In the limit of continuum flow (\(Kn \to 0\)), the model converges to a Poiseuille flow profile, \(U^*=2[1-(r/(d/2))]^2\). The shape of velocity profile is a parabola shifted in the axial direction by \(2Kn/(1+Kn)\), with a shrinkage of the maximum velocity. Here, the Kn is a local Knudsen number. Then, the volumetric flow is obtained by integrating the velocity equation derived from Navier-Stokes equation with Maxwell’s slip boundary condition over the cross-section of the channel,

\[
Q = -\frac{\pi(d/2)^2}{8\mu_o} \frac{dP}{dx} (1+\alpha Kn) \left[ 1 + \frac{4Kn}{1+Kn} \right]
\]  

where \(\mu_o\) and \(\alpha\) are the bulk dynamic viscosity and the model parameter accounting for the rarefaction effect, respectively. Here, Kn is a global Knudsen number, which is determined at the average pressure between upstream and downstream. Rarefaction coefficient \((1+\alpha Kn)\) accounts for a hybrid length combining the channel diameter \(d\) and the MFP \(\lambda\), giving variation to the dynamic viscosity \(\mu_o\). The length scale used in determining dynamic viscosity in kinetic theory is the MFP \(\lambda\). As Kn increases and the flow enters transition regime, channel dimension and MPF become comparable.
and the fluid viscosity is determined by the combinatorial effects of these two lengths: \[ \mu(Kn) = \mu_0 \left[ \frac{1}{1+Kn} \right] \] (6)

When the experimental results were compared with the unified flow model prediction, DWCNTs/SiN\(_x\) (d=1.6 nm) membrane showed still an order of magnitude higher flow rate while MWCNTs/PS (d=7 nm) and PC (d=15 nm) membranes showed within the order of magnitude flow rate.

Several MD simulations had predicted the enhanced gas flow through the CNT channel even before experimental results became available. Skoulidas et al. have reported that the transport diffusivities of light gases (H\(_2\) and CH\(_4\)) are orders of magnitude greater in SWCNTs than in zeolites, attributing to the inherent smoothness of the CNT wall. Later on, they presented a detailed picture on the behavior of gas molecules (CO\(_2\) and N\(_2\)) inside a SWCNT, providing a density profile and molecular trajectories of gas molecule. At 1 bar, most gas molecules adsorb on the CNT wall, forming a gas nanotube (Figure 4.45a).

**Figure 4.45.** MD simulation; (a) density profiles of CO\(_2\) inside a (40,40) SWCNT as a function of the bulk gas pressure and (b) trajectories of CO\(_2\) molecules in a (40,40) SWNT at 298 K and a pressure of 1 bar. [45]
Owing to the weak interaction between gas molecules, they cannot move collectively as we observe in a constrained single file water chain. Instead, gas molecules diffuse toward a lower potential, following the surface of the gas nanotube. The pressure-dependent adsorption gradient (assuming local equilibrium) will drive surface diffusion. At the same time, collisions between traveling gas molecule and CNT wall exist (Figure 4.45b). Thus, the smoothness of CNT may augment the contribution of specular reflection to gas transport.

Figure 4.45a also shows that as the pressure increases, more gas molecules enter the CNT, another gas nanotube form on top of the first layer, trapped by the long range vdW potential. However, the more gas nanotubes form, the more they shield the attraction from the wall. Eventually at much higher pressures, gas molecules in the middle of CNT rather flow with a form of chunk than a layered gas nanotube. This layering effect of gas nanotube, highly dependent on the CNT diameter seem to play a significant role in gas transport in small diameter CNTs. Several following works showed even when CNT are allowed some flexibility, the transport efficiency remain extraordinary high, but the presence of any source (defect, impurity having high affinity to CNT) that can disrupt the atomic smooth gas molecule-CNT potential energy surface have an adverse influence on the transport diffusivity. [352, 353] On the other hand, gas permeation through CNTs involves not only the diffusion within the channel but the surface resistance from the gas molecules entering and leaving the pores. Newsome et al. have reported that the surface resistance is expected to increase as the adsorption strength of the gas species such as $n$-alkanes increases, or equivalently, as the temperature is lowered. [354]
4.6.1.2 Water Transport

Unique nanoscale fluid transport properties of CNTs have inspired researchers for over a decade, initially with their analogies to various transmembrane protein channels such as aquaporins, proton and ion selective channels in terms of having a narrow hydrophobic passage with entrances enriched with charged residues selective of a certain type of ions and later with the potential impacts on water purification, desalination and energy applications. [355-357] As observed for biological channels, water can flow through a CNT channel at rates far exceeding those predicted by Hagen-Poiseuille formulation and measured in nano-conduits made up of different materials, attributed to nanoconfinement, hydrophobicity, and smooth potential energy landscape. [20, 22, 298, 308] Exciting progress has been made so far by simulating and experimentally observing intriguing nanofluidic phenomena. However, the underlying mechanisms remain marginally understood and the detailed quantitative aspects of nanofluidic flow behaviors remain to be further investigated mainly due to the difficulties in fabricating a reliable platform of CNT membrane with precisely controlled and characterized properties.

When considering the thermodynamics and kinetics of water flows through CNTs, a set of fundamental questions arise. First, a large mismatch in length scale questions the validity of classical continuum fluid theory for the transport in nanoconfinement. Constrained water flow behavior inside CNT breaks the assumption of treating water as a continuous medium, or a pseudo-particle composed of a chunk of molecules and cannot be described by the continuum hydrodynamics that is governed by the Navier-Stokes equation with no consideration of the changes in molecular structure and configuration. For the water fluids to be treated as a continuum with less than 1 % statistical fluctuation or statistical resolution of a physical property, it requires more than ten thousand equidistant molecules, corresponding to the diameter about 6 nm. [299] The length scale considered in carbon nanofluidics is often smaller than this size criterion and therefore, it is very unlikely that continuum hydrodynamics theory works for the water flow under graphitic nanoconfinement where the physical and chemical properties of water significantly vary over the molecular configuration and relaxation time scales.
Figure 4.46. Hydrodynamic flow profile described with a concept of slip length, $L_s$. [307]

Classical theory describes the fluid flow by using a conceptual length scale called slip length ($L_s$) (Figure 4.46). A no-slip boundary condition as presumed in continuum fluid dynamics demands a fluid close to a solid boundary to obtain the same tangential velocity ($v_{t,\text{wall}}$) as the solid ($v_{\text{wall}}$). The degree of enhanced flow rates relative to no-slip Hagen-Poiseuille prediction has been practically used in experimental studies using CNT membranes. The laminar volumetric flow rates through a uniform circular pipe of Radius ($R$) for non-slip Hagen-Poiseuille flow having a parabolic velocity profile and for slip flow having a plug like velocity profile with respect to the distance from the center ($r$) are given by:

$$U(r, L_s) = -\frac{1}{4\mu} \frac{dp}{dz} \left( R^2 - r^2 + 2RL_s \right)$$  \hspace{1cm} (7)

$$Q_{\text{HP}} = \int_0^R 2\pi r U(r, 0)dr = -\frac{dp}{dz} \frac{\pi R^4}{8\mu}$$  \hspace{1cm} (8)

$$Q_{\text{slip}} = \int_0^R 2\pi r U(r, L_s)dr = Q_{\text{HP}} \left( 1 + \frac{4L_s}{R} \right)$$  \hspace{1cm} (9)

where $dp/dz$ represents the pressure drop along the pipe length. As seen, it is expected that the water flow rate linearly increases with the pressure drop. Note that there is a transition state theory proposed
for the very high pressure regime, predicting that the same increase in
driving force causes less of an increase in the flow rate. The
pressure range experimentally approached with CNT membrane so
far is limited up to several bars due to the challenges in building a
robust nanofluidic devices and thus it would be very interesting
subject to investigate further.

When \( \nu_{t,\text{wall}} \) is not the same as \( \nu_{\text{wall}} \), it is described as the fluid slips on
the surface. This concept has been adopted to describe the non-
continuum water transport phenomena in CNTs within the frame of
continuum dynamics. Slip length \( (L_s) \) is defined according
to the Navier boundary condition as follows;

\[
L_s \frac{\partial \nu_t}{\partial n}_{\text{wall}} = \nu_{t,\text{wall}} - \nu_{\text{wall}}
\]

where \( n \) and \( t \) denote normal and tangential directions of the wall,
\( \nu_{t,\text{wall}} \) is the velocity of a fluid tangential to the wall, and \( \nu_{\text{wall}} \) is the
velocity of the solid wall (Figure 4.46). A large slip length can be
related with a low friction at interface between liquid fluid and solid
surface. In this context, the slip length of water flow through CNT
membrane, larger than CNT diameter refers that water molecules
experience negligible friction at the curved CNT surface and the
velocity profile becomes a plug-like. The low friction of water is
predicted and also measured on hydrophobic surfaces. Flow
enhancement reached by the CNT membranes, however, is orders of
magnitude higher than these results measured for the chemically
modified interfaces. As well summarized in Falk et al.’s work [22],
the surface fluid-solid friction force \( (F_{\text{wall}}) \) is linearly proportional to slip
velocity \( (\nu_{\text{wall}}) \): \( F_{\text{wall}} = -A_L \lambda (\nu_{t,\text{wall}} - \nu_{\text{wall}}) \), where \( \lambda \) is the friction
coefficient, \( A_L \) is the lateral area, and by definition the slip length \( (L_s) \)
is inversely proportional to the interfacial friction coefficient \( (\lambda) \) via
\( L_s = \mu / \lambda \) (\( \mu \): dynamic viscosity of bulk water).

An approximation of the Green-Kubo relation can relate the friction
coefficient to a correlation function of a fluctuating microscopic
variable at equilibrium as follows [360, 361]:

\[
\lambda = \frac{1}{A_L k_B T} \int_0^\infty < F_{\text{wall}}(\tilde{t}) F_{\text{wall}}(0) >_{\text{equ}} \cdot \tilde{d}\tilde{t} \approx \frac{\tau}{A_L k_B T} < F_{\text{wall}}^2 >_{\text{equ}}
\]
where $\tau$ is the relaxation time, $<F_{\text{Wall}}^{2}>_{\text{equ}}$ is the rms friction force, and $k_B T$ is the reference thermal energy. Here, the relaxation time ($\tau$) is $\sim \sigma^2/D$, where $\sigma$ is the scale of molecular diameter and $D$ is the fluid diffusion coefficient. According to these relations, a large slip length ($L_s$) can be observed at high temperatures ($k_B T$) or smooth surfaces ($<F_{\text{Wall}}^{2}>_{\text{equ}}$).

Second question is how the polar liquid such as water and aqueous solution can enter and flow over hydrophobic surface of CNT interior. Whitby et al. [309] have attempted to describe the thermodynamics of capillary filling based on the Kelvin equation and the dynamics of a liquid meniscus by the Washburn equation using Hagen-Poiseuille law with the driving force given by the Laplace equation for the pressure difference across the meniscus of invading liquid. [362] The Kelvin equation describes the higher vapor pressure on a curved liquid/vapor interface (meniscus):

$$\ln \left( \frac{p(R_m)}{p_o} \right) = -\frac{(\gamma_{vw} - \gamma_{wl}) \cdot V_m}{k_B T R_m}$$

(12)

where $p$, $p_o$, $R_m$, $V_m$, $\gamma_{vw}$ and $\gamma_{wl}$ are the water vapor pressure near CNT channel entrance, the saturated vapor pressure of water, the pore radius where a meniscus forms, the molar volume of liquid water and the surface tensions of CNT wall-water vapor and CNT wall-liquid water, respectively. The Washburn equation describes the penetration length ($L$) at time $t$ of a fluid in a capillary of radius $R_m$ with an assumption that there is no fluid motion at the wall (stick boundary condition):

$$L^2 = \frac{R_m \cdot (\gamma_{vw} - \gamma_{wl})}{2 \mu} \cdot t$$

(13)

When $p_o$ is comparable to $p(R_m)$, water molecules in vapor and liquid phases coexists in equilibrium near the CNT wall and only when $p_o$ exceeds $p(R_m)$ water can condense and fill the CNT. Here, the equilibrium vapor pressure depends on $R_m$, which is determined by the tube diameter for a CNT channel. As the CNT diameter ($\geq R_m$) decreases, $p(R_m)$ increases and thus it is unlikely that liquid water condense and fill the CNT. Also, in a hydrophobic CNT pore, $\gamma_{wl}$ is expected to be larger than $\gamma_{vw}$, and thus the pore wall would prefer to
be in contact with vapor than liquid water. For nanoscale capillaries
the flow behavior is dominated not by bulk properties such as $\gamma$ and $\mu$
but by the interaction of the fluid with the capillary walls and the
classical hydrodynamics cannot explain the hydration of hydrophobic
CNT pore entrance and channel.

A counter-argument against these classical theories has been made
based on the thermodynamic consideration of the constrained water
structure. In 2001, Hummer et al.'s MD simulations on a (6,6) CNT
(0.8 nm in diameter) solvated in a water reservoir for the first time
showed that water molecules spontaneously occupy and continuously
diffuse through the CNT channel. [23] Water molecules are observed
to form a single file chains in the CNT, having only two hydrogen
bonds (H-bonds) to adapt to a narrow CNT and show two state
transitions between empty and filled states. (cf. 3.6 H-bonding per
water molecule in bulk state). The persistent water occupancy inside a
CNT is explained by the free energy of confined water relative to the
bulk. In the constrained single file water chain, water molecules can
rotate freely along their aligned H-bonds, increasing the rotational
entropy significantly compared to the hindered rotation in tetrahedral
bulk state water network. Also, they are more tightly bound with an
extended H-bond lifetime than in bulk state (5.6 ps in a constrained
single file and 1.0 ps in bulk water) and highly aligned with CNT axis,
collective flipping direction every 2-3 ns on average. In summary, the
water molecules gain enough entropy by entering the hydrophobic
CNT channel, which outweighs the energy losses incurred by breaking
some of its hydrogen bonds. Thus, the water flows spontaneously into
the CNTs (Figure 4.47a).

Later, Pascal et al. have expanded the thermodynamic considerations
of the constrained water chain to CNTs of larger diameters and
reported three different reasons why water flows freely into CNT at
different CNT diameter ranges. [363] For the smallest CNTs (0.8-1.0
nm in diameter), water molecules line up nearly single file within
them and take on a gas-like state. The normal bonded structure of
liquid water breaks down, giving the molecules greater freedom of
rotational and translational motion. Such increase in entropy draws
water into the tubes. For the CNTs having diameters between 1.1 and
1.2 nm, confined water molecules arrange themselves in stacked and
ice-like crystals that are energetically very stable due to the increased
average number of H-bonds compared to bulk at the expense of reduced entropy by the rigidity of the ice-like water structure. These crystal bonding interactions, not entropy, make it favorable for water to flow into the tubes. For the larger CNTs (1.4-2.7 nm), the confined water molecules behave more like liquid water, but, some of the normal hydrogen bonds are broken. Similar to the smallest CNTs, the entropy drives the favorable free energy for spontaneous water filling of CNT despite the unfavorable enthalpy change (Figure 4.47b).

Figure 4.47. (a) Structure of the constrained single file water chain inside a CNT and the number of water molecules ($N_t$) inside CNT as a function of time, simulated with modified carbon-water Lennard–Jones parameters of $\sigma_{CO} = 3.41 \text{ Å}$ and $\varepsilon_{CO} = 0.065 \text{ kcal/mol}$; adapted from ref. [23]. (b) Comparison of enthalpy versus entropy contributions to the free energy of constrained water inside CNTs of different diameters and correlation of the average number of H-bonds/molecule with enthalpy ($\Delta U^0$). [363].
4.6.2 Gas transport experiments

Parts of this section have been submitted for publication in: S. K. Youn, J. Buchheim, H. G. Park, “Fabrication of the first vertically aligned single walled carbon nanotube membrane and the diameter dependent mass flow enhancement,” 2014 (in preparation)

Using fabricated SWCNT membranes, we studied the gas transport characteristics. The details about the membrane specifications are given in table 4.2 of section 4.5.3. A commercially available anodic aluminum oxide (AAO) membrane (Synker Technologies Inc.) of 5 nm in diameter (pore density of $2.0 \times 10^{11}/\text{cm}^2$) and 1 μm in thickness is tested for comparison. The AAO membrane was bonded on a robust patterned Si support by using epoxy glue and the effective area is defined as $9.16 \times 10^{-2} \text{ cm}^2$. For investigating gas flow properties, we measured the pressure-driven flow, that is, the gas flow rates at the given constant pressures.

Figure 4.48 shows a flow cell and an experimental setup used for gas flow, or permeance measurements. The membrane flow cell is made out of transparent polycarbonate or polyoxymethylene (POM, DuPont\textsuperscript{TM} Delrin). The contact surface of the two parts of the cell has an indent in which two PTFE O-rings press to seal the membrane of interest mounted on them. The two parts are tightened to be hermetic by using the four screws. The membrane fixture assembly is connected to other compartment by stainless tubes with Swagelok sealing. A pressure regulator controls the upstream pressure of a membrane, which is measured by a digital manometer with high precision. A mass flow controller (MFC, MKS instruments Inc.) is connected to the downstream of the membrane to measure the gas flow passed through the membrane. The MFC (measurement range of 0.1-10 sccm, accuracy of ± 0.5 % of reading plus 0.02 sccm), and repeatability of ± 0.02 sccm) is calibrated for nitrogen and for other gases the measured values need to be multiplied by gas correction factor (GCF). For example, GCFs of N\textsubscript{2}, Ar, CO\textsubscript{2}, CF\textsubscript{4}, He, Kr, Ne, O\textsubscript{2} and Xe are 1, 1.39, 0.70, 0.42, 1.4, 1.543, 1.46, 0.993 and 1.32 at 1 atm and 0 °C condition, respectively. All the measurements were done at room temperature around 23-26 °C. If necessary, temperature correction can be made based on the relation of (corrected GCF) =
GCF × actual temperature/273.15 K (=0 °C) While the upstream of membrane is connected to the pressurized gas line, the outlet of the MFC in the downstream of membrane is open to the laboratory ambient at 1 atm. A control experiment utilizing a non-porous Si frame of the same dimension as CNT membranes confirmed that all connections were leak tight, such that the pores of the membrane would be the only gas transport path.

**Figure 4.48.** Gas flow or permeance measurement setup used in this study.

Gas flow measurement using this setup was performed to check the pore opening during membrane fabrication process prior to the actual measurement to study the gas transport characteristics as mentioned
in section 4.4.6. Once the excess PE or ALD deposited alumina on the top side and the catalyst layer on the bottom side of a patterned Si supported CNT membrane are more or less removed (checked by SEM imaging), we began to measure gas permeance through the membrane. We verified that the membrane was impermeable at this stage. In case that the membrane showed gas permeance at this stage, we checked the sample thoroughly by SEM and in most cases found local defects or breakages, which can be sealed by epoxy glue. Only membranes that are impermeable at this stage are used to open up pores with further ion milling process with durations of 2-3 min and the gas permeance was checked after every etching step. Once the membrane showed permeance (when we consider that some pores are opened), additional etching step continued to increase the permeance.

![Graph](image)

**Figure 4.49.** Nitrogen flow rate versus applied pressure drop as ion milling steps accrue; the more the SWCNTs are exposed by the etching steps, the more permeable a membrane becomes. Symbols and lines represent measure data and linear curve fittings, respectively.

Figure 4.49 shows an example of the permeance increase as the surface etching adds up for the membrane 1 in Table 4.2. The applied pressure drop represents the pressure measured by the manometer.
on the upstream of membrane. The slope of the plot \( (Q_{\text{N}_2}/\Delta P) \), that is, the nitrogen permeance increases as etching steps accrue and stabilizes in the end. Once the membrane permeance was stabilized, the etching process was stopped. The measured volumetric flows of nitrogen \( (Q_{\text{N}_2}) \) are linearly proportional to the pressure difference across the membrane. We did not observe any possible anomaly such as a threshold pressure drop that might exist if the membrane bending is accompanied when pressurized or temporarily lower permeance at high pressure by the buckling of protruding CNTs.

In order to investigate the diameter dependence on the gas flow enhancement, we first measured the flow rate of \( \text{N}_2 \) gas as a function of pressure drop across the membrane. Same as shown in Figure 4.48, \( \text{N}_2 \) flow rate increases linearly as the applied pressure rises, revealing that the gas permeance is independent of an applied pressure drop. This evidences that no viscous flow takes place and thus the prepared SWCNT membrane is free of any large pinholes or cracks. It is again supported by the non-correlation between gas permeability and viscosity. For most gases including \( \text{N}_2 \) at room temperature the mean free paths \( (\lambda) \) are significantly larger than the pore sizes of our SWCNT membranes \( (d_{\text{CNT}}) \), showing Knudsen numbers \( (\lambda/d_{\text{CNT}}) \) in the range of 10-70. Hence, one would expect the gas transport through the SWCNT membrane enters free molecular flow regime where molecule-membrane wall collisions dominate over molecule-molecule collisions which implies that only the average molecular speed (thermal speed) determines the molecule mobility. In the kinetic gas theory the average speed of gas molecules is expressed as

\[
\sqrt{\frac{8\pi N_A k_B T}{M}}
\]

with \( N_A \) being the Avogadro number, \( k_B \) the Boltzmann constant, \( T \) the absolute temperature, and \( M \) the molecular weight of the gas.

Table 4.3 summarizes the observations of \( \text{N}_2 \) flow enhancements through the fabricated SWCNT membranes of different diameters. The degree of flow enhancement can be described by the ratio of the observed \( \text{N}_2 \) flow rate \( (Q_{\text{Exp}}) \) to that \( (Q_{\text{Kn}}) \) predicted by the Knudsen diffusion model using the specifications of the membranes provided in Table 4.2 of section 4.5.3. This way of presenting the enhancement degree captures flow enhancement arising from the unique physicochemical properties of CNT nanochannels with respect to the classical flow model prediction and allows direct comparisons with
other literatures. In calculating the Knudsen flow, either the average or weighted average diameter can be used however the difference between the two results are negligible thanks to the even and narrow distribution of the SWCNT diameter. The error range in Knudsen prediction is mainly originated from the uncertainty still existing on the pore density quantification and the correction of CNT channel length by HOF factor does not significantly alter the calculation results.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>$N_2$ permeability, $Q_{Exp}$ (m$^3$/Pa·s·m$^2$)</th>
<th>Knudsen prediction, $Q_{Kn}$ (m$^3$/Pa·s·m$^2$)</th>
<th>Enhancement ($Q_{Exp} / Q_{Kn}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW 1</td>
<td>$3.25 \times 10^{-7}$</td>
<td>$1.24-2.33 \times 10^{-8}$</td>
<td>14-19</td>
</tr>
<tr>
<td>SW 2</td>
<td>$1.54 \times 10^{-7}$</td>
<td>$1.00-1.19 \times 10^{-8}$</td>
<td>13-15</td>
</tr>
<tr>
<td>SW 3</td>
<td>$5.69 \times 10^{-8}$</td>
<td>$1.58-2.38 \times 10^{-9}$</td>
<td>24-36</td>
</tr>
<tr>
<td>SW 4</td>
<td>$1.99 \times 10^{-7}$</td>
<td>$3.13-3.62 \times 10^{-9}$</td>
<td>42-49</td>
</tr>
<tr>
<td>SW 5</td>
<td>$4.85 \times 10^{-8}$</td>
<td>$1.59-1.98 \times 10^{-9}$</td>
<td>24-30</td>
</tr>
<tr>
<td>AAO</td>
<td>$5.83 \times 10^{-7}$</td>
<td>$\sim 5.37 \times 10^{-7}$</td>
<td>$\sim 1.08$</td>
</tr>
</tbody>
</table>

Table 4.3. Comparisons of nitrogen flow rates measured for several SWCNT membranes and an AAO membrane with Knudsen model predictions; the lower and upper bounds of Knudsen predictions are mainly originated from the uncertainty still existing on the pore density quantification. Specifications of the membranes are provided in Table 4.2. $N_2$ permeability is defined as the volumetric flow rate (m$^3$/s) per effective membrane area (m$^2$) per applied pressure drop (Pa).

For the five membranes studied, absolute $N_2$ fluxes measured through the SWCNT membranes exceeded the fluxes predicted by Knudsen diffusion model by 13-49 folds (Figure 4.50). Interestingly, for an AAO membrane with comparable pore sizes of 5-6 nm, the gas transport magnitudes were consistent with Knudsen diffusion predictions. Note that previously a factor of 10 and 2.1 enhancements over Knudsen diffusion were observed for 10 m and 15 nm track etched polycarbonate membranes. [20, 364] These observations show that the surface properties of the vertically oriented nanochannels are critical in obtaining the enhanced transport rate of gases. Many other simulation results that predicted such enhancements in the graphitic
CNTs attributed it to the combined effect of nanoconfinement and graphitic surface properties. [44, 365] At the very lubricous surface, molecular collision with the wall do not randomly scatter as in the Knudsen diffusion instead keep all tangential forward momentum upon reflections. [44] Such specular momentum transfer can increase the gas diffusivities, to an extent higher than kinetic theory. Our observations with the SWCNT membranes are also consistent with previous experimental work where enhancement of 1-2 orders of magnitude is observed (Figure 4.51). [20, 31, 301, 313, 366]

![Histogram of the measured nitrogen gas permeances scaled in mol/m²·Pa·s and the enhancement factors over Knudsen diffusion for each membrane.](image)

**Figure 4.50.** Histogram of the measured nitrogen gas permeances scaled in mol/m²·Pa·s and the enhancement factors over Knudsen diffusion for each membrane.

Previously, using MD simulations, Skoulidas *et al.* have reported the transport diffusivities of CO₂ gas through armchair type SWCNTs with five different diameters of 1.08, 1.36, 1.63, 2.71 and 5.42 nm at 298 K (Figure 4.50). [45] Over the whole pressure ranges, smaller diameters SWCNTs shows relatively higher transport diffusivities than larger diameters SWCNTs, which is attributed to the increased smoothness of the interaction potential energy surface of traveling gas molecules and the interior surface of CNT channel, brought about by the decrease in the effective distance between the carbon atoms in the CNT with the decrease in diameter. The transport diffusivities are observed to be virtually independent of pressure for SWCNTs larger than 2 nm while the other smaller SWCNTs show slight increase at
pressures beyond 1 bar where the internal spaces of the small CNT channel start being fully occupied, resulting in a large value of the thermodynamic factor for driving rapid surface diffusion of confined gas molecules. The nearly constant gas diffusivities through larger diameter SWCNTs is due to that even if large spaces are available, the density of gas away from the CNT wall is very low even at the pressure of about 100 bar, meaning that the surface diffusion is still dominant mechanism, not the Knudsen diffusion.

Figure 4.51. MD simulation results on the transport diffusivities of CO$_2$ gas at 298 K through SWCNTs with various diameters as a function of pressure. Overall, smaller diameters SWCNTs reveals relatively higher transport diffusivities than larger diameters SWCNTs and shows a slight increase in the diffusivity at pressures higher than 1 bar. [45].

The reported CO$_2$ transport diffusivities can be used to predict flow enhancement; for example, SWCNTs with diameters of 1.08, 1.36, 1.63, 2.71 and 5.42 nm showed 0.35, 0.11, 0.06, 0.04, and 0.03 cm$^2$/s at 1 bar, respectively. We calculated the volumetric flow rate of CO$_2$ per each SWCNT pore and compared with the Knudsen predictions to derive the enhancement factor (Figure 4.51), based on the following equations where $V_m$, $D_{MD}$ and $M_{CO_2}$ are molar volume, transport diffusivity obtained from MD simulations and molar mass of CO$_2$. 

![Graph showing transport diffusivity vs pressure for different SWCNT diameters.](image-url)
The absolute flow rate of CO₂ gas decreases with an increase of CNT diameter but again increases when the CNT diameter becomes larger than about 2 nm due to the increasing absolute permeation area. The enhancement factor is a better measure for direct comparison between the CNT membranes of different dimensions.

Figure 4.52. Diameter dependence of the absolute gas flow rate per CNT pore and gas flow enhancement predicted by Skoulidas et al.’s MD simulations. [45]

Figure 4.52 shows the strong CNT diameter dependence of gas flow enhancement that in sub-2-nm regime the gas transport is almost 2-3 orders of magnitude faster than Knudsen prediction, however, the confinement effect drastically decreases beyond this size regime. Less than an order of magnitude flow enhancements are predicted for CNT whose diameters are larger than 3 nm. In order to compare our experimental data with the simulation results, we plotted the gas flow enhancement factors through our SWCNT membranes as a function
of average tube diameter in Figure 4.53. All available data in the literatures are also included in this plot for comparison.

**Figure 4.53.** Gas flow enhancements through CNT membranes that are previously reported (black squares) and obtained in the present study (red circles), plotted as a function of average CNT diameter; five SWCNT membranes (3-8 µm thick) with average diameters of 1.93 (4), 2.15 (5), 2.39 (3), 3.62 (1), and 4.15 nm (2). Previously reported membranes of DWCNTs ($d_{CNT}=1.6$ nm, $L=2-3$ µm, ref. [20]), MWCNTs ($d_{CNT}=6.5$ nm, $L=2.5$ µm, ref. [300]), MWCNTs ($d_{CNT}=5.1$, $L=105$ µm and 7.7 nm, $L=110$ µm, ref. [313]), MWCNTs ($d_{CNT}=7$ nm, $L=34-126$ µm ref. [366]), a mixture of SW- and DWCNTs ($d_{CNT}=3.3$ nm, $L=20-50$ µm ref. [315]) and DWCNTs ($d_{CNT}=7$ nm, $L=8-10$ µm ref. [31]), respectively. The blue solid line denotes the MD simulation results described in Figure 4.51.

Our data clearly reveal the overall trend of increasing enhancement factors for the gas flows through the smaller diameter SWCNTs, having slightly higher enhancement factors than the predicted values. The small deviation between simulated and measured enhancement factors can be accepted because the experimental values are ensemble averaged data of CNTs whose diameters vary within the range of ± 1.0-2.0 nm. Interestingly, except the Holt and Park et al.’s results with sub 2 nm DWCNT membranes, all other previous experimental demonstrations do not agree with the diameter dependence observed in our results and predicted in MD simulations, reporting at least an order of magnitude higher gas flow enhancement factor. Plausible
explanations for the overestimated values are the underestimation of the CNT pore density and/or the presence of additional gas transport paths such as cracks or voids as mentioned in section 4.5.3 or the uncompensated effects of the different structural parameters such as structural defect density, membrane thickness et cetera.

Next, we performed single gas selectivity measurements in the same setup shown in Figure 4.48. Prior to each measurement with different gases, both sides of the membrane mounted in the gas flow cell as well as the entire gas lines were evacuated till the mass spectroscopy connected to the outlet did not detect any residual gas molecules, then, filled with the gas of interest to a pressure of around 200 mbar while the exit value is opened to continuously release the supplied gas. This process is repeated 3-5 times to ensure the constant pressure gradient at the set value over the course of the experiment. A bypass line connecting upstream and downstream of the membrane is required in order to avoid membrane breakage, which may occur if pressure difference between vacuum and 200 mbar is directly imposed across the membrane.

Figure 4.54 shows the single gas selectivities relative to He, exhibiting that all gases (He, CH₄, N₂, Ar, CO₂, Kr, CF₄, and SF₆) tested in this study follows the expected inverse-square-root scaling of molecular mass, reflecting the mass dependence of molecular velocity. On the other hand, our SWCNT membranes do not show higher selectivity for carbon-containing gases. Previously, Ban et al. reported molecular simulation result that ~3 fold higher selectivities towards CO₂ over N₂ is expected than Knudsen selectivity for a SWCNT with a diameter of 1.36 nm although the pronounced difference of single gas transport diffusivities diminishes for CO₂/N₂ mixtures due to the correlation effect in a gas mixture. [367] As an experimental evidence, Bittner et al. observed the strong adsorption of hydrocarbons (i.e., hexane) on bulk SWCNTs relative to more polar molecules (i.e., ethanol) using a pulse mass analyzer. [368] Also, Holt and Park et al. reported an experimental observation that linear hydrocarbon gases such as CH₄, C₂H₆, C₃H₆, C₄H₆, and C₄H₈ shows similar mass dependence but a slightly higher selectivity in sub 2 nm DWCNT membranes. [20] Such enhancement is attributed to the strong adsorption strength of CO₂ with CNT walls and its influence on the surface diffusion mechanism. The observed Knudsen-like selectivity of our SWCNT membrane may
suggest that the effect of strong interaction of travelling molecules with CNT wall is less pronounced in weak confinement condition by the contribution of gas phase ballistic transport to the gas permeance. [354, 368, 369]

Figure 4.54. Single gas selectivities (defined as permeability relative to He) for SWCNT membranes (1: orange squares, 2: blue triangles, 3: pink circles, 4: green diamonds, 5: violet pentagons), AAO membrane with an average pore diameter of 5 nm (red crossings) and polycarbonate membrane with an average pore diameter of 15 nm (gray stars); all data show good agreements with the Knudsen model scaling that is indicated by the dashed line.
4.6.3 Water transport experiments

Parts of this section have been submitted for publication in: S. K. Youn, J. Buchheim, H. G. Park, “Fabrication of the first vertically aligned single walled carbon nanotube membrane and the diameter dependent mass flow enhancement”, 2014, in preparation.

Through the comprehensive review and problem-posing in previous sections of 4.2 and 4.3, we have claimed that the experimental verification especially for CNTs with small diameters and narrow distribution is still needed in the study of water transport through CNTs. The details about the structural properties of membrane 1 and 2 used for water transport experiments are provided in table 4.2 of section 4.5.3. Size exclusion tests with 5 nm gold nanoparticles were performed for the two SWCNT membranes of 1 and 2 used for water transport experiments in order to once again confirm the absence of leakage path for water transport. We measured the pressure driven water flow rate by pressuring a given volume at constant pressure and monitor the volumetric change as a function of time. Experimental setup for measuring water flow rate is similar to the set up for gas flow rate measurement.

![Figure 4.55. Schematic of water flow or permeance measurement setup.](image)

Figure 4.55 shows the schematic of experimental set up. Initially, the upstream side of a membrane in a flow cell and the connected 1/8 inch capillary tube (PFA-T2-030-100, Swagelok) are filled with 5-7
259 mL water and pressurized with dry N₂ gas in the range of 0-1 bar. Since the downstream of the membrane is open to ambient, the effective pressure drop across the membrane is the same as the applied N₂ pressure (ΔP). The bottom side of membrane is pre-wet by water droplet to lower the energy barrier for water at the exits of CNT channels if exist. [370] The flow rate is measured by the change in the height of the upstream water column over time.

Figure 4.56. (a) Volumetric changes of liquid water as a function time with respect to the initial volume, converted from experimentally measured height changes of upstream water column at ΔP=250 mbar (300 K, 40 % relative humidity) and (b) the calculated water flow rate plotted as a function of an applied pressure across SWCNT membrane 1; The solid lines are linear curve fittings, indicating the constant water flow rate at a given pressure drop and a linear pressure dependence of water flow rate.

Figure 4.57a shows raw data of a water flow rate through a SWCNT membrane 1 at ΔP of 250 mbar. The measured height change (ΔH) of the water column inside the capillary tube whose cross sectional area
is measured to be 2.256 mm² is converted to the volume change (ΔV) with respect to the initial volume in the y axis. The upstream volume of water column kept decreasing linearly over 5 hours, indicating the constant water flow rate through the membrane at a fixed pressure drop. Further, the water flow rates were measured at several different ΔP to check its pressure dependence. Figure 4.55b shows the linear increase of water flow rate with the imposed pressure gradient across the SWCNT membrane, consistent with Walther et al.’s work. [370] After the experiments, we observed a water film or droplets on the initially dry downstream side of the membrane, confirming the water flows through the membrane (Figure 4.57).

Figure 4.57. Water droplets smeared out from the downstream side of the SWCNT membrane and accumulated during water flow measurement.

Evaporation of water from the surface of upstream water column could occur upon continuous exposure to the pressurized N₂ flow, thereby lowering the measurement accuracy. The saturation pressure of water vapor at around room temperature where we perform the measurement is ~33 mbar. The maximum water vapor content in dry N₂ can then be 2.64 % (33 mbar/ 1250 mbar). A control experiment was performed by monitoring the time dependent volume change of upstream water column with an impermeable Si chip. About 3-5 % error is observed and accordingly corrections can be made in the determination of volume change over time. The height change of water column was manually marked and measured using a digital caliper. The error that can be introduced by manual readings can be minimized by collecting large number of data points over long measurement time.
Membrane permeation of liquids is usually described by classical model as a low Reynolds number flow in cylindrical tubes with no-slip boundary condition, yielding the Hagen-Poiseuille formalism. MD simulations, however, have shown that water molecules conduct at extremely high speed through the near zero friction CNT channels by the cooperative movement of a hydrogen-bonded water network. Breakdown of the continuum model is not very surprising for only a few nanometers wide nanochannels. Taking the formalism used for predicting gas transport mechanism, one can define the characteristic length in liquid water as the molecular diameter (0.25 nm for H$_2$O) and then Kn number for the waters inside CNTs of 3-4 nm in diameters is calculated to be 0.06-0.08. These values lie in transition flow regime where continuum theory concepts such as velocity profile may not be applicable, which is why MD simulations are often used for studies in nanofluidics.

$$Q_{\text{HP}} = \frac{\pi}{8\mu} \left( \frac{d_{\text{CNT}}}{2} \right)^4 \frac{\Delta P}{L}$$  \hspace{1cm} (16)

$$Q_{\text{slip}} = Q_{\text{HP}} \left( 1 + 8 \frac{L_s}{d_{\text{CNT}}} \right); \quad \frac{L_s}{d_{\text{CNT}}} = \frac{EF-1}{8}$$ \hspace{1cm} (17)

<table>
<thead>
<tr>
<th>SWCNT Membranes</th>
<th>H$<em>2$O permeability, $Q</em>{\text{Exp}}$ (m$^3$/Pa·s·m$^2$)</th>
<th>Hagen-Poiseuille prediction, $Q_{\text{HP}}$ (m$^3$/Pa·s·m$^2$)</th>
<th>Enhancement ($Q_{\text{Exp}}/Q_{\text{HP}}$), Slip length ($L_s$, nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.82 × 10$^{-11}$</td>
<td>1.24-1.65 × 10$^{-12}$</td>
<td>47-106, 19-48</td>
</tr>
<tr>
<td>2</td>
<td>6.46 × 10$^{-11}$</td>
<td>0.87-1.03 × 10$^{-12}$</td>
<td>46-94, 23-48</td>
</tr>
</tbody>
</table>

Table 4.4. The experimentally obtained water permeability for SWCNT membranes of 1 (average d$_{\text{CNT}}$=3.62 nm) and 2 (average d$_{\text{CNT}}$=4.15 nm) with Hagen-Poiseuille model predictions. Detailed specifications of the membranes are provided in Table 4.2. H$_2$O permeability is defined as the measured volumetric flow rate (m$^3$/s) per effective membrane area (m$^2$) per applied pressure drop (Pa).
Same as in gas transport studies, water flow enhancement can be assessed by the enhancement factor (EF), the ratio of the measured water flux over the water flux calculated by no-slip Hagen-Poiseuille equation and the slip length ($L_s$), an extrapolated distance relative to the wall where the tangential velocity component vanishes. The measured water flow rates reveal 46-77 fold enhanced flows, 1-2 orders of magnitude faster than the no-slip Hagen-Poiseuille model predictions. It corresponds to slip lengths ranging from 19-35 nm, much larger than the CNT diameter (Table 4.4). Note that several previous works reported that nanoporous polycarbonate or AAO membranes shows slip lengths smaller than pore dimension and the slip length of water-graphene without a curvature is around 30 nm. [372]

![Figure 4.58.](image)

**Figure 4.58.** Water flow enhancement factors through CNT membranes versus the average CNT diameter ($d_{CNT}$); the observed water flow enhancements through the SWCNT membranes of 1 and 2 (pink and violet circles) are in line with the simulation results (green pentagons, [308] and dark yellow stars, [298]) by Thomas et al. but bit lower than Falk et al.’s prediction (navy squares, [22]). The gray circles correspond to previous experimental results; Holt and Park et al., [20, 300] Kim et al., [315], Majumder et al., [366], Du et al., [30] and Whitby et al.’s results. [309]
Next, we plotted the measured water flow enhancement factors through our SWCNT membranes along with all available data in the literatures as a function of average CNT diameter in Figure 4.58 to compare our new data with other simulation and experimental results and to discover the diameter dependence of liquid water flow enhancement. Briefly summarizing up to this time, Majumder et al. reported an enhancement of 4 to 5 orders of magnitude with average $d_{\text{CNT}}=7$ nm MWCNT membrane [301], while Holt, Park et al. evaluated an enhancement of 2 to 4 orders of magnitude with average $d_{\text{CNT}}=1.6$ nm DWCNT membrane. [20] Recently, Du et al. have reported water flow enhancement that is about 5 orders of magnitude faster with MWCNT membrane with average $d_{\text{CNT}}=10$ nm. [30] The pore size distribution and structural properties of these membranes are summarized in Figure 4.59 for comparative analysis.

<table>
<thead>
<tr>
<th>CNT Membranes</th>
<th>$d_{\text{CNT}}$ (nm)</th>
<th>CNT density (cm$^{-2}$)</th>
<th>Membrane thickness ($\mu m$)</th>
<th>Tortuosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. [20]</td>
<td>1.3-2.0</td>
<td>$2.5 \times 10^{11}$</td>
<td>2-3</td>
<td>~1</td>
</tr>
<tr>
<td>Ref. [301]</td>
<td>7</td>
<td>$1-3.4 \times 10^{9}$</td>
<td>34-126</td>
<td>~1.10</td>
</tr>
<tr>
<td>Ref. [30]</td>
<td>8-12</td>
<td>$2.4 \times 10^{10}$</td>
<td>~4,000</td>
<td>~1</td>
</tr>
<tr>
<td>SWCNT 1</td>
<td>$3.62 \pm 1.1$</td>
<td>$&lt;1.1 \times 10^{11}$</td>
<td>3.143</td>
<td>~1.3</td>
</tr>
<tr>
<td>SWCNT 2</td>
<td>$4.15 \pm 1.5$</td>
<td>$&lt;1.0 \times 10^{11}$</td>
<td>8.48</td>
<td>~1.38</td>
</tr>
</tbody>
</table>

Figure 4.59. Comparison of the pore size distribution, wall number and the structural parameters of various CNT membranes reported in present and previous studies; ref.[20] (navy), ref. [301] (olive), ref. [30] (red), and our SWCNT membrane 1 (filled green bars) and 2 (filled pink bars).
As shown in Figure 4.58, the water flow enhancement factor obtained from SWCNT membrane 1 and 2 lie in the range reported in the Thomas et al.’s simulation [308], however, are slightly lower than Falk et al.’s prediction. [22] Earlier, the fast water transport through a CNT was explained by the surface hydrophobicity to have a depletion region at the water-CNT interface. Then, Thomas et al. reassessed the water flow enhancement (EF) in CNT by deriving a continuum-based pressure-driven flow model, incorporating the variation of water viscosity ($\mu(d_{CNT})$) and slip length ($L_s$) with respect to CNT diameter ($d_{CNT}$) with an assumption that the origin of water flow enhancement is mainly caused by the nearly frictionless surface. [308]

$$EF = \left[ 1 + 8 \frac{L_s(d_{CNT})}{d_{CNT}} \right] \frac{\mu_\infty}{\mu(d_{CNT})}$$  \hspace{1cm} (18)

$$L_s (nm) = 30 + \frac{352}{d^3}$$  \hspace{1cm} (19)

$$\mu(d_{CNT}) = \mu_{int} \frac{A_{int}(d_{CNT})}{A_{CNT}(d_{CNT})} + \mu_\infty \left[ 1 - \frac{A_{int}(d_{CNT})}{A_{CNT}(d_{CNT})} \right]$$  \hspace{1cm} (20)

where $\mu_\infty$, $\mu_{int}$, $A_{int}$, and $A_{CNT}$ are the viscosity of bulk water, the viscosity of the water-CNT interface region, the area of the water-CNT interface region, and the total cross sectional area of CNT. This model is valid for CNTs with diameters larger than 1.6 nm. This model well supports our new results with SWCNT membranes, Holt, Park et al.’s [20] and Whitby et al.’s results [309], and yet does not agree well with Du et al. [30] and Majumder et al.’s results. [301, 366] Note that this equation uses several parameters that has not been determined either by experiment of exact theory and therefore its validity needs further verification. The strong deviations of the Majumder et al.’s [301, 366] and Du et al. [30]’s results may be caused by an uncompensated length effect causing an artificially low reference permeation through the nanotube and thus inflating the enhancement value beyond expectations. Recently, Walther et al. have deduced the following expression of EF as a function of CNT diameter ($d_{CNT}$), slip length ($L_s$), and pressure entry/exit losses ($C$) from the slip and entrance/exit loss modified Hagen-Poiseuille model. For infinitely long CNTs ($L>300$ nm), the second term of eq. (21)
becomes negligible and the degree of enhancement can be determined by $d_{CNT}$ and $L_s$. Based on the $L_s$ of 63 nm determined from their own simulation results, they reported the maximum theoretical EF value of 253.

$$\frac{1}{EF} = \frac{1}{1 + \frac{4L_s}{d_{CNT}/2}} + \frac{C\pi(d_{CNT}/2)}{8L} \xrightarrow{L \to \infty} EF = 1 + \frac{4L_s}{d_{CNT}/2}$$ (21)

For shorter CNTs, the calculated EF value rises with CNT length ($L$). Previously, Su et al. and Nicholls et al. have shown the similar CNT length dependence of water flow enhancement in CNT channels (Figure 4.60). [373, 374]

![Figure 4.60. MD simulation results of linear CNT length ($L_{CNT}$) dependence of water flow enhancement factor: (a) For a given $d_{CNT}/2=1.08$ nm, the EF factors increases almost linearly with $L_{CNT}$ (red circles) while for a given $L_{CNT}=2.56$ nm the EF factors reduces as CNT diameter ($d_{CNT}$) increase (green starts), adapted from ref. [373]. (b) EF factors of water flow through (7,7) CNTs with $L_{CNT}$ in the range of 2.5-50 nm. [374]]

Su et al. [373] reported EF values near the values predicted by the Walther’s model, while Nicholls et al. [374] showed one to two orders of magnitude higher EF values. Different approaches of estimating the transport rates and selecting the potential model and parameters to model the system result in such a huge deviation or contradiction in the MD simulation results. [21] To assess the effect of CNT membrane thickness on the calculation of water flow enhancement,
we plotted the experimental and simulation results again versus the ratio of membrane thickness to CNT diameter ($L/d_{\text{CNT}}$) (Figure 4.61). Interestingly, all the data points collapsed to a line in the plot of $E_F$ versus $L/d_{\text{CNT}}$. It hints about the length effect on the water flow enhancement factors.

**Figure 4.61.** A log-log plot of water flow enhancement factors ($E_F$) through CNT membranes versus the ratio of membrane thickness over CNT diameter ($L/d_{\text{CNT}}$), exhibiting a linear relation, a power-law dependence; the hollow gray symbols correspond to various MD simulations [370] and the color-filled circles correspond to new data points obtained from SWCNT membranes (green and pink circles) and previously reported experimental results: navy (DW- [20], MWCNT [300]), green (MWCNT, [366]), orange (SW- and DWCNTs [315]) and red (DWCNT [30]) circles.
4.7 Summary

We present a new membrane design and a universal fabrication method that enable the direct integration of as-grown small diameter VA-SWCNTs into a robust membrane platform, which has been desired for investigating unique molecular transport characteristics through CNTs as well as for achieving the best performance as a membrane for many potential applications such as reverse osmosis, water purification and desalination, etc. Along with the VA-SWCNTs grown in a controlled manner (preferably, shorter than 20 µm, high quality and low tortuosity), the new membrane fabrication includes a characteristic step of mechanical reinforcement of VACNTs prior to the typical polymer gap-filling process by coating them with thin layer of oxide or other available materials using ALD process. The ALD coated VACNT structure, then, no longer suffers from the common problems in polymer infiltration and thus becomes easily processable. Polyethylene is chosen as a matrix material due to its high availability and material properties that could be useful for the commercialization and practical applications. Using this method, we for the first time succeed in the fabrication of SWCNT membranes that are used for measuring the transport characteristics of various gases and water through SWCNTs of 2 to 5 nm in diameters. The measured gas fluxes through the fabricated SWCNT membranes reveal the Knudsen-like selectivity with no indication of preferential interaction of CNT walls toward hydrocarbons and the diameter dependence of gas flow enhancement; the smaller the CNT diameters, the higher the degree of gas flow enhancement becomes, in good agreement with previous MD simulation results. SWCNT membranes with average diameters of around 3 nm and 4 nm show water flow rate, 1-2 orders of magnitude faster than the no-slip, Hagen-Poiseuille model predictions. Along with the Holt, Park et al.’s previous work, our new data agree well with the MD simulation results, completing the map of water flow enhancement factor over CNT diameter. In addition, a new way of presenting the water flow enhancement factor as a function of the ratio of membrane thickness to CNT diameter reveals the length effect on the overestimated water flow enhancement factors reported from the hundreds to thousands of µm-thick CNT membranes.
Epilogue
5 Epilogue

5.1 Key contributions of this work

Fast mass transport inside a graphitic nanochannel of CNT has made CNT membrane as an emerging branch of membrane science and technology, which can spawn numerous applications particularly in current energy and environment issues. Nevertheless, the difficulties and complexities in fabricating CNT membrane, the lack of sufficient experimental demonstrations and the large discrepancies in the flow enhancement among previous simulation and experimental results have been hampering the progress in both fundamental studies and practical applications. This thesis has investigated the CCVD process of VA-SWCNTs and CNT membrane fabrication towards the goal of studying the effect of confinement (imposed by CNT diameter) on mass transport enhancement.

Work towards this goal included: the understanding of diameter modulation mechanism of VACNTs, the catalyst design for growing small diameter VACNTs, a systematic study of CVD parameters influencing the structural properties of VACNTs, the fabrication and characterization of SWCNT membranes, and the evaluation of gas and water transport properties through the fabricated SWCNT membranes with different diameters. This thesis made meaningful contributions towards the advancement of not only the process technologies for the production of VA-SWCNTs and CNT membranes but also the scientific understanding on the CVD growths of VACNTs on supported metal catalyst and the nanofluidic phenomena inside a CNT. The key contributions of this thesis include:

- Development of ultrathin Fe catalysts on granular alumina supports for diameter controlled growth of VA-SWCNTs via acetylene based CVD [132]:
  - Observation of the critical role of alumina support in the morphological evolution of catalyst particles during CVD
  - Demonstration of a direct correlation between the initial catalyst film thickness and SWCNT diameter
- Achievement of VA-SWCNTs with an average diameter decreased to 1.25 nm, in the range of current minimum
- Observation of the significant subsurface diffusion of surface metallic atoms and its contribution to the size control of catalyst particle remaining on the surface
- Observation of the gradual change of CNT diameter and density along the height of VACNTs.

- Design and use of bimetallic catalysts composed of Fe and Mo for diameter and density controlled growth of VACNTs [142]:
  - Observation of the differences in the growth dynamics of VACNTs depending on the composition and stacking order of bimetallic catalyst
  - Systematic analysis of morphological and compositional evolution of the two types of bimetallic catalysts, Fe-on-Mo and Mo-on-Fe through a thorough AFM and XPS analysis
  - Elucidation of a strong correlation between catalyst particle size and spacing, and CNT diameter and spacing
  - Strategic use of Mo in tuning catalyst activity and lifetime

- New findings on the use of the thick trilayered metallic catalyst composed of Fe, Mo and alumina for growing VA-SWCNTs:
  - Understanding of the catalyst formation mechanism based on thorough catalyst characterization results using AFM, ToF-SIMS, FIB, and TEM: metallic interdiffusion
  - A new concept of catalyst configuration weakening the strong dependence of CNT diameter on initial catalyst film thickness
  - Demonstration of a 4inch wafer-scale uniform growth of high quality VA-SWCNTs with diameters in sub 3 nm range

- Novel concept, design and optimization of a thermal gradient CVD reactor (TGCVD) [164]:
  - Systematic control of gas phase thermal gradient in a cold-wall CVD reactor using two independent thermocouples
  - Observation of the effect of different thermal treatment of precursor gases on the growth results of VACNTs
- Identification of important gas thermal zone in the range of 600-700 °C for growth enhancement of VACNTs
- Control of diameter and wall number distribution of CNTs simply by changing the thermal gradient in the gas phase at a fixed catalyst substrate temperature
- Simulation results revealing the presence of secondary carbonaceous precursors along with intact acetylene as a result of gas phase reactions such as polymerization and decomposition during CVD process

• Systematic studies of the influences of the key CVD parameters (acetylene partial pressure, temperature, growth time, catalyst pretreatment) on the growth dynamics, diameter distribution and defect density of VA-SWCNTs:
  - Standardization and preconditioning of a CVD reactor, improving process consistency and repeatability
  - growth temperature predominantly determining the size distribution of catalyst nanoparticles and acetylene partial pressure tuning the size range of catalyst particles allowing the formation of stable CNT cap and continuous growth
  - Transition of rate determining step for the initial growth rate and defect density of VACNTs
  - Acetylene partial pressure dependence of the transition temperature; the higher the acetylene partial pressure, the higher the transition temperature becomes
  - Time evolution of the growth rate of VACNTs originated from the gradual catalyst evolution at CVD condition and its relation to growth termination
  - Suppression of catalyst particle coarsening by the early nucleation of CNT
  - Fine tuning of the size and reactivity of catalyst particles by means of the duration and hydrogen concentration during catalyst preannealing

• Demonstration of the CNT membrane fabrication, for the first time integrating as-grown VA-SWCNTs:
  - Identification of the critical issues in applying the previous membrane fabrication methods to VA-SWCNTs
- A newly developed CNT membrane configuration and fabrication process that includes a characteristic step of mechanical reinforcement of VACNTs by ALD process prior to the typical polymer gap-filling process
- Structure properties of VA-SWCNTs that are preferable for membrane fabrication process; height shorter than 20 µm, intermediate density, less entanglement, low tortuosity, and the presence of small amount of amorphous carbon

- Mapping of the degree of gas and water flow enhancement through CNTs as a function of CNT diameter:
  - Evidencing the effect of CNT confinement on the gas flow enhancement through the fabricated SWCNT membranes whose average diameters are in the range of 2 to 5 nm
  - Observation of one to two orders of magnitude enhanced liquid water flow from SWCNT membranes with average diameters of around 3 nm and 4 nm
  - Good agreement with previous MD simulation results
  - Identification of the length effect on the overestimated water flow enhancement factors reported from the several hundreds to thousands of µm-thick CNT membranes

In addition to the work presented in this thesis, a collaborative effort with M. A. Zeeshan established the conformal graphitic coatings of magnetic iron nanowires by thermal CVD process for nanorobotic applications. [375] A collaboration work with J. W. Choi reported a one-step growth of a unique carbon nanostructure of graphene on VA-MWCNTs that pose potential for (electro) chemical applications. [376] Collaboration works with A. O. Altun and N. Yazdani presented the use of controllably grown VA-MWCNTs in the applications of dye sensitized solar cells and surface enhanced Raman spectroscopy. [377, 378] A collaboration work with N. Yang further studying the TGCVD growth kinetics of VACNTs and an analytical model relating the acetylene pyrolysis product to the growth kinetics is on progress.
5.2 Outlook

- High Flux CNT Membranes For Energy and Water Purification

The studies presented in this thesis have been exclusively concerned with the diameter modulation of VACNTs and the fabrication of pore-size controlled CNT membranes towards the superfast mass transport through CNTs. The new findings and approaches introduced in this thesis offer potentially useful insights and methodologies into the development of next generation membrane, particularly in the field of osmotic power generation [43], taking the full advantage of high flux CNT membrane. Whether the large mechanical energy of fast flowing water through a CNT membrane can be converted to electrical energy (hydroelectric voltage generation [379]) is also an interesting subject. In a short term, our CNT membranes can be directly applied to the forward osmosis process with wastewater or size controlled synthetic draw solutions for water purification. Compared to the other existing polymer membranes, CNT membranes can achieve higher process efficiency by the beneficial effects of solvent flow enhancement, high solute rejection and lower fouling tendency.

- Future Directions in CNT Membrane Fabrication

The first experimental demonstration of the unusually rapid water transport was only made in 2005 and as described a comprehensive understanding of the nanofluidic phenomena is still lacking mostly due to the difficulties in building an experimental platform to study carbon nanofluidics. All the VACNTs based membranes reported so far suffer from rather small membrane area, long fabrication process, poor mechanical stability, local agglomeration of CNTs, and low CNT packing density. A novel design and fabrication method of CNT membrane achieved in this study has just lowered this barrier, in particular significantly improving membrane integrity and preserving not only the straightness of individual CNTs but their entanglements. Techniques involved in the developed fabrication approach can be used for wafer-scale processing. However, new advances are still needed in densifying and straightening the CNT channels for making
ultrahigh flux nanoporous membrane. Moreover, so far, most of works in the field have overlooked the possibly significant effects of the structural properties of original VACNTs such as the straightness of individual nanotube, the broadness of diameter range, the presence of heteroatoms having higher affinities toward certain molecules and the transparency of the CNT channel that might be controllable by the wall numbers or by the variation of matrix material properties. For example, membranes made out of the CNTs having high density of structural defects that become additional diffuse scattering sites per unit length is expected to lower the transport efficiency \([353]\). Accordingly, in-depth investigations on such effects along with the further fine control of CNT channel dimension and surface properties should be followed.

- Reduction of CNT Diameter to Sub-nm and Scaling-up

![Figure 5.1](image)

*Figure 5.1.* Comparison of the diameter range and size control of VA-SWCNTs achieved in this thesis by varying catalyst and support material and configuration to those reported in state-of-the-art literature \([24, 64, 127, 129, 380, 381]\)

This thesis presents a wide range of average diameter control of VA-SWCNTs by rational catalyst design and CVD process optimization, which rivals the state-of-the-art results in the field (Figure 5.1). The smallest average CNT diameter realized in this work is \(1.1 \pm 0.31\) nm. Reducing the absolute diameter and narrowing the distribution of CNTs are considered to be the highest priority mission for realizing
the greatest performance in membrane applications. New approaches for the diameter modulation of SWCNTs hinted from this thesis work are as follows; pre-coating of catalyst surface with a protective layer at low temperature to suppress particle coarsening, a stepwise or short-pulsed introduction of carbon precursors with different reactivities for the decoupled nucleation and growth steps, and surface roughness modulation of catalyst support. As shown in this thesis work, the strategic use of secondary metal as support or multilayered metallic film stacks is a very promising approach for scale-up production of uniform VACNTs without sacrificing the nanotube quality and small diameters. Follow-up experiments for optimizing the interdiffusion process for diameter modulation are in progress. Modulating the surface properties of CNT channels can be assessed by incorporation of heteroatoms to a sp² graphitic network [382] at the CCVD process.
Appendix
Appendix

A.1 Techniques for catalyst surface analysis

AFM, Atomic Force Microscopy

Since the first demonstration of the use of ultra-small probe tip at the end of a cantilever for investigating surface of insulators by Binnig et al. in 1986, AFM has been the most commonly used technique to image the surface with nanometer to atomic level resolution. [383] The scanning mechanism works via a piezoelectric transducer which is brought into close proximity with the tip on the sample surface and moved relative to each other in a raster pattern. And a laser beam made to focus on the cantilever and reflected onto a photodiode enable the detection.

![Figure A.1. Schematic of basic AFM operation and SEM image of the super sharp silicon tip (Nanosensors™, SSS-NCHR) used for the surface analysis of supported metal catalysts throughout the thesis.](image)

Figure A.1 shows a schematic of the basic AFM operation. The interaction between the tip and sample surface are measured by monitoring the displacement of the cantilever via the changes in the position of the reflected beam on the photodiode. At very short distance in the range of few Å, a very strong repulsive force exists between the tip and surface atoms of the sample. This is called exchange interactions, which arise due to the overlap of the electron orbitals at atomic distances. When this repulsive force is dominant, the tip and sample are considered to be in contact mode. Besides, when an instantaneous polarization of an atom induces a polarization
The silicon tip on the cantilever is driven to oscillate at its resonance frequency. As the tip approaches the sample surface, the amplitude and the resonance frequency change drastically. This provides the feedback to the scanner. The AFM system can image the topography using contact, non-contact or tapping modes. Imaging in tapping mode, having the tip touch the surface only for a short time is proven to take advantages of the contact and non-contact imaging. It eliminates friction force by intermittently contacting the surface and oscillating with sufficient amplitude to prevent the tip from being trapped by adhesive forces from the contaminant surface of the sample, in turn providing higher lateral resolution and protecting the tip from the scratching effects of non-rigid samples. [384]

Optical and electron microscopes can easily generate two dimensional images of sample surface at a broad range of magnifications but cannot provide information on the vertical dimension (z-direction) of the sample, the height (i.e., metal nanoparticles, diameter of laterally lying CNTs) or depth (i.e., grain boundaries of a copper foil, granular structure of oxide support) of the surface features. AFM is the most appropriate tool to characterize the three dimensional surface of various metallic catalysts investigated throughout this thesis works. AFM analyses of the various catalyst surface for the presented thesis work were made using the AFM (Asylum Research, MFP-3D™) at FIRST (Frontiers In Research: Space and Time) and in the tapping mode. Because the lateral resolution depends on the tip sharpness, a supersharp tip (SSS-NCHR, tip radius of smaller than 5 nm) available from Nanoscience™ is used for the characterizations.

**XPS, X-ray Photoelectron Spectroscopy**

XPS is a surface sensitive technique widely used to determine the chemical composition of surfaces and obtain information about the types of bonding that occurs within various compounds based on the photoelectric effect. In the photoelectron effect, atoms emit electrons when absorbing energy from light. This process requires photons with energies from a few eV to over 1 MeV in case for high atomic number elements. For surface analysis, photons created by an X-ray source strike atoms on surface and transfer their energy to electrons within
atoms. If a sufficient energy is transferred, the electrons within the surface atoms escape out of the atoms, becoming a photoelectron. The detection can be done by comparing the kinetic energy of escaping photoelectrons to the initial energy of the photons, which corresponds to the strength of attraction the electron has with the nucleus to break it (binding energy) and the amount of energy the particle loses in transit from the sample to the analyzer (work function). The work function is consistent for each sample on a specific XPS analyzer but the binding energy is dependent on the type of atom the electron came from as well as the environment it came from. Here, the photo-emitted electrons remain within a range of binding energies, thereby can be used to identify the element and the types of bonds.

**Figure A.2.** (a) A schematic of XPS process and (b) an example of using XPS technique in the field of CNT synthesis to characterize the catalyst properties; *in situ* XPS Fe 2p\textsubscript{3/2} core level lines of Fe catalyst on SiO\textsubscript{2} support. [385]

As shown in Figure A.2, in the field of CNT synthesis, XPS has been frequently used to determine the metallic state of catalyst whether it is in metallic or oxide state or in carbide form. For instance, Amama *et al.* investigated the influence of annealing ambient (N\textsubscript{2}, Ar and H\textsubscript{2}) on the Fe\textsubscript{2}O\textsubscript{3} nanoparticles employed for CNT growth using XPS and Hofmann *et al.* observed that the oxidized Fe does not catalyze CNT growth and the active state of the catalyst is a crystalline metallic with no contributions of metal carbide forms. [202, 385]
Typical XPS analysis uses an incidence angle normal to the sample surface. Photons from the x-ray source then penetrate into the sample as deep as about 1 µm, further than merely the top layer of surface atoms. Because the atoms in the subsurface of the sample outnumber the interfacial atoms, the majority of the signal comes from the interior, reflecting in general the information at 5 to 20 Å below the interface of the sample with surrounding environment. In order to distinguish more clearly between the surface and bulk photoelectrons, we can alter the angle of incidence, changing the sampling depth to a level that includes almost exclusively the surface atoms. In that case, the contribution of the surface portion can be significantly boosted in signal strength. (Figure A.3) The penetration depths are decreased by a factor of \( \cos \theta \), as seen in Figure A.3. [386]

![Figure A.3. A schematic of angle-resolved XPS analysis: greater surface contribution in the XPS signal intensity at more grazing emission angles and diagrammatic XPS spectra of a metal surface covered with a thin metal oxide.](image)

XPS analyses of the various catalyst surface for the presented thesis work were made using the PHI Quantum 2000 microprobe spectrometer at EMPA with base pressure of \( 8 \times 10^{-7} \) Pa and monochromatic Al K\( \alpha \) (1486.6 eV) radiation. To increase the surface contribution, the XPS spectra were made at two different incident angles of 17° and 45°. The surface elemental composition was determined using MULTIPAK software (Physical Electronics), which uses proprietary relative sensitivity factors to calculate element concentrations in atomic percentages.

**SIMS, Secondary Ion Mass Spectroscopy**

Time-of-Flight (ToF)-SIMS is widely used technique for analyzing trace elements in solid materials, especially thin films. The SIMS ion source is one of only a few to produce ions from solid samples without
prior vaporization. During the SIMS analysis, the surface is slowly sputtered away by a pulsed primary ion beam. The bombardment generates monatomic and polyatomic particles of sample material and re-sputtered primary ions, along with electrons and photons whose kinetic energies are in the range of zero to several hundred eV. The desorbed and ionized species from sample surface are accelerated into a mass spectrometer, where their masses are analyzed based on their ToF from the sample surface to the detector. Mass spectra from ToF-SIMS analysis reveal the elemental and molecular species on a surface. Further, spatial mapping of the mass spectra can visualize the distribution of individual species on the surface (Static SIMS).

![Diagram of multilayered films](image)

**Figure A.4.** An example of depth profiling using ToF-SIMS; compositional profiles of the multilayered films of ZnO (20 nm, top), ZnS (31 nm), SnS$_2$ (37 nm), and Cu$_2$S (24 nm) on Si. [387]

A continuous analysis while sputtering with a relatively fast sputtering rate a few nm/s in dynamic SIMS mode determines the distribution of various chemical species with high mass resolution simultaneously and the secondary ion count rate of selected elements as a function of depth from the surface, called depth profile. Depth resolution below 1 nm can be achieved. This ToF-SIMS depth profiling has been performed at EMPA using a ToFSIMS5 (IonTof GmbH) for characterizing the interfacial diffusion phenomena occurring in the newly designed trilayer catalyst in the presented thesis work. The quantitative analysis by SIMS uses relative sensitivity factors (RSF), which is a function of the element of interest and the sample matrix. The RSFs of the two components in the catalyst of interest, Fe and Mo are in the same range of $1.0 \times 10^{22-23}$ atoms/cm$^3$, measured for oxygen primary ion bombardment. [388]
A.2 Techniques for CNT characterization

SEM, Scanning Electron Microscopy

Various structural features of CNTs including their dimensions, orientations and macroscopic morphology of VA-CNTs can be easily detected using SEM with high resolutions. SEM scans the surface of the specimen mounted using a conductive carbon tape with a focused electron beam. Upon beam impingement, the specimen emits both secondary and backscattered electrons that are collected by a detector for imaging. Material-dependent backscattering (i.e., specimen with a high mean atomic number yields greater backscattered electron signals which can be used for determining the chemical composition) and charging effects as well as the topography of the specimen (i.e., secondary electrons can more easily escape at the edges) contribute to the image contrast. The resolution is intrinsically limited by the penetration of electron beam into the mass of the specimen. The higher the acceleration voltage (i.e., speed or energy of the electrons), the smaller the spot size, the higher the beam current and the smaller the atomic mass of the sample, the deeper the beam penetration depth (the larger the interaction volume) becomes, from where secondary electrons are ejected. The penetration depth \( H, \mu m \) is described by

\[
H = \frac{0.0276 A \cdot V^{1.67}}{z^{0.89} \rho},
\]

where \( A \) is the atomic mass (g/mol), \( V \) is the accelerating voltage (keV), \( z \) is the atomic number, and \( \rho \) is the density (g/cm\(^3\)). [389]

SEM images of the CNTs synthesized for the presented thesis work were made using Zeiss ULTRA 55, ULTRA plus at FIRST (Frontiers In Research: Space and Time) and FEI Quanta 250 at BRNC (Binning and Rohrer Nanotechnology Center), the clean room facilities at ETH Zurich. Substrate-bound CNTs appear bright and blurred at low acceleration voltages due to beam-induced charge accumulation on CNTs. Li et al. reported an observation that metallic (bright) and semiconducting SWCNTs (dark) have different contrast in SEM images due to the effect of their conductivity difference on beam-induced surface potential. [390] Followingly, He et al. reported a new approach of imaging Schottky barrier formed at the metal-SWCNT contact for evaluation bandgap information of CNTs based on the
relation of the length of charge depletion to the diameter of semiconducting SWCNTs (Figure A.5). [391]

Figure A.5. (a) cross-sectional SEM images of VA-SWCNTs providing information on their height and alignment and SEM techniques useful for the characterization of SWCNT properties, adapted from (b) ref. [390]: identification of metallic and semiconducting SWCNTs by the SEM image contrast and (c) Ref [391]: evaluation of band gap energies of semiconducting SWCNTs by the charge depletion length that can be imaged using SEM.

Raman Spectroscopy

Raman spectroscopy is an important technique, which can provide information on the structural properties of a CNT in a non-destructive manner; for example, clustering of the sp² phase, the presence of sp²-sp³ hybridization and the introduction of chemical impurities, the magnitude of the mass density, optical energy gap, elastic constants, doping, defects and other crystal disorder, nanotube diameter, chirality, curvature, and metallic versus semiconducting behavior, etc.
Figure A.6. Representative Raman spectrum of VA-SWCNTs.

All carbon allotropes show two common spectral peaks: a G peak at 1580-1600 cm$^{-1}$ and a D peak at 1350 cm$^{-1}$ (Figure A.6). [280] The G peak feature stems from the first order scattering of the E$_{2g}$ phonon at the Brillouin zone center of sp$^2$ carbon bonds while the defect induced D peak feature arises from the C-C breathing modes of six-fold rings of K-point phonons of A$_{1g}$ symmetry. [281] Often, the D-to-G ratio is used as a measure of the degree of disorder in the sp$^2$ network of CNT. The RBMs are in particular useful for the determination of the diameter of a nanotube through the dependence of $\omega_{\text{RBM}}$ on nanotube diameter and for relating the $\omega_{\text{RBM}}$ and the resonant optical transition energies $E_{ij}$ for a given tube (the Kataura plot). The relation between $\omega_{\text{RBM}}$ and nanotube diameter can be generally described by

$$\omega_{\text{RBM}} = \frac{277}{d_t^2} \sqrt{1 + C_\epsilon d_t^2},$$

where the parameter $d_t$ and $C_\epsilon$ describes nanotube diameter and environmental effects. Lastly, the $(n,m)$ dependence of the optical transition energies ($E_{ij}$) can be studied by the RBM resonance window analysis. Raman spectrosocopes (WiTec confocal CRM200 with a 532 nm laser and Renishaw RM 1000 with a 785 nm laser) are used throughout the presented thesis work.

**TEM, Transmission Electron Microscopy**

The first discovery of CNT was enabled by the use of TEM. [5] Since then, high resolution TEM (HRTEM) has been the most powerful instrument, which provides information on diameters, wall numbers, structural distortion and catalyst position of CNT. Moreover, the electron diffraction pattern helps identify the chirality (helicity) as well as the nature of the catalyst. [392, 393] In TEM, an electron
beam passes through thin specimen and the transmitted electrons are projected on a screen for imaging. The diffracted electron pattern can be used to determine the atomic structure and defects present in the specimen.

**Figure A.7.** (a) A representative high magnification TEM image of a good quality SWCNT and (b) the contrast profile along the dotted line in the image showing the nanotube diameter of 4 nm.

TEM analysis of the CNTs synthesized for the presented thesis work was examined by a FEI CM12 microscope at EMEZ, the Electron Microscopy Facility of ETH Zurich. The typical acceleration voltages are in the range of 100-120 keV. For the beam energies larger than 139 keV, carbon atoms can be knocked out and small diameter CNTs can suffer beam-induced damage even at lower energies around 80 keV. For TEM sample preparation, VACNTs were detached from catalyst substrate by the sonication and dispersed in ethanol. The samples were prepared by dropping the suspension onto a holey carbon TEM grid (Ted Pella) and dried in air. The nanotube CNT wall appears as dark lines accompanied by bright lines farer away from the nanotube axis can be well-imaged at slight underfocus. The nanotube diameters can be experimentally defined by the distance of the two dark lines (Figure A.7) but such values have been reported to be slightly smaller than the real diameters. The discrepancy was found to be typically less than 10 % for nanotubes larger than 1 nm.
A.3 Symbols and abbreviations

S.I. units have been used throughout this thesis, except in the case of gas flow rates, which are noted in standard cubic centimeters per minute (1 sccm = $1.67 \times 10^{-8}$ m$^3$/s) and pressure (mbar, 1 mbar = 100 Pa).

Unless stated otherwise the notation and symbols have the following meanings:

- $A$ Membrane area (m$^2$)
- amu Atomic mass unit (g)
- $a.u$ Arbitrary Units
- at. % Atomic Percentage
- $d_{CNT}$ CNT diameter (nm)
- $E$ Energy (eV)
- $E_a$ Activation Energy (eV)
- $E_g$ Band gap (eV)
- $G$ Gibbs free energy (J/mol)
- $\Delta G_f$ Gibbs free energy of formation (J/mol)
- $J$ Molar flux (mol/m$^2$·s)
- $k$ Wavenumber (cm$^{-1}$)
- $k_B$ Boltzmann constant (J/K)
- $L_s$ Slip length (m)
- $L$ Membrane thickness or CNT length (m)
- $M$ Molar mass (kg/mol)
- sccm Standard cubic centimeters per minute
- $t$ Time (s)
- $T_m$ Melting temperature (K)
- $T_s$ Softening temperature (K)
- $P$ Pressure (bar, Pa)
- $Q$ Volumetric flow rate (m$^3$/s or sccm)
\( R \) Universal gas constant \((8.314 \text{ J/mol}\cdot\text{K})\)

\( V \) Volume \((\text{m}^3)\)

\( \sigma_v \) TMAC

\( \mu \) (Dynamic) viscosity \((\text{Pa}\cdot\text{s})\)

\( \lambda \) Wavelength \((\text{nm})\)

\( \nu \) Wavenumber \((\text{cm}^{-1})\)

\( \rho \) Density \((\text{g/cm}^3)\)

In the first instance, all abbreviations are written in the text and are denoted in the parenthesis immediately following the first usage. Abbreviations used in this thesis have the following meanings.

AFM Atomic Force Microscopy
APCVD Atmospheric Pressure Chemical Vapor Deposition
\( \alpha \)-C Amorphous carbon
CNT Carbon Nanotube
CCVD (Catalytic) Chemical Vapor Deposition
DWCNT Double Walled Carbon Nanotube
EF Enhancement Factor
EDX Energy Dispersive X-ray Spectroscopy
FWCNT Few Walled Carbon Nanotube
FWHM Full Width Half Maximum
GCF Gas Correction Factor
HP Hagen-Poiseuille
IGR Initial Growth Rate
Kn Knudsen number
MWCNT Multi Walled Carbon Nanotube
MD Molecular Dynamics
MFP Mean Free Path
MFC Mass Flow Controller
PVD Physical Vapor Deposition
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>vdW</td>
<td>van der Waals</td>
</tr>
<tr>
<td>Parylene-C</td>
<td>Poly-para-xylylene C</td>
</tr>
<tr>
<td>PAHs</td>
<td>Polycyclic Aromatic hydrocarbons</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>POM</td>
<td>Polyoxymethylene</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PSf</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>RBM</td>
<td>Radial Breathing Mode</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>RMS</td>
<td>Root Mean Square</td>
</tr>
<tr>
<td>RSF</td>
<td>Relative Sensitivity Factor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single Walled Carbon Nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGCVD</td>
<td>Temperature Gradient Chemical Vapor Deposition</td>
</tr>
<tr>
<td>TMAC</td>
<td>Tangential Momentum Accommodation Coefficient</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of flight</td>
</tr>
<tr>
<td>TWCNT</td>
<td>Triple Walled Carbon Nanotube</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>Ultraviolet-Visible</td>
</tr>
<tr>
<td>VOCs</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>VA(CNT)</td>
<td>Vertically Aligned (Carbon Nanotube)</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoemission Spectroscopy</td>
</tr>
</tbody>
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Curriculum Vitae

Personal Details

Name: Seul Ki Youn
Birth: February 27\textsuperscript{th}, 1983, Seoul, Republic of Korea
Nationality: Republic of Korea

Education

01/2010 ETH Zurich, Switzerland
- present Department of Mechanical and Process Engineering
   Institute of Energy Technology
   Supervisor: Prof. Hyung Gyu Park

09/2004 Korea Advanced Institute of Science and
Technology, Republic of Korea
- 01/2008 Graduation with Master’s degree
   Department of Chemistry
   Supervisor: Prof. Jin Baek Kim
   Thesis: A new approach in top surface imaging
   through the selective adsorption of
   poly(dimethylsiloxane) derivatives
   KRF global internship scholarship

03/2001 Sogang University, Republic of Korea
- 08/2005 Graduation with Bachelor’s degree
   Department of Chemistry,
   Department of Business administration
   Advisor: Prof. BongJin Moon
   Magna Cum Laude, BK 21 undergraduate research
   fellowship from KOSEF
Work Experience

01/2009  
Albert-Ludwigs-University Freiburg, Germany
-12/2009  
Research Scientist; ZnO nanowire-based gas sensor

08/2008  
Kimberly-Clark Innovation Center Asia, U.S.A
-02/2009  
Research Scientist; Packaging plastics from CO₂

08/2007  
CSIRO Melbourne, Australia
-07/2008  
Internship; Polysiloxanes for intraocular lenses

07/2004  
POSTECH, Republic of Korea
-09/2004  
Internship; dynamic kinetic resolution of phenylalanine
Publications

Peer-reviewed Journal Publications (during PhD studies)


8. S. K. Youn, C.E. Frouzakis, B. P. Gopi, K. Teo, J. Robertson and H. G. Park*. Temperature Gradient Chemical Vapor Deposition


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Conference Proceedings and Talks


**Book chapter**


**Poster presentations**


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