Collective Mechanism for the Evolution and Self-Termination of Vertically Aligned Carbon Nanotube Growth

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We explain the evolution and termination of vertically aligned carbon nanotube (CNT) “forests” by a collective mechanism, which is verified by temporal measurements of forest mass and height, as well as quantitative spatial mapping of CNT alignment by synchrotron X-ray scattering. We propose that forest growth consists of four stages: (I) self-organization; (II) steady growth with a constant CNT number density; (III) decay with a decreasing number density; and (IV) abrupt self-termination, which is coincident with a loss of alignment at the base of the forest. The abrupt loss of CNT alignment has been observed experimentally in many systems, yet termination of forest growth has previously been explained using models for individual CNTs, which do not consider the evolution of the CNT population. We propose that abrupt termination of CNT forest growth is caused by loss of the self-supporting structure, which is essential for formation of a CNT forest in the first place, and that this event is triggered by accumulating growth termination of individual CNTs. A finite element model accurately predicts the critical CNT number density at which forest growth terminates and demonstrates the essential role of mechanical contact in maintaining growth of self-assembled films of filamentary nanostructures.

Despite recent advances in our understanding of the multivariate nature of carbon nanotube (CNT) growth by chemical vapor deposition (CVD), the mechanism of growth termination is still not fully understood. This limits the efficiency of CNT manufacturing, restricts commercial viability of applications that require bulk quantities of CNTs, and prevents us from realizing indefinitely long strands of continuous CNTs as next-generation structural fibers and electrical transmission lines. Significant study has focused on understanding the mechanisms that limit the growth of individual CNTs, and it has been suggested that growth termination can be caused by evaporation, contamination, alloying, or overcoating of the catalyst particle that resides at the base or tip of the growing CNT.2–4 Interestingly, the longest known CNTs have been grown as “floating” isolated CNTs in the CVD atmosphere,5 suggesting coupling inherently present among CNTs within a forest are a limiting condition for achieving indefinite CNT growth. However, considering that at least tens of thousands of CNTs must be packed to create even a micrometer diameter fiber, self-assembly of CNTs during growth is likely necessary for efficient manufacturing of large-scale aligned CNT materials.

Vertically aligned CNT “forests” typically comprise billions of CNTs per square centimeter on a substrate and are a model system for understanding the collective mechanics of CNT growth. Further, owing to their anisotropic structure and the outstanding properties of individual CNTs, CNT forests are widely attractive for use as mechanical, electrical, and thermal interface layers,7–9 electrochemical storage devices,10 and membranes for gas, liquid, and biological separations.11–14 For these and other applications, it is critical to manufacture CNT forests having spatially uniform characteristics.

A CNT forest forms when CNTs self-orient due to crowding during the initial stage of growth, and along with appropriate control of the CVD conditions, CNT forests can reach heights of several millimeters or more. Recent studies have shown the importance of oxygen,15 hydrogen,15 water vapor,16 and carbon dioxide17,18 in mediating gas-phase reactions in the CVD atmosphere, controlling deposition of carbon at the nanoparticle growth sites, and prolonging the duration of catalyst activity. Small amounts of these species, in addition to fluctuations in ambient pressure,4 have been shown to affect consistency and repeatability of experimentation. CNT forest growth was also prolonged by adjusting the stoichiometry of bimetallic catalyst particles19 and by stabilizing the underlying Al2O3 support by doping with a rare earth element such as lanthanum (La).20 The latter approach was used to grow CNT forests as high as 18 mm.21 However, in spite of all these efforts, termination of CNT forest growth has not been overcome.

Further, previous attempts to understand the limiting mechanisms of CNT forest growth have represented the growth kinetics by the evolution of the forest height with time. These studies have assumed that the areal density of CNTs remains constant throughout the forest and have explained forest termination using behavior expected for an individual CNT–catalyst system. However, considering that a forest is a population of CNTs having a certain diameter distribution and that interactions among CNTs create and maintain the aligned morphology, it is necessary to adopt a holistic approach that accounts for the collective behavior of CNTs.
In this study, we explain the evolution and termination of CNT forest growth based on a collective model consisting of four stages, as illustrated in Figure 1A:

I. Nucleation and self-assembly of randomly oriented CNTs into a vertically aligned forest structure.

II. Steady growth, wherein the number density of growing CNTs remains constant with time.

III. Density decay, wherein the number density of CNTs within the forest decreases with time.

IV. Abrupt self-termination, wherein forest growth ceases suddenly, and is accompanied by a loss of CNT alignment at the interface between the CNTs and the substrate.

This model is verified by combining in situ measurements of forest height during growth, spatial mapping of CNT alignment by synchrotron X-ray scattering, and ex situ measurements of CNT forest mass versus height and growth time. Further, a finite element model considering the effect of CNT–CNT spacing and contact on the mechanical stiffness of a CNT forest accurately predicts the CNT areal density at which termination is observed experimentally.

Therefore, we suggest that abrupt termination of CNT forest growth is caused by loss of the self-supporting structure that is essential for organization of a CNT forest in the first place. The proposed mechanism supports several previously unexplained observations of abrupt growth termination using both in situ and ex situ height measurements of single-wall (SWNT) and multiwall CNT (MWNT) forests. Further, filamentary nanostructures are replete in man-made and natural systems, and this study further reveals how interactions among such structures not only govern their collective behavior but are also critical to their self-organization and morphological evolution.

CNT growth was performed using both a horizontal quartz tube furnace (Thermo-Fisher Mini-Mite, 22 mm inner diameter, 12 in. heated length), and a “cold wall” reactor system (Absolute Nano SabreTube) wherein the growth substrate rests on a resistively heated silicon platform. 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 min. The growth process parameters are further detailed in the Supporting Information. Feedback control of temperature and flow was automated using LabVIEW (National Instruments). With the heated-platform reactor, forest height was measured in real time during growth using a noncontact 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. X-ray scattering was performed at the G1 beamline at the Cornell High Energy Synchrotron Source (CHESS), with a slit-collimated beamspot size of ≈100 μm.

SEM images (Figure 1B) show the morphological evolution of a CNT forest during growth, starting (stage I) with formation of a thin “crust”30 of randomly oriented CNTs that resides on the top of the forest after alignment emerges. The forest sidewall then exhibits a uniform, aligned, and dense texture (Figure 1C) that extends downward below the crust and into the density decay region (Figure 1D). It is important to note that SEM images are not used to infer information about the CNT number density, as the CNTs are likely bundled together, and the focal depth of SEM makes it difficult to precisely discern density differences unless more involved techniques (e.g., stereo imaging31) are used. Nevertheless, SEM confirms the evolution of CNT alignment and morphology. Finally, the base of a CNT forest, which has been grown until self-termination occurs (stage IV), transforms to a distinctly rippled and tangled morphology (Figure 1E, F). This morphology is typically restricted to within several micrometers from the substrate and has been observed in several previous studies but has not yet been explained.4,27 It is important to note that this bottom layer may appear to have a high packing density of unoriented CNTs even though the number density of CNTs (i.e., the number of continuous CNTs that are growing from the substrate) is low. This is presumably because the CNTs continue to grow and crowd one another for a short duration after the forest loses its self-supporting structure. Nevertheless, owing to the small thickness of this layer as compared to the forest height, its contribution in the total forest mass is believed to be negligible.
The abrupt termination of CNT forest growth is further demonstrated by quantifying the evolution of CNT forest height and alignment during growth. Figure 2A shows a schematic representation of our unique reactor configuration which enables in situ measurement of CNT forest height during growth, and acquisition of small-angle X-ray scattering (SAXS) patterns by positioning the synchrotron beam (by moving the reactor on a motorized stage) to pass through at a desired section of the forest. Scattering data were obtained during growth, by positioning the X-ray beam just above the interface between the CNT forest and the substrate; and after growth, by scanning the forest from bottom to top. The CNT alignment within a forest is quantified by calculating the Hermans orientation parameter \( H \):\(^{32} \)

\[
H = \frac{1}{2} (3 \langle \cos^2 \phi \rangle - 1) \tag{1}
\]

\[
\langle \cos^2 \phi \rangle = \frac{\int_0^{\pi/2} (I(\phi) \sin \phi \cos^2 \phi) \, d\phi}{\int_0^{\pi/2} (I(\phi) \sin \phi) \, d\phi} \tag{2}
\]

Here, \( \phi \) is the azimuthal angle, shown in the inset of Figure 2A. \( I(\phi) \) is the corresponding scattered intensity, measured at the radial location corresponding to the local maximum of intensity arising from form factor scattering of the CNTs.\(^{33} \) The morphological evolution was corroborated by scattering data taken both during and after growth, and data discussed below was taken by scanning the forests mounted in the reactor immediately after growth.

Figure 2B shows in situ measurements of the height evolution of a forest that self-terminates and of forests which are terminated prematurely by rapidly cooling the substrate or stopping the flow of \( \text{C}_2\text{H}_4/\text{H}_2 \) while maintaining the substrate temperature. As seen in Figure 2C, \( H \) increases sharply at the top of a forest, representing the transition from tangled to vertically aligned morphology during the first stage 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 morphological evolution indicated by the calculated \( H \) values, SEM images (Figure 2D) show that the self-terminated forest exhibits disorder at its base, yet the intentionally terminated forests exhibit strong alignment at the base. This demonstrates that the loss of alignment is a signature of growth self-termination, and is not caused by cooling the reactor or by an abrupt decrease in the carbon concentration in the CVD atmosphere, as demonstrated in Figure 2B. The \( \approx 100 \mu \text{m} \) height of the X-ray beamspot limits the spatial resolution of \( H \); therefore, the apparent thickness of the tangled crust is much larger than observed by SEM imaging, and the rate of decline in alignment during the decay and termination stages is more rapid than determined by SAXS mapping.

While measurements of the CNT forest height versus time have previously been used as a direct estimate of the reaction rate,\(^{34-36} \) measuring the time evolution of CNT forest mass provides a needed complement to the forest height data in revealing the true growth kinetics. Figure 3A 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 \( \times \) 5 mm\(^2 \) area), all grown in the same position along the length of the tube furnace, 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. Significant amorphous carbon accumulates\(^{37} \) on the CNT sidewalls when the sample is left in the furnace for a long duration after growth termination; however, before termination, amorphous carbon accumulation is an insignificant fraction of the measured mass and therefore does not affect the kinetics. This is shown by thermogravimetric analysis (TGA) of CNT forests grown in the same hot-walled reactor, which we have reported in another publication.\(^{38} \)

The faster rate of height increase, as compared to mass increase during the later stage of growth, indicates that the number density of CNTs growing at the substrate begins to decrease long before termination occurs. The time evolution of the CNT number density during growth is shown in Figure 3B.
and is estimated by first calculating the differential change in the mass density between forests grown for slightly different durations. From this differential mass density, the CNT number density is calculated as

\[ \rho_n = \frac{\rho_m}{\pi \left( \frac{d_o^2}{4} - \frac{d_i^2}{4} \right)} \]  

(4)

For this calculation, we consider the CNTs to be continuous straight hollow cylinders of graphite (\( \rho = 2.2 \text{ g/cm}^3 \)), having outer diameter \( d_o = 11 \text{ nm} \), and inner diameter \( d_i = 6 \text{ nm} \). The diameters are measured by fitting the SAXS patterns with a form factor model for a lognormally distributed population of hollow cylinders, and this method agrees closely with TEM diameter measurements in our previous work.33,38 A ratio of 0.6 between the inner and outer diameter of the CNTs appropriately fits the scattering data and agrees with TEM analysis. Using SAXS to map the CNT diameter versus vertical position in these forests suggests that the CNT diameter may change only by 5–10% during growth (Figure S3). Therefore, our assumption of constant CNT diameter along the forest height does not significantly affect the number density calculations. Clearly, 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.39

The analysis of the time evolution of forest density allows us to elucidate the proposed stages of the collective growth mechanism, as indicated in Figure 3. Steady growth (stage II) occurs when the differential mass density remains essentially constant (\( \approx 24 \mu g/mm^3 \)) with growth time, and this lasts for \( \approx 15 \text{ min} \). Then, the density decays (stage III) sharply by nearly an order of magnitude (\( \approx 3 \mu g/mm^3 \)). Termination (stage IV) occurs 10–15 min later (\( t = 25 \text{ min} \)), when the forest height abruptly stops increasing. CNT forests grown for different durations in a tube furnace were also mapped by SAXS after growth, and the resulting trends of Hermans orientation parameter are shown in Figure 4. This corroborates the emergence, stabilization, and decay of CNT alignment that is also observed in Figure 2C, suggesting that the collective growth mechanism applies to both “hot wall” and “cold wall” CVD systems. Further, even considering that the X-ray beam height is \( \approx 100 \mu m \) compared to the maximum forest height of \( \approx 600 \mu m \), it is apparent that the CNT alignment decays gradually before suddenly transitioning to a random morphology when growth self-terminates.

Raman spectroscopy, shown in Figure S4, was used to compare the quality of CNT forests grown for different times. The slight variation in the G/D ratio obtained from sample to sample suggests that the quality of CNTs does not deteriorate significantly throughout the growth process. Nevertheless, a slight decrease in G/D ratio was observed within each sample when scanning from top to bottom. This may be caused by the accumulation of defects in CNTs prior to their individual growth termination or may be an effect of the increasing tortuosity of CNTs as the number density decays. Further understanding of this behavior is beyond the scope of this paper, and this is a subject of ongoing study.

Our experiments demonstrate that the decay of the number density of growing CNTs within the forest eventually renders the forest incapable of sustaining a self-supporting morphology, and that abrupt termination of growth occurs when the CNT number density at the base of the forest drops below a critical value. This behavior is captured analytically using a finite element model (ABAQUS), which enables us to study the dependence of self-supporting CNT–CNT interactions on the

![Figure 3](image-url) Ex situ measurements of the time evolution (A) forest mass and height, and (B) differential mass density and CNT number density, for samples grown in a conventional “hot wall” tube furnace.

![Figure 4](image-url) Time evolution of Hermans orientation parameter for forests grown for different durations in a “hot wall” tube furnace.
spacing between CNTs within the forest. We consider a
simplified two-dimensional case where a pair of CNTs that lie
in the same plane (Figure 5A), are modeled as hollow cylinders
(d, = 6 nm, d, = 10 nm, E = 1 TPa, ν = 0.3) fixed to a rigid
top panel and pinned to a bottom substrate. We believe this
simplification is justified by the presence of the attractive van
der Waal’s potential between CNTs, which is expected to draw
CNTs together when they are in proximity. To simulate the
deforation of this two-CNT system, we first perform an
eigenvalue analysis to determine the shape of the first buckling
mode of an individual CNT and then impose the buckled shape
as the starting condition for each CNT in the two-CNT system.
Then, the two-CNT system is deformed by applying a downward
pressure to the top panel, which is restricted to move only in
the vertical direction. The initial buckled shape guarantees that
the two CNTs will deform toward each other and is representa-
tive of the actual case where CNTs are inherently tortuous and
thus will not behave as perfect columns.

An effective modulus of the two-CNT system is defined as
K = σεt, where σ = F/2ad is the force per unit area (pressure)
acting on the top panel, where d is the inter-CNT spacing, and
ε = δ/h is the ratio of displacement (δ) divided by the initial
length (h) of the CNTs. By changing the distance between the
pair of CNTs in this simple postbuckling mechanical model,
we study how the effective modulus of a CNT forest depends
on the number of CNTs per unit area (areal density), as shown
in Figure 5B. In a sparse arrangement, CNTs do not contact
each other, and consequently, stiffness increases linearly with
number density. This linear increase proceeds until a critical
value of ≈8 × 10^8 CNTs/cm^2, at which point the CNTs contact
after deformation, resulting in a nonlinear increase in K with
increasing number density. This critical value, noted by a vertical
line in Figure 5B, is believed to correspond to the threshold
CNT number density needed to maintain a self-supporting
structure. This is close to the value of ≈1.7 × 10^9 CNTs/cm^2
measured in our experiments at the transition between density
decay (stage III) and termination (stage IV) and may also
represent the threshold density^40 needed to form the self-
supporting forest structure at the start of the growth process.
As the number density increases beyond the threshold, the
consequent deformation needed to establish contact between
neighboring CNTs decreases. Therefore, the alignment of a CNT
forest decreases gradually as the number decays before reaching
the threshold for self-termination. Although this model simplifies
the true structure of a CNT forest, which contains isolated CNTs
and bundles, the qualitative insights complement the experi-
mental observations that CNT forest number density and
alignment are coupled and that CNT–CNT contact creates
essential mechanical reinforcement. Further details and results
from the model are in the Supporting Information.

Previous investigations of the time evolution of CNT forest
height have concluded that, depending on the reaction condi-
tions, the growth rate may be limited by the reaction rate at the
catalyst or by diffusion of the carbon precursor to the catalyst.34
In the former case, the forest height is linear with time,35 and
in the latter case, quadratic decay (h ≈ t^{1/2}) is observed.36 Our
investigation shows that these kinetic models may be appropriate
for the steady growth stage, as indicated by the fits to our real
time height data (Figure 2B); however, these models predict
that forest growth will proceed beyond the abrupt halt that is
observed in the real time data and therefore do not address the
termination mechanism. Further, the rate of mass accumulation
is a more direct measure of the reaction rate and therefore is
a necessary complement to the CNT forest height in understanding
the growth kinetics. Because the rate of mass increase begins
to decay while the rate of height increase remains constant, it
is evident that some CNTs stop growing individually before
the forest height stops increasing. Meanwhile, the forest height
rises in an undisturbed fashion as a result of the growth of the
remaining population that has not terminated yet.

Recent attention has focused on the use of oxygen-containing
carbon precursors and additives to increase the catalyst activity
and possibly extend the lifetime of CNT forest growth. It has
been demonstrated that presence of water vapor in the growth
atmosphere can slow Ostwald ripening of Fe by hydroxylation
of the alumina support.41 Studies of water-assisted16,42 CVD
proposed that the rate of forest height increase decays expo-
entially due to gradual catalyst poisoning.43 or that forest
growth stops abruptly when the catalyst is overcoated with
amorphous carbon,4 even though a small (∼100 ppm) water
concentration in the CVD ambient can enhance the catalyst
lifetime by etching amorphous carbon from the catalyst
surface.44,45 Further, past studies considered the behavior of an
individual CNT as representing the kinetic behavior of the forest.
It was also shown that the mass of a forest grown by water-
assisted CVD evolved linearly with growth time,46 yet this study
only addressed the steady growth stage. We have found that
adding a small concentration of ethanol to our C_2H_4/H_2/He
atmosphere prolongs the catalyst lifetime to over 60 min;47
however, SAXS mapping demonstrates that the alignment
decays in a similar fashion to the forests grown without added
ethanol. Therefore, we believe the density decay mechanism
governs collective termination even in the presence of oxygen-
containing additives.

We hypothesize that growth termination of an individual CNT
is governed by the lifetime of the catalyst particle, which
depends on its diameter, surface conditions, and other factors.
Chemical analysis performed on catalyst substrates after manual
delamination of CNT forests indicates that Fe diffuses through

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Figure 5. Finite element modeling of CNT buckling and pairwise
reinforcement: (A) dependence of the effective modulus on the areal
density of CNTs, with inset showing the model for a pair of CNTs;
(B) representative deformed configurations of pairs of CNTs.
the supporting Al$_2$O$_3$ layer and into the underlying SiO$_2$, and thus diffusion of Fe could be responsible for the observed density decay. This behavior may be affected by engineering the morphology (e.g., porosity) and thickness of the supporting Al$_2$O$_3$ layer. However, our ongoing work also demonstrates that the forest growth rate and catalyst lifetime (i.e., the duration before self-termination occurs) strongly depend on the hydrocarbon composition of the reactant atmosphere. Therefore, multiple factors may contribute to collective termination, and one factor may dominate under particular conditions. The same is likely true for the rate of decay in the number density of growing CNTs, which may differ considerably on the basis of the growth conditions (i.e., catalyst, carbon source, temperature). As an opposite limiting case, simultaneous growth termination with a loss of CNT alignment has been observed in many recent studies using widely different CNT forest growth recipes.

Further, it was recently suggested that deactivation of an individual CNT causes buildup of mechanical stress in the forest due to coupling among the tubes at the tangled top layer and that the resulting force at the forest base eventually exceeds the driving chemical potential for the growth reaction, halting forest growth. While this mechanochemical termination mechanism may be possible, in our experiments the decay of the CNT population is gradual and that the role of CNT–CNT interactions in maintaining a self-supporting structure is essential for continued forest growth. Further, application of external compressive force to a growing forest can decrease the growth rate and cause significant defects in the CNTs themselves, yet the mechanical energy output of CNT growth in these experiments was orders of magnitude below the chemical energy of the C$_2$H$_4$ decomposition reaction. A decrease in the self-supporting CNT–CNT interactions as the number density decays, as verified by the finite element model, may also permit growth of more defective CNT structures under stresses present in the CNT forest, and this could accelerate the collective termination process.

Last, variation in the rate of density decay may underlie nonrepeatability of CNT forest height under identical growth times and conditions, which is widely discussed in this field but currently met with a lack of practical understanding. We find that the forest mass per unit area of substrate is far more repeatable in our process than the terminal forest height, suggesting that duration of the steady growth stage is far more repeatable than the duration of the density decay stage.

In conclusion, we propose a collective mechanism for the evolution and termination of CNT forest growth, which is supported experimentally by measurements of the time evolution of forest mass and height and mapping of the Hermans orientation parameter using synchrotron X-ray scattering. We present that forest growth consists of four stages: self-organization; steady growth with a constant CNT number density; decay with a decreasing number density; and abrupt termination, which is coincident with a loss of alignment at the base of the forest. Thus, termination is driven by a declining population density of CNTs, which deactivate individually yet must vitally support one another for collective growth to continue. The observed density decay would also considerably degrade the through-thickness properties of CNT forests, such as their electrical and thermal conductivity, and therefore, it is essential to consider the uniformity of forest density for future developments of these new materials. Our findings support previously unexplained observations of abrupt self-termination of SWNT and MWNT forest growth and may be generalized to further understand the collective growth mechanics of filamentary nanostructures. Thus, in situ monitoring of the CNT morphology and density during growth has the potential of providing a means for spotting the early indicators of a decay in the number density of growing CNTs. This information may be used to change the process parameters such as temperature, pressure, and the reaction environment to delay and/or eliminate growth termination.

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Supporting Information Available: Detailed CNT growth methods of both the “hot wall” reactor and the “cold wall” reactor, Raman spectroscopy analysis of CNTs grown for 5 and 30 min in the “hot wall” reactor, and spatial mapping of CNT diameter across the height of a sample that was grown for 20 min in the “hot wall” reactor; further description of the finite element models of CNT–CNT buckling and contact. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes