COLLECTIVE MECHANISMS LIMITING THE INDEFINITE GROWTH OF CARBON NANOTUBE ASSEMBLIES

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ABSTRACT
While carbon nanotubes (CNTs) have been produced industrially in ton-scale quantities for nearly two decades, scalable manufacturing processes that precisely control the structure, length, and alignment of CNTs are needed to realize the exceptional properties of CNTs at larger scales. Specifically, vertically aligned CNT forests are a model system for further understanding what limits the growth of indefinitely long CNTs, and are building blocks for novel microstructures and multifunctional thin films. This paper will present our current understanding of the limiting mechanisms of CNT forest growth by chemical vapor deposition (CVD). Interactions among a population of CNTs govern their collective growth behavior, and in combination with the performance of individual catalyst particles, prevent indefinite CNT growth using known methods. To understand these effects, we examine the dynamics of catalyst formation, CNT forest self-organization, steady growth, and termination using a holistic approach, combining in situ and ex situ X-ray scattering with spatiotemporal mapping of CNT forest mass, height, and density. While indefinite CNT growth may remain a dream, the present findings have enabled scalable production of CNT forests and horizontally-aligned thin films via continuous CVD, rolling, and printing schemes. These technologies have been realized in our laboratory using prototype bench-scale machines and show promise for cost-effective manufacturing of large-area, organized CNT films.

INTRODUCTION
Carbon nanotubes (CNTs) are hollow cylindrical molecules of graphitic carbon, and have exceptional properties including several times the strength of steel piano wire at one fourth the density, at least five times the thermal conductivity of pure copper, and high electrical conductivity and current-carrying capacity [1]. CNTs have likely been around civilization for thousands of years and are natural outgrowths of exposure of carbon containing gases to nanoscale particles of common transition metals such as iron, cobalt or nickel. Evidence even exists that CNTs are present within ancient steel swords [2] where they may grow by solid diffusion of carbon to nucleation sites within the steel. The first documented deliberate production of carbon nanotubes was in 1952 by Radushkevich and Lukyanovich [3], followed by work of Bacon [4] on graphite single crystals, and Endo [5] who later pioneered the use of the floating catalyst method [6] and was instrumental in scaling this technology for mass production. TEM studies by Baker [7] and Bethune [8] from IBM helped understand of the distinct cylindrical morphology of CNTs, and structural characterization by Iijima [9] stimulated wide attention to the unique form of CNTs. Large quantities of multi-wall CNT (MWNTs) powders have been produced commercially by floating catalyst chemical vapor deposition (CVD) since
the late 1980's [10], and over 300 tons per year are now used primarily as additives in plastics for
electrostatic discharge and rechargeable batteries having increased cycle life [11]. Several
companies also produce single-wall CNTs (SWNTs) in annual volumes of several tons.

Current industrial production methods focus chiefly on manufacturing of CNTs in powder form.
Due to difficulty in exfoliating, dispersing, and mixing large quantities of CNTs, these products
can be used only as bulk material additives, and it is very difficult to make high performance
materials from CNTs in powder form. The scientific methodology and knowledge base that has
worked toward optimizing bulk CNT powder synthesis has also limited our ability to isolate and
understand the limiting mechanisms of growth. Understanding these issues is to create a next
generation of high performance materials using long and highly ordered CNTs, and to approach
the long-sought goal of continuous production of indefinite CNTs. While significant advances
have been made recently in production of CNT yarns and nonwoven sheets (e.g., Nanocomp
Technologies, Baughman et al. [12]), extreme potential for CNT materials will remain untapped
until we understand how to grow CNTs of indefinite lengths, and understand how to control
CNT diameter and structure (e.g., defect density, chirality) with high precision and continuity.
Likewise, advances in understanding the limiting mechanisms of CNT growth will be useful for
advancing current and emerging CNT production methods.

![Figure 1: (a) schematic of CNT growth from catalyst nanoparticle on a substrate; (b) millimeter-scale CNT forest during growth.](image)

Catalytic CVD is the most versatile and scalable method of CNT production, owing to its high
yield (relative to arc, laser, and flame methods), versatility for many reactor configurations, and
relative simplicity of operation [13, 14]. In the CVD method, nanoscale particles serve as
templates for deposition and reorganization of gaseous carbon into solid carbon (Figure 1a);
after initial organization of a carbon “cap” on the surface of the particle, the CNT forms and
lengthens until growth stops. The particles are typically called “catalysts”; however, the details
of how carbon is incorporated into a growing CNT are not yet fully understood. The energy for
conversion of carbon at the catalyst particles is typically supplied by heating the catalyst to
elevated temperature, and historically (and in most methods used today), the catalyst particles are
transition metals or alloys that have a non-negligible carbon solubility and very high rates of
carbon surface diffusion, such as Fe, Co, Ni, Fe/Mo, and Co/Mo. While some techniques
including plasma-enhanced CVD (PECVD) methods have produced CNTs at relatively low
temperatures (e.g., 200-500 °C, which is useful for CMOS electronics and polymer substrates),
CNT structural quality and growth rate increases with temperature. Therefore, high temperature
CVD (e.g., 800-1300 °C) is best for achieving high quality CNT products and will be the focus
of our discussion and study.
In order to create functional materials that comprise indefinitely long CNTs, we must design synthesis processes that fulfill three main requirements:

I. Maintenance of catalyst health to prevent termination of growth;

II. Maximization of CNT structural quality (i.e., low defect density);

III. Control of CNT organization to minimize tortuosity and thereby enable high packing density.

It is also imperative to realize that CNT growth is a multi-stage and dynamic process, starting with formation of the catalyst particle and ending with a CNT (or assembly of CNTs) having desired structural characteristics (i.e., chirality, diameter, length). A large number of variables (i.e., pressure, temperature, catalyst, substrate, feedstock, etc.) are involved in CNT synthesis, and most studies rely primarily on *ex situ* measurements [15] to create models of the growth process. We use synthesis of vertically aligned forests by chemical vapor deposition (CVD) as a model system for studying the process and limitations of CNT production. Figure 1b shows a typical vertically aligned CNT “forest” during growth on a resistively heated substrate platform [16-18]. Just as the forest looks like a little “black box”, many important details of CNT forest growth are still unknown. In the following sections we discuss how to look inside the black box of CNT forest growth, and thereby elucidate the limiting mechanisms of this important process.

**EXPERIMENTATION**

CNT growth was performed using both a horizontal quartz tube furnace (Thermo-Fisher Mini-Mite, 22 mm inner diameter, 12” heated length), and a “cold wall” reactor system (Absolute Nano SabreTube) wherein the growth substrate rests on a resistively heated silicon platform [16, 17]. In all experiments, the growth substrate was 1/10 nm Fe/Al₂O₃, deposited on thermally oxidized (100) silicon wafers by electron beam evaporation. After installing the substrate and purging the reactor, the catalyst was heated to the growth temperature in flowing H₂/He, and then C₂H₄ was added for the growth duration (t), which ranged from 2.5 to 30 minutes. The growth process parameters are further detailed in Figure 2. Feedback control of temperature and flow was automated using LabVIEW™ (National Instruments). In the cold walled reactor (Figure 2c), the substrated is locally heated (Tₐ); however, the gaseous precursors are preheated before entering the reactor (Tₚ). With the cold-wall system, CNT forest height is measured in real time during growth using a non-contact laser displacement sensor (Keyence LK-G152). This sensor was also used for *ex situ* forest height measurements. Forest mass was measured using an electronic scale (Ohaus Discovery DV215CD) with accuracy 0.01 mg, by weighing the silicon substrate after CNT growth, before and after delaminating the CNT forest. SEM imaging was performed using a Philips XL30-FEG. Small Angle X-ray scattering (SAXS) was performed at the G1 beamline at the Cornell High Energy Synchrotron Source (CHESS). AFM imaging was performed in tapping mode (MultiMode AFM, Nanoscope IIIa controller) and results were analyzed using WSxM 5.0 Develop 2.0 (Nanotec) [19]. Samples were prepared by heating the substrate in 310/300 sccm H₂/He for 2 minutes, and then rapidly cooling the substrate in H₂/He without exposure to C₂H₄.
RESULTS

Catalyst formation

In order to grow CNT forests, the shape and size of the catalyst particles needs to be controlled in the nanometer scale. In order to achieve this, the catalyst formation process starts with a thin metal film deposited by physical vapor deposition (PVD) that agglomerates into nanoparticles upon heating in a process known as dewetting. In order to study this process, AFM is used to characterize the topography of the as-deposited and the annealed catalyst surfaces for samples in prepared in the cold-walled reactor. As shown in Figure 3, the nanoparticles formed after heating the substrate for 2 minutes in an ambient of H₂/He at Ts = 825 °C.

To further study the kinetics of this catalyst formation process, in situ grazing incidence small angle scattering is used (GI-SAXS), as shown in Figure 4a. In this study, the substrate was heated from room temperature up to 820 °C in 2 minutes in an ambient of H₂/He (310/300 sccm). The scattering patterns collected by the area detector are correlated to the temperature in Figure 4b. The evolution of these nanoparticles is elucidated by taking horizontal line scans in these patterns at the vertical location of highest average intensity and plotting the intensity as a function of the inverse-space parameter q (Figure 4c). With heating the structure factor peak starts showing only at high temperatures (about 700 °C) and becomes well-defined at 820 °C. Thus, the catalyst particles form rapidly, at temperatures as low as 700 °C.
Height and rate kinetics

As shown in Figure 2c, a non contact displacement sensor is used to measure the in situ height and rate kinetics during CNT forest growth in the cold-walled reactor [20]. Figure 5 shows the results of CNT growth kinetics in the cold-walled reactor at a substrate temperature of 825 °C, and varying $T_p$ (1010, 1040, 1070, and 1120 °C). The average growth rates before termination were found to be 4.7, 6.0, 7.2, and 8.5 μm/s, respectively. This result emphasizes the impact of the thermal gas decomposition of the precursor gases on the CNT growth process. This also indicates the ability to decouple the gas decomposition process from the substrate temperature [18]. Also, as can be clearly observed in all cases, the growth terminates abruptly [20].
Quantification and spatial mapping of CNT alignment in CNT forests

In order to quantify the alignment of CNTs within a forest, an orientation parameter is determined from X-ray scattering data. Figure 6a shows a schematic representation of our reactor configuration which enables, in addition to the in situ measurement of CNT forest height during growth, the acquisition of small-angle X-ray scattering (SAXS) patterns. Scattering data was obtained by positioning the X-ray beam just above the interface between the CNT forest and the substrate, and then scanning the forest from bottom to top by moving the sample stage.

The CNT alignment within a forest is quantified by calculating the Hermans orientation parameter ($H$) [21],

$$H = \frac{1}{2} \left( 3\langle \cos^2 \phi \rangle - 1 \right), \quad \langle \cos^2 \phi \rangle = \frac{\int_{0}^{\pi} (I(\phi) \sin \phi \cos^2 \phi) d\phi}{\int_{0}^{\pi} (I(\phi) \sin \phi) d\phi}$$

Here, $\phi$ is the azimuthal angle, shown in the inset of Figure 6a. $I(\phi)$ is the corresponding scattered intensity, which is measured at the radial location corresponding to the local maximum of intensity arising from form factor scattering of the CNTs[22]. The morphological evolution was corroborated by scattering data taken both during and after growth. Data shown below was taken by scanning the forests mounted in the reactor immediately after growth.

In Figure 6b, the evolution of the orientation parameter is shown for three samples: a forest that self-terminates, and two forests that are terminated prematurely by rapidly cooling the substrate, or stopping the flow of C$_2$H$_4$/H$_2$ while maintaining the substrate temperature. $H$ increases sharply at the top of a forest, representing a transition from tangled to vertically aligned morphology as the CNTs self-organize at the start of growth. $H$ then remains approximately constant as growth proceeds, and then it decays steeply toward zero before growth terminates, indicating the onset of disordered CNTs. In agreement with the $H$ values, SEM images (Figure 6c) show that the self-terminated forest exhibits disorder at its base, and the intentionally
terminated forests exhibit strong alignment at the base. Thus, the loss of alignment is a signature of self-termination of CNT forest growth.

**Figure 6.** Characterization of CNT alignment. (a) schematic of the experimental setup mounted in synchrotron beamline, (b) evolution of Hermans parameter, (c) SEM of the base morphology of the forest (adapted from [23]).

**Figure 7.** Measurement of the lengthening kinetics of a CNT forest: (a) cross section of the setup used for focusing the synchrotron X-ray beam, (b) schematic of the transformation scheme, (c) time evolution of forest height and average CNT length, showing that CNT length is linear with time (adapted from [24]).

### Measurement of CNT lengthening kinetics

Owing to the inherent tortuosity of VA-CNT forest as shown in **Figure 6c**, its collective height does not equal the average length of the constituent individual CNTs, and therefore temporal height measurement is not an accurate measure of the genuine growth kinetics. We uniquely use high-resolution spatial mapping of alignment by SAXS (**Figure 7a**) to transform real-time
measurements of array height (Figure 7b) to the average length of the CNTs comprising this forest [24]. Applying this approach, as shown in Figure 7c, shows that the actual length of CNTs is much longer than the apparent height measurements. Also, this transformation changes the shape of the kinetics curve from a slightly sub-linear to a true linear relationship with time. This has important implications for interpretation of the growth kinetics, because many previous studies [25-28] have used sublinear relationships between CNT height and time to suggest that growth is limited by gas diffusion or catalyst rate decay.

Evolution of mass density during CNT forest growth

While measurements of the CNT forest height versus time have previously been used as a direct estimate of the reaction rate [26, 27, 29], measuring the time evolution of CNT forest mass provides a needed complement to the forest height data in revealing the true growth kinetics. Figure 8a shows how both the forest height and the mass per unit area change with time. Each point on this plot is an average of three forests (5×5 mm² area), all grown in the same position along the length of the tube furnace (hot-walled reactor), and measured after growth. As was also observed in situ, the forest height increases in an essentially linear fashion with time until abrupt termination occurs; however, the rate of mass increase begins to decrease long before the forest height stops increasing. Amorphous carbon accumulation is an insignificant fraction of the measured mass and therefore does not affect the kinetics [18].

Because the rate of height increase is much greater than the rate of mass increase during the later stage of growth, we conclude that the number density of CNTs growing at the substrate begins to decrease long before termination occurs. Accordingly, the time evolution of the CNT number density during growth is shown in Figure 8b and is estimated by first calculating the differential change in the mass density (ρm) between forests grown for slightly different durations. From this differential mass density, the CNT number density (ρn) is calculated as

$$\rho_n = \frac{\rho_m(t_n) - \rho_m(t_{n-1})}{h(t_n) - h(t_{n-1})}, \quad \rho_n = \frac{\rho_m/\rho}{\pi/4(d_o^2 - d_i^2)}$$

We consider the CNTs to be continuous straight hollow cylinders of graphite (ρ=2.2 g/cm³), with outer diameter do = 11 nm, and inner diameter di = 6 nm. The diameters are measured by fitting the SAXS patterns with a form factor model for a lognormally distributed population of hollow cylinders. This method agrees closely with TEM diameter measurements in our previous work [18, 22], and the diameter varies by only 5-10% through the forest. A ratio of 0.6 between the inner and outer diameter of the CNTs appropriately fits the scattering data and agrees with TEM analysis. As discussed in the previous section, it is not fully accurate to assume that the CNTs are straight, and this assumption becomes less accurate as the CNT alignment within the forest degrades. The assumption of straight CNTs therefore underestimates the magnitude and rate of the number density decay, as the true length of a CNT will be greater if it is not fully perpendicular to the substrate [24].

As indicated on Figure 8, there is a stage of density decay that precedes growth termination to from ≈ 24 to 3 μg/mm³. Before the density decay stage, a steady growth stage is shown, in which the differential mass density remains essentially constant (≈24 μg/mm³) with growth time, and this lasts for approximately 15 minutes. The analysis of the time evolution of forest density allows us to elucidate the successive stages of the collective growth mechanism, which will be discussed next.
DISCUSSION

Stages of the growth process

By combining *in situ* and *ex situ* experimental characterization, a deeper understanding of the CNT growth process is formed. Figure 9 depicts the sequential stages of CNT forest growth that are identified based on our results. First, the catalyst particles are formed on the substrate, by depositing a thin metal film that is typically less than 5 nm thick (stage 0). This film agglomerates upon heating (stage 1). When the carbon source is introduced it dissociates at the catalyst and organizes into a CNT “nucleus” (i.e., the “cap”) (stage 2). As a result of the uniform nucleation, CNTs start growing in random orientations, and due to the attractive van de Waals forces, they crowd and form an entangled layer (later becoming the top “crust” of the forest) that causes the CNTs to form a vertically aligned forest (stage 3). The CNTs then grow in the vertically aligned morphology (stage 4), and all the CNTs grow in parallel. This “steady growth” stage continues until the growth of individual CNTs begins to terminate; thus the number density of CNTs growing at the substrate begins to decay (stage 5). Thus, while the CNT forest grows in a coordinated fashion, it is vital to consider that the CNTs have a distribution of growth characteristics. Growth termination of an individual CNT is governed by the lifetime of the catalyst particle, which depends on its diameter, surface structure, and other factors. Collective growth termination of the forest, as indicated by an abrupt halt in forest height increase [20], happens when the CNT number density becomes too low for self-supporting the aligned forest structure (stage 6) [23]. This leads to a loss of alignment that was revealed by electron microscopy and quantified by small-angle X-ray scattering (SAXS) [22]. Due to the presence of a small percentage of the catalyst particle population that is still active, a tangled mat continues to form at the interface between the forest and the substrate in a post-termination regime (stage 7).
Figure 9. Collective mechanism of CNT forest growth: (a) sequential stages of catalyst formation, nucleation, self-organization, evolution, and termination; (b,c,d) SEM images of representative morphology of top, middle, and bottom of a CNT forest.

Mechanisms of CNT growth termination

Despite understanding of the succession of events leading to collective termination of CNT forest growth, the specific and underlying causes of growth termination of individual CNTs remain unresolved. Further, these causes are difficult to ascertain using metrology approaches that have been pursued by this study and the work of many other groups. Nevertheless, all experiments to date indicate that CNT growth self-terminates. Depending on the reaction conditions:

- The catalyst may evolve in size (e.g., by diffusion, ripening/coalescence, or evaporation) and thereby become incompatible with the reaction conditions;
- The surface of the catalyst may become isolated from the hydrocarbon supply by the formation of a carbonaceous overcoat, or the catalyst may become an inactive carbide phase.
- Termination may be caused by an insufficient supply of carbon in the atmosphere surrounding the catalyst, such as by diffusion limitation due to the height of the forest.

Carbon overcoating: If the rate of hydrocarbon surface adsorption exceeds the rate of incorporating carbon atoms into the growing CNT, a layer of either amorphous or graphitic carbon will form, coating the catalyst particles [25, 30-32]. This isolates the catalyst from the hydrocarbon atmosphere and prevents continued growth. Also, catalyst particles may be “buried” by the accumulation of large hydrocarbon molecules that are not efficient carbon sources for CNT growth. These molecules, including polycyclic aromatic hydrocarbons (PAHs), are formed by thermal decomposition of the reaction atmosphere in typical CNT growth processes [33]. Importantly, a small (∼100 ppm) water concentration in the CVD ambient can enhance the catalyst lifetime by etching amorphous carbon from the catalyst surface [34]. Similarly, introducing other oxygen containing growth enhancers such as alcohols can extend the catalyst lifetime [35].
**Catalyst poisoning:** Poisoning of catalyst nanoparticles by gas-phase pyrolysis products has frequently been regarded as the cause of catalyst deactivation during CNT growth [36]. Also, carbide formation has been suggested as a mechanism for deactivation of Fe growth [37]; however, a recent study also claims CNT growth from Fe carbide nanoparticles [38].

**Ostwald ripening of the catalyst particles:** At elevated temperatures, the size distribution of metal nanoparticles on a substrate evolves with time according to the mechanism known as Ostwald ripening. In Ostwald ripening, particles that are larger than a critical radius grow larger (via atomic diffusion between particles) at the expense of particles that are smaller than the critical radius in order to minimize the total surface energy [39, 40]. This process leads size evolution of the catalyst nanoparticles, and if its kinetics are fast enough, growth may stop early due to this size change. It was shown that this occurs during CNT growth, where nanoparticles increase in size while decreasing in number density. Adding water vapor to the growth atmosphere was shown to inhibit this Ostwald ripening, by reducing the diffusivity of Fe atoms on a Al₂O₃ support layer by OH- functionalization [41]. Also, hydrogenation increases the mobility of the metal atoms, thus leads to faster ripening kinetics [42]. CNT growth atmospheres typically contain excess hydrogen.

**Catalyst evaporation:** In CVD processes where the growth temperature is very high, the loss of catalyst atoms by evaporation becomes more rapid. This causes the size of the catalyst particles to decrease until a threshold size is reached at which the catalytic reaction cannot proceed. It is likely that evaporation is not significant at lower growth temperatures (600-900 °C) typically used for substrate-bound growth, and is significant at higher temperatures (1100-1300 °C) which are typically used for gas-phase (floating catalyst) growth. Importantly, due to their nanoscale size, CNT growth catalysts exhibit melting points significantly lower than the bulk value and therefore have significantly higher vapor pressures.

**Catalyst migration into the substrate:** Atomic diffusion of the catalyst down into the support layer beneath is another route for reducing the size of the catalyst nanoparticles [23]. Ongoing investigations in our group using Rutherford backscattering spectroscopy (RBS) and X-ray photoelectron spectroscopy (XPS) are studying this behavior; for example, we have quantified diffusion of Fe into the Al₂O₃ support.

**CONCLUSIONS AND OUTLOOK**

Using CNT forest growth as a model system, we advance the current understanding of the CNT growth process and its limiting mechanisms. Using a combination of in situ and ex situ methods to probe the spatial and temporal evolution of CNT forest growth, we demonstrate that interactions among the growing population of CNTs govern their collective growth behavior. These interactions, in combination with the performance of individual catalyst particles, currently limit indefinite CNT growth. It is likely that competition among these mechanisms governs growth termination under any particular process conditions. Further, these mechanisms depend intimately on the size, surface structure, and other aspects of the individual catalyst particles. Therefore, understanding the statistical behavior of the CNTs during growth is important for controlling CNT growth in a collective fashion. Based on this understanding, new reactor designs, new catalyst designs, and new methods of controlling the collective growth of large numbers of CNTs are necessary to overcome existing limits to growth of long CNTs, as well as controlling the spatial variation of morphology and properties.
While indefinite CNT growth may remain elusive, our new understanding is enabling scalable production of CNT forests and horizontally-aligned thin films via continuous CVD, rolling, and printing schemes. These technologies have been realized in our laboratory using prototype bench-scale machines and show promise for cost-effective manufacturing of large-area, organized CNT films. For example, by spatially separating the annealing, growth and delamination processes within a single apparatus, the catalyst can be recycled for successive growth of CNT forests on a recirculating substrate (Figure 10) [43]. Additionally, CNT forests which have a low as-grown density can be transformed into dense horizontally aligned (HA-CNT) thin-films by mechanical rolling as shown in Figure 11. The VA-CNT “blades” are grown to mm scale height (Figure 11c) and subsequently rolled by a stainless steel pin (0.6 mm diameter) to orient the CNTs parallel to the substrate and simultaneously control the film thickness and areal density (Figure 11d). By changing the preload of the roller on the substrate, the thickness of the resultant HA-CNT films can be adjusted and hence the packing fraction of the CNTs in the film is controlled.

Figure 10. Schematic and prototype for continuous CNT forest growth on a recirculating substrate.
Figure 11. Preparing HACNT, (a) schematic of rolling, (b) machine used for rolling, (c-f) SEM showing the morphology before and after rolling.

REFERENCES


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