Population Growth Dynamics of Carbon Nanotubes

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ABSTRACT

Understanding the population growth behavior of filamentary nanostructures, such as carbon nanotubes (CNTs), is hampered by the lack of characterization techniques capable of probing statistical variations with high spatial resolution. We present a comprehensive methodology for studying the population growth dynamics of vertically aligned CNT forests, utilizing high-resolution spatial mapping of synchrotron X-ray scattering and attenuation, along with real-time height kinetics. We map the CNT alignment and dimensions within CNT forests, revealing broadening and focusing of size distributions during different stages of the process. Then, we calculate the number density and mass density of the CNT population versus time, which are true measures of the reaction kinetics. We find that the mass-based kinetics of a CNT population is accurately represented by the S-shaped Gompertz model of population growth, although the forest height and CNT length kinetics are essentially linear. Competition between catalyst activation and deactivation govern the rapid initial acceleration and slow decay of the CNT number density. The maximum CNT density (i.e., the overall catalyst activity) is limited by gas-phase reactions and catalyst-surface interactions, which collectively exhibit autocatalytic behavior. Thus, we propose a comprehensive picture of CNT population growth which combines both chemical and mechanical cooperation. Our findings are relevant to both bulk and substrate-based CNT synthesis methods and provide general insights into the self-assembly and collective growth of filamentary nanostructures.

KEYWORDS: carbon nanotubes · kinetics · filaments · X-ray · characterization · population · chemical vapor deposition · catalyst

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Received for review August 16, 2011 and accepted October 23, 2011.

Published online October 23, 2011
10.1021/nn203144f
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Highly uniform ensembles of monodisperse CNTs are needed for electrical interconnects,10–12 filters,13 gas sensors,14–16 and structural composites.17 Also, consistent morphology is required for post-synthesis processing such as the spinning of CNTs from forests into yarns and sheets,18,19 which was shown to depend on the CNT areal density and bundle organization within a forest.20

An accurate picture of the internal structure of CNT forests is also essential for understanding how to control the growth process to approach the ideal structure. In fact, the kinetic picture of how a population of CNTs evolves with time during synthesis is still largely incomplete. The CNTs within a forest nucleate from a population of catalyst nanoparticles having a distribution of sizes and shapes, whose morphology was shown to evolve during growth,21 resulting in a distribution of CNT sizes, and likely a polydispersity of growth rates. On the basis of our recent observation that the number and mass density of CNTs change during growth and considerably decay (by almost an order of magnitude) toward termination,1 the apparent forest height kinetics measured in situ22–28 or ex situ29–31 must be complemented by a measure of the mass kinetics. The discrepancy between forest height kinetics and mass kinetics further explains the abruptness of forest growth self-termination,1 which we25 and others27,32–36 have observed.

Several in situ and ex situ methods for nondestructively measuring CNT forest height have been developed, such as optical photography and videography,24,27 optical interference,23 single-slit laser diffraction,37 time-resolved reflectivity,23 and cycling of growth conditions to form marks that are visible in electron microscopy.30,31,38 Methods of accurate and nondestructive mass measurements are fewer and generally use a microbalance either in situ39 or ex situ,40 which is limited by the resolution of the balance and cannot be used for spatial mapping. Alternatively, the changes in contrast from ex situ Z-contrast transmission electron microscopy (Z-STEM) images, as well as changes in the estimated effective extinction coefficient from time-resolved optical reflectivity (TRR), were used to infer information about CNT forest density.41 Although these methods can be used for spatial profiling, they can only provide relative measures of density and cannot give absolute density values.

In addition, in situ Raman spectroscopy has been used to infer CNT growth kinetics from real-time monitoring of the area under the G-band.42–45 Because the CNT–laser coupling strength depends on the structure, diameter, and number of walls of a CNT, it is unlikely that the G-band intensity is directly proportional to the total mass of a polydisperse CNT population.46 For both single-wall (SWNT) and multiwall (MWNTs) CNTs, the line shape of the G-band is a superposition of multiple peaks which depend on the CNT chirality, conductivity, and charge transfer with the surroundings.46,47 Further, for a typical millimeter-sized CNT forest, Raman spectroscopy cannot be reliably used to get population measurements because the laser beam cannot fully penetrate the forest. The presence of non-CNT graphitic deposits can also contribute to the G-band intensity. Hence, Raman studies require either a single CNT or a relatively limited number thereof to give relative mass measurements and require small diameter SWNTs to give structural information about size and chirality.

We previously showed how small-angle X-ray scattering (SAXS)48,49 and ultra-small-angle X-ray scattering (USAXS)50 can provide precise measurements of the diameter, bundle size, and alignment of CNTs within a forest. Here we present a comprehensive nondestructive characterization methodology for CNT materials, which enables identification of the population kinetics of the CNT growth process. This method combines high-resolution spatially resolved X-ray scattering and intensity attenuation measurements after growth, with real-time measurements of CNT forest height during growth. The spatial and temporal evolution of the mass density, number density, and cumulative CNT areal density are analyzed with unprecedented accuracy from the initial CNT self-organization stage until growth termination. On the basis of these findings, we can explain growth of a CNT forest as a time-varying population. This population behavior results from a statistical ensemble of individual particles and CNTs having polydisperse reaction behavior, contrasting previous studies that explained CNT forest growth kinetics based on models for a single particle and/or CNTs.23,32,51,52 Population growth models indicate that CNT synthesis exhibits an autocatalytic and cooperative nature, and that the maximum density of CNTs is limited by the process conditions. Finally, surface analysis of the catalyst gives insight into how competition between catalytic activation and deactivation rates prevent indefinite growth of CNTs using current CVD methods.

RESULTS AND DISCUSSION

Our methodology for CNT population analysis begins with high-resolution spatial mapping of the forest using synchrotron X-ray scattering. We place an already-grown CNT forest (Figure S1 in Supporting Information) on a motorized stage in the beampath of a synchrotron X-ray beam that is focused using monocular optics, as shown in Figure 1A. By scanning the forest from top to bottom at increments of 10 μm, which is approximately equal to the beam size, we discretize the forest into a stack of differential volumes that we refer to as “slices”. Two different types of data are acquired for each slice: (1) X-ray scattering patterns, collected using a 2D area detector; and (2) X-ray intensity, collected using detectors placed upstream and downstream of the CNT forest. We also measure
the CNT forest height versus time in situ during growth (see Methods section). Both the in situ and ex situ data are inputs to the quantitative analysis procedure shown in Figure 1B.

First, we use the measurements of X-ray intensity to calculate the local mass density of the CNT forest within the beampath, according to the Beer–Lambert–Bouguer law. This relates the density of a material to the X-ray intensity attenuation due to both scattering and absorption, such that

$$\rho_m(z_l) = \frac{\ln \left( \frac{i_0}{i} \right)}{t \left( \frac{\mu}{\rho} \right)} \quad (1)$$

Here $\rho_m(z_l)$ is the local mass density obtained from each forest slice (index $l$), defined as the mass of CNTs in each slice $(dm)$ per unit volume $(dv = t \times w \times dz)$; $z$ is the distance from the top of the forest to the forest slice; $t$ is the CNT forest depth in the direction of the X-ray beam; $i_0$ is the X-ray intensity upstream of the CNT forest; $i$ is the X-ray intensity downstream of the CNT forest; and $\mu/\rho$ is the total mass attenuation coefficient. The index is counted starting at the top of the forest, that is, for a 2 mm forest, $i = 200$ at the base.

The Beer–Lambert–Bouguer law is applicable for a homogeneous medium. This assumption is valid for the CNT forest because the waviness of the CNTs is on a much smaller length scale than the beam, and the variations in morphology (discussed later) occur over a much larger length scale. Throughout our analysis, we also assume that the forest is homogeneous in the X–Y plane, that is, along the direction of the X-ray beam, which we have validated in previous work.

For X-rays with energies below 20 keV, absorption is the primary contribution to X-ray attenuation, compared to both elastic and inelastic scattering. Hence, using the absorption mass attenuation coefficient instead of the total mass attenuation coefficient would have only resulted in a small error in the density calculation. Further, because there is only a small amount of absorption compared to the overall X-ray intensity (i.e., $i_0 \approx i$), noise in the measurements leads to an apparent fluctuation in the calculated vertical profile of density. We estimate that the signal-to-noise ratio (SNR) of density measurements is equal to $\approx 2$. The SNR is calculated as the ratio between the mean and the standard deviation (Figure S2D). Nevertheless, due to the high spatial resolution of our mapping technique, this noise is inconsequential when the local...
density measurements are integrated as discussed later.

Using the mass density \( \rho_m(z) \) of each slice with known thickness (\( \Delta z = 10 \mu m \)) and relating the slice mass (\( m_i \)) to the unit cross forest sectional area (\( a = t \times w \)), we calculate the areal mass density of each slice

\[
m_a(z_i) = \rho_m(z_i) \Delta z \quad (2)
\]

Next the cumulative areal density (\( m_{ac} \), total CNT mass per unit area) versus position in the forest is calculated by summing the areal density of all slices

\[
m_{ac}(z_i) = \sum_{i=0}^{z_i} m_a(z_i) \Delta z \quad (3)
\]

The areal mass density per slice represents how much CNT mass was created for that specific 10 \( \mu m \) of the forest, and the cumulative areal density represents the mass of the CNT forest above (and including) the indexed slice.

We performed X-ray mapping of tall CNT forests (up to 2 mm) grown in both cold-wall (heated substrate, Absolute Nano SabreTube) and hot-wall (heated tube, Thermo-Fisher MiniMite) systems (Figure S1). Each forest was discretized into up to 200 slices with 10 \( \mu m \) thickness by scanning the X-ray beam vertically, as shown in Figure 2A,B. The mass density varies throughout the forest (Figure 2C,D): it increases in a closely linear trend from the top surface (“crust”) of the forest until it reaches a maximum and brief plateau, then it decays gradually toward the bottom of the forest. The formation of a tangled crust at the start of growth is well-known; however, this density map reveals, for the first time, a subsequent “crowding” stage where the CNT density increases substantially as new CNTs begin to grow even long after the forest self-organizes and starts to thrust upward. The distance of this density increase (\( \approx 300 \mu m \)) is significantly larger than the non-uniformity of the top surface of the forest (Figure 2A,B), which we estimate to be less than 100 \( \mu m \) (Figure S3), and larger than any errors expected from sample tilt or beam divergence, which we estimate to be less than 50 \( \mu m \) (Figure S2B). Also, the employed alignment procedure (Figure S4), utilizing X-ray intensity scans ensures that the sample tilt (about y-axis) is within \( \approx 0.01^\circ \) of the substrate plane. Hence, the slope of the density increase predominately represents the kinetics of the crowding stage, that is, the rate at which new CNTs begin growing from catalyst particles that were inactive during the self-organization stage. Even considering the non-uniformity of the top surface and the beam divergence, the measured CNT density increase during crowding would be at least 5-fold.

We also observe that the kinetics of crowding depends on the process conditions, suggesting that the rate of crowding and the maximum density represent the efficiency of CNT nucleation from the population of catalyst particles on the substrate. For instance, as can be seen by comparing Figure 2C,D, the slope of CNT density increase for the sample grown in a hot-wall reactor is approximately twice that of the sample grown in a cold-wall reactor. We attribute this to the different process parameters used in the two systems, which are documented in Figure S1 (Supporting Information). Both samples were annealed at 775 °C in H\(_2\)/He; however, the rate of heating and duration of annealing in the cold-wall system was much shorter than that in the hot-wall system. A long annealing duration may be necessary for catalyst nanoparticles to be fully reduced from a higher oxide state (Fe\(^{2+}\) or Fe\(^{3+}\)) to a lower one (Fe\(^{3+}\) or Fe\(^0\)) in order to become active.\(^{55,56}\) This could also explain why the hot-wall
sample has a higher maximum density, indicating that a larger fraction of the catalyst nanoparticles becomes active for CNT growth.

After the maximum density is reached, the density remains approximately constant at this value for a small (∼300 μm or less) portion of the forest (<20% of the forest height). Hence, only a small portion of the forest is truly uniform, and this observation may highlight the general difficulty of producing highly uniform and tall CNT ensembles even though many CVD methods of growing millimeter-scale CNT forests have assumed overall uniformity. Then, after the brief steady growth stage, the density decays due to accumulated deactivation of individual catalyst particles and proceeds until eventual self-termination. The shape and/ or the slope of the decay also depends on the growth conditions, representing variability in the catalyst deactivation kinetics. Nevertheless, a universal observation in all samples we have tested is that both the initial density at the top of the forest (including the crust) and the final density are approximately 1 order of magnitude below the maximum density. Thus, the same critical CNT density forms the self-supporting structure that enables “lift-off” of the CNT forest and causes collective self-termination at the end of the growth process.

The spatial evolution of the cumulative areal mass density (mg/cm²) is also shown in Figure 2. The last point on this curve corresponds to the bottom of the forest and therefore represents the total areal density of the sample. For the cold-wall forest, we compare this value to a direct measurement of the CNT forest mass which was measured using a microbalance. We therefore confirm that the calculated density value based on X-ray mass attenuation is very close to the true density. Using thermogravimetric analysis (TGA), shown in Figure S5, we find that the contribution of amorphous carbon and any other low evaporation temperature carbonaceous impurities is limited to about 10% of the total mass of this sample (recipe in Figure S1). Hence, the mass measurements are dominated by CNTs rather than carbonaceous impurities.

The cumulative areal density follows an S-shaped curve with increasing distance from the top crust. This shape is explained by the spatial evolution of local mass density along the forest height. The initial acceleration (concave up region) in the cumulative areal density results from the newly identified crowding stage, and the deceleration (concave down region) results from the density decay stage. The intermediate steady growth stage results in an approximately linear relationship between total mass and vertical position.

Now, we proceed to analyze the population dynamics within the forest based on spatial mapping of the CNT diameter and alignment. This information is necessary to build a comprehensive picture of the forest internal structure and is needed to calculate the evolution of CNT number density. Then, these results are combined with real-time height kinetics to calculate the time evolution of forest mass and density. Because real-time height kinetics can only be measured during growth in the cold-wall system, the remainder of analysis in this paper uses results from the cold-wall growth process.

Although transmission electron microscopy (TEM) has been customarily used for measuring CNT diameters and number of walls,5,6 it is painstaking to obtain reliable descriptive statistics from measurements of a limited number of CNTs, compared to the inherent ability of SAXS to probe at least 10⁶ CNTs in the beampath. It is also perhaps impossible to do accurate spatial profiling of size distributions using TEM at the high spatial resolution (10 μm) enabled by the capillary optics used with our SAXS setup. Analysis of the radial breathing modes (RBM) using two-wave-length in situ Raman spectroscopy has been used to obtain the diameter distribution of single-walled CNTs (SWNTs),57 however, this is only suitable for SWNTs, or double-wall CNTs (DWNTs), within an incomplete diameter range, and it requires that the CNTs be resonant with the incident laser energy. On the other hand, X-ray scattering methods inherently enable characterization of any CNT based on its dimensions.

Hence, we use the X-ray scattering 2D image collected on the area detector (Figure 1A) to map the CNT size distribution by fitting the peak (or shoulder) observed in a linescan with a mathematical form factor model for hollow cylinders28,48,49 having a log-normal distribution of diameters (Figure S6). Figure 3A shows the SAXS I–q profiles along with model fits for forest slices selected every 0.1 mm throughout the forest height. This model-fitting procedure is repeated for each of the 156 slices (images) for the studied forest, resulting in a spatial map with unprecedented resolution compared to previous studies of CNT forest morphology.1,5,6,28,49,58 Because of the large number of images, we developed an automated algorithm for choosing the fitting range based on the key features of the linescan, as described in Figure S7. The blue marks in Figure 3A indicate the lower and upper limits for the fitting range and the peak (shoulder) position determined using this algorithm. A trend of decreasing CNT outer diameter (CNT OD) can be inferred from the position of the peak (or a shoulder in cases in which there is no well-defined peak) relative to the inverse space parameter q because the peak (or shoulder) position correlates inversely with CNT diameter. The peak moves from q ≈ 0.75 to 0.9 nm⁻¹ (≈20% increase) from top to bottom of the forest.

As seen in Figure 3, the mathematical model provides excellent fits to the scattering data, throughout the forest. The probability density functions (PDFs) of CNT OD distribution for each forest slice are laid together in Figure 3B, along with the normalized histogram of CNT OD measurements collected using
TEM. There is a good agreement between the diameter values as well as the PDF obtained from SAXS fitting with TEM measurements, validating the accuracy of the SAXS measurement technique. The inset to Figure 3B shows a TEM micrograph of a representative CNT with six walls. The smoothness of the spatial trends of CNT dimensions and their variance highlights the precision of our technique because the mathematical model fit produces a highly confident and accurate result for each slice. Also, the resolution of size measurement is effectively atomic because a scattering model is based on the coherent elastic interactions between X-rays and carbon atoms forming the CNTs. Due to the large number of scatterers (atoms of more than 10^6 CNTs) in the beampath through the CNT forest, high confidence descriptive statistics are obtained.

As shown in Figure 3C, the mode of CNT OD shifts from 9.7 to 8.1 nm as growth proceeds (from top to bottom of the forest), which is a 16.5% decrease, and the arithmetic mean shifts from 12.9 to 10.8 nm, which is a 16.3% decrease. The difference between the mode and arithmetic mean highlights the skewness of the log-normal distribution of the CNT population throughout the forest.

In spite of the overall decay in CNT diameter during growth, we find that both the CNT OD and its coefficient of variation (CV) are constant during the crowding stage when the CNT number density increases to the maximum. This shows that the density increase represents an increasing population of active (i.e., CNT-bearing) catalyst particles with an invariant diameter distribution. In other words, there is no preferential nucleation of smaller or larger diameter CNTs within the population under the tested growth conditions (Figure S1). After the crowding stage, the CNT OD decreases until growth stops, and the CV decreases until the onset of the termination stage at which time the CV increases rapidly until growth stops. During the termination stage, the corresponding lowest part (base) of the forest exhibits significant broadening of the diameter distribution. This broadening, along with a continued decrease of the mode and mean OD, may suggest that growth of larger diameter CNTs is halted more abruptly during collective termination. Although the forest height abruptly stops increasing when the CNT density drops below the critical threshold, smaller diameter CNTs may continue to grow and attempt to...
push up into the forest. This can also explain the shifts in the OD and CV values in the termination region.

Another parameter of the CNT scattering model is the diametral ratio (\(c = \text{ID}/\text{OD}\)), which is the ratio between the average inner diameter (ID) and outer diameter (OD). This enables calculation of the average number of CNT walls \((n_{\text{wall}})\), shown in Figure 3D. The number of walls is unchanged during crowding, then decreases from \(\approx 7\) to \(5\) walls during density decay and remains fairly constant through the termination stage as a result of the decay in both the CNT OD and the diametral ratio (c). These changes can perhaps be linked to the morphological evolution of the catalyst nanoparticles, which is discussed later.4,60

Now, the CNT number density profile (i.e., the total number of CNTs at each vertical position) can be calculated by combining the profiles of areal mass density and the measured CNT dimensions. However, owing to the skewness of the log-normal distributions, a single value OD (mean or mode) cannot be used in this calculation; that is, the average CNT mass of a skewed population is not equal to the mass of CNTs having the average diameter. Hence, the entire PDF must be used to assign the proportion of the population that belongs to a specific narrow bin of diameters, and we must also correct for the CNT tortuosity by calculating the corrected CNT length from alignment and height data for each slice.

Accordingly, the CNT OD range of 5–40 nm is divided up into small diameter bins of width \(\Delta D_{\text{bin}} = 0.5\) nm. Now, the ratio between the number of CNTs within each bin \(N(D_i)\) centered at the outer diameter \(D_o\) and the total number of CNTs \((N)\) within each forest slice is calculated from the PDF of each slice \(i\)

\[
\left(\frac{N(D_i)}{N}\right) = \frac{1}{D_o - D_{\text{bin}}/2} \int_{D_o - \Delta D_{\text{bin}}/2}^{D_o + \Delta D_{\text{bin}}/2} \text{PDF}_{D_{\text{OD}}} dD
\]

(4)

To accurately calculate the total volume of the tortuous CNTs within each slice and therefore calculate the mass, we must know the actual CNT length rather than just the height of the slice. So, we calculate a height-to-length transformation factor based on the CNT alignment within each slice. To quantify the CNT alignment, we use the orientation parameter \(f(z)\) calculated from azimuthal scans at the \(q\) location of maximum intensity1,3,48,49,61

\[
f(z_i) = \frac{1}{2} \left(3 \cos^2 \phi_i - 1\right)
\]

(5)

where

\[
\langle \cos^2 \phi_i \rangle = \int_0^{\pi/2} \int_0^{\pi/2} l(r) \sin \phi \cos^2 \phi d\phi d\phi = \int_0^{\pi/2} \int_0^{\pi/2} l(r) \sin \phi d\phi d\phi
\]

(6)

Here, \(\phi\) is the angle between the CNT direction and the z-axis direction, and \(l(r)\) is the azimuthal intensity distribution of scattered X-rays from the SAXS image of slice \(i\).

A transformation factor \((\Lambda)\) is then calculated to convert the apparent forest height (slice thickness \(\Delta z\)) to the average CNT length \((\Delta l)\) within that slice3

\[
\Delta l(z_i) = \Lambda(z) \Delta z
\]

(7)

where

\[
\Lambda(z) = \left(\frac{3}{2f(z) + 1}\right)^{1/2}
\]

(8)

Now, we can calculate the total number of CNTs within each slice \((N)\) by dividing the previously calculated (eq 2) mass of each slice \((m_i)\) by the weighted average mass of a CNT \((m_{\text{CNT}})\) of the population based on the obtained PDF of CNT OD distribution and using the corrected average CNT length \((\Delta l)\) in each slice. This follows as

\[
N(z_i) = \frac{m_i(z)}{m_{\text{CNT}}(z_i)}
\]

(9)

where

\[
m_{\text{CNT}}(z_i) = \rho_g \Delta l(z_i) \sum_{D_\text{OD}=5nm}^{D_\text{OD}=40nm} \left(\frac{N(D_i)}{N}\right) \pi D_\text{OD}^2 (1 - c(z_i)^2)
\]

(10)

The bulk density is taken as the value for graphite, \(\rho_g = 2.2\) g/cm\(^3\).

The orientation parameter \(f(z)\) and the height-to-length transformation factor are shown in Figure 4A. The tangled top “crust” layer is typically no more than a few micrometers thick; however, the first points of the X-ray map are affected by non-uniformity in the top surface of the forest. As a result, there is an apparent slight decrease of the orientation parameter at the top of the map, until the beam has passed through the non-uniform region. After this, the orientation parameter increases to a maximum at the end of the steady growth stage, then decreases gradually through the density decay stage, and then decreases rapidly during the termination stage. The transformation factor varies inversely (eq 8) with the orientation parameter and therefore is greatest at the top and bottom of the forest.

We can now derive the profile of CNT number density versus position, which is shown in Figure 4B. The number density increases during crowding, reaching a maximum of \(\approx 9 \times 10^9\) CNTs/cm\(^2\), and then decays. The maximum is about an order of magnitude higher than the initial density and then decreases by about an order of magnitude before termination. Compared to the mass density profile (Figure 2C), the number density profile is curvier and less steep due to the diameter change and the tortuosity correction of CNT length. In spite of the noise in the X-ray density measurements, we suggest that the beginning and ending CNT number density values represent the critical value for the self-supporting structure. The
horizontal red line marks the estimated threshold value (≈10^9 CNTs/cm²) based on a finite element model of postbuckling behavior of CNTs in contact.1

Combining these spatial mapping results with the real-time forest height measurements (dz/dt) obtained in situ during growth, we determine the time evolution of CNT length, number density, and, more importantly, cumulative areal density (mass per unit area). The lengthening kinetics \( l(t) \), the cumulative areal density kinetics \( m_\omega(t) \), and the total number density kinetics \( N(t) \) are calculated

\[
\begin{align*}
    l(t) &= \int_{0}^{t} \omega \left( \frac{dz}{dt} \right) dt \quad (11) \\
    m_\omega(t) &= \int_{0}^{t} \frac{dm_a}{dz} \left( \frac{dz}{dt} \right) dt \quad (12) \\
    \frac{dN(t)}{dt} &= \left( \frac{dN(z)}{dz} \right) \left( \frac{dz}{dt} \right) \quad (13)
\end{align*}
\]

In Figure 5, the CNT lengthening kinetics is compared to the height kinetics, showing that the measurements of apparent forest height significantly underestimate the actual CNT length. Owing to the initial increase followed by a decrease in the orientation parameter across the forest, the slightly sublinear curvature of the apparent height kinetics becomes more linear when transformed into true CNT length.3 Nevertheless, the evolution of forest mass is a more accurate measure of reaction kinetics, as it directly represents the rate at which carbon is incorporated in the growing CNT population. Incidentally, we observe that, for the same growth conditions, the areal mass density of CNT forests (i.e., the total mg/cm²) is more repeatable than the forest height or the volume density (mg/cm³). In other words, for the same growth time, many grown forests may have a considerable variation in height, but the mass output of each experiment is more consistent (Figure S9).

Therefore, the culmination of our comprehensive analysis is a measure of the time evolution of the total cumulative areal density and the total CNT number density, shown in Figure 6. Due to the nearly linear height kinetics, both curves closely resemble the spatial profiles shown in Figures 2 and 4, and the total CNT forest mass versus time is an S-shaped curve. In addition, by processing atomic force microscopy (AFM) images, we calculate the mean number density of nanoparticles (Figure S10) on samples annealed according to the recipe in Figure S1 to be ≈8 × 10^10 particles/cm² (about 2 orders of magnitude higher than the CNT lift-off threshold ≈10^9 CNTs/cm², identified in Figures 4 and 5). As shown in Figure 6, this results in a calculated catalyst activity that increases from ≈1 to ≈11% at the maximum CNT density during the steady growth stage.

The significant spatial variations in CNT morphology during growth confirm that the apparent forest height depends on the interplay between CNT number density, diameter, stiffness, tortuosity, and possibly the hierarchal bundling structure. However, many previous
studies that have represented CNT growth kinetics by forest height, and less commonly by forest mass, have found an S-shaped growth curve. Some have identified its key features including an initial acceleration, an inflection point, and a deceleration that concludes in termination. In general, growth models for individual CNTs and CNT–particle systems have been used to interpret these stages. The initial acceleration has been explained by the presence of an incubation/induction stage, in which the processes of carburization of the catalyst particles and nucleation of CNTs were proposed to exhibit an autocatalytic nature. The final decelerating part was explained by catalyst deactivation kinetics based on various limiting mechanisms, such as catalyst poisoning, overcoating, evaporation, or diffusion. However, the noted discrepancy between CNT forest height and mass, along with the frequent reliance of sparse (i.e., ex situ) time points data to fit height kinetics to different kinetic models without obtaining representative statistics, highlights the importance of obtaining a population-based picture of the growth kinetics. An ideal model of CNT forest growth would therefore consider a distribution of individual growth behaviors and how these behaviors result in a drastic variation in CNT density throughout the growth process, which results in the observed true kinetic behavior of the population.

To obtain further insight about the S-shaped reaction kinetics, we investigated three known models that are ubiquitous to analysis of population growth in natural systems: the monomolecular model (eq 14), the autocatalytic model (eq 15), and the Gompertz model (eq 16)

\[
m_a(t) = \frac{\alpha}{1 + e^{-kt}} - \tau
\]  
\[
m_a(t) = \alpha e^t - e^{-e^{-e^{-kt}}}
\]  
\[
m_a(t) = \alpha e^t - e^{-e^{-kt}} - \tau
\]

In these models, \( \alpha \) is the asymptotic final cumulative mass of growth, \( k \) is a reaction rate, and \( \tau \) is the time origin.

We find that the Gompertz model is an excellent fit to the CNT mass kinetics in Figure 6 and compare all three fits in Figure S11. In fact, only the monomolecular (aka exponential decay) model was previously used to fit CNT growth data. While the monomolecular model fits the decay part of the cumulative mass kinetics, the model fails to fit the initial accelerating part because it does not have an inflection point. On the other hand, both the autocatalytic and Gompertz models are sigmoidal equations that have inflection points. Further, the autocatalytic curve is symmetric about the inflection point, while the Gompertz curve is asymmetric. Hence, the Gompertz model fits our data best because the different rates of acceleration (crowding) and deceleration (decay) can be accommodated by the asymmetry of the curve (Figure 5B). The Gompertz model has been extensively applied to population growth in animal systems and has been applied to tumor growth and bacterial growth. This analogy can give insights into possible competition among the population of growing CNTs because tumor growth involves a population of cells that grows in a confined space, with a limited supply of nutrients. While it is possible that catalyst deactivation and density decay in CNT forest growth analogously result from shortage of necessary growth precursors at the
The deactivation rate eventually supersedes the continuous activation rate that dominates during the initial crowding stage. The asymmetry around the inflection point, as well as the catalyst lifetime, may be controlled by changing the growth conditions, affecting this activation–deactivation competition. Thus, we explain that the ubiquitous growth-enhancing agents, such as water or ethanol, can result in high activation and deactivation of catalyst nanoparticles. For instance, the decomposition of hydrocarbon gas (C2H4 in our case) may be catalyzed by products or intermediates expelled from the dissociation reactions at the catalyst, even if they are unstable groups or short-lived free radicals. Thermal decomposition and rearrangement of C2H4 and H2 is a multistep chain of gas-phase reactions yielding a plurality of compounds, and in light of the sigmoid-shaped population kinetics, it is possible that some of these reactions manifest an autocatalytic nature and, depending on the product/compound, contribute to activation or deactivation of CNT growth. For instance, while alkynes have been specifically shown to accelerate CNT growth, PAHs (precursors to soot) are also generated in thermal CVD, and there are many other compounds that are apparently benign. CH2 was also identified as a possibly active species. Measurements of the time-varying concentrations of both reactants and products will give further insights into the chemical causes and effects of changes in the density of growing CNTs.

Regardless of the exact interplay or competition between these compounds and mechanisms, termination of CNT growth is currently inevitable because the deactivation rate eventually dominates. In fact, this deactivation has been attributed to various mechanisms that are consequential of the gas-phase chemistry such as catalyst poisoning, overcoating with amorphous carbon, or steric hindrance, indicating that manipulating the gas chemistry is an attractive route for controlling deactivation. Another universal observation from our work, as well as others, is that carbonaceous deposits on reactor walls from previous growth cycles can improve CNT nucleation and growth, possibly due to the presence of active species that desorb from the reactor wall surface when the furnace tube is heated.

CNT growth deactivation can also be influenced by morphological evolution of catalyst nanoparticles such as by migration and coarsening. In our system, we hypothesize that accumulating CNT deactivation is in large part due to evolution of the catalyst particles, especially atomic diffusion of the catalyst into and beyond the supporting alumina layer. Indeed, using ex situ X-ray photoelectron spectroscopy (XPS), as well as Rutherford backscattering spectroscopy (RBS) (results not shown), we observe significant diffusion of Fe catalyst into the substrate in samples that are processed in the hot-wall reactor. Figure 7A quantifies changes in the percentage of surface Fe after annealing and after growth (and delamination of the CNT forest), based on the area under the Fe2p peaks from survey scans (Figure S12). While the Fe concentration after growth and delamination can possibly be affected by

![Image](https://example.com/image.png)

**Figure 7.** XPS analysis of catalyst evolution during annealing and growth: (A) atomic concentration of surface Fe based on the areas under the peak of Fe2p peaks of the survey spectra (Figure S12) for three samples (as-deposited, after annealing, and after growth); (B) comparison of normalized Fe2p1/2 and Fe2p3/2 peaks for samples as-deposited, after annealing (10 min ramp-up to 775 °C and hold for 10 more min), and after growth (for 15 min at 775 °C) and CNT delamination. To calibrate binding energy values, these spectra were shifted by +3.2 eV based on the measured C1s peak location (Figure S13).
mechanical removal of some catalyst particles (i.e.,
attached to the CNTs), the significant loss of Fe after
annealing is evidence of catalyst diffusion through
subsurface layers because the annealing temperature
(775 °C) is not high enough to cause evaporation of the
Fe catalyst. Nevertheless, in this base growth process,
the catalyst nanoparticles are bound by strong interac-
tions between Fe and Al2O3,21,88 as demonstrated in
literature for similar growth systems by means of back-
scatter electron imaging that showed no traces of metal
particles on the top of grown CNT forests.32

Figure 7B is a superposition of the Fe2p spectral lines
for three different samples (as-deposited, after anneal-
ing, and after growth). All spectra were collected during
the same run and are plotted after applying a correction
factor for line positions in order to accurately compare
the binding energy values of spectral lines. A correction
factor of +3.2 eV is calculated based on the commonly
used value of 285 eV for the binding energy of the
ubiquitous C1s peak (Figure S13). Results show that
there is no significant change in the binding energy of the
Fe2p3/2 and Fe2p1/2 lines (2p3/2 peak remains at
about 711.7 eV), indicating that Fe is in essentially the
same oxidation state on all three samples. This is likely a
combination of F2+ and F3+ based on the corrected
binding energy values34,55,56,89 and the asymmetry of the
peaks. This can be attributed to the ambient oxygen
exposure90 after annealing and after growth which
results in oxidation of Fe even if it was reduced to
metallic Fe during the high-temperature process. Never-
theless, the appearance of a low binding energy Fe2p3/2
peak at 708.2 eV indicates that there is some metallic Fe
that did not oxidize upon exposure to atmosphere
because it is trapped beneath the surface. Notably,
after subsequent heating in a reducing environment of
H2/He, this peak becomes more significant, while after
heating in air, the peak completely disappears (results
not shown). Also, after heating in H2/He, there is no shift
in the C1s peak position (Figure S13), and we find
(Figure S12) that the carbon signal decays while the
aluminum signal increases after growth. These observa-
tions indicate that the low binding energy 2p3/2 peak in
fact represents subsurface metallic Fe and not iron
carbide or Fe particles encapsulated with graphitic
carbon. Because XPS penetrates only a few nanometers
into the sample, these findings can only prove the
diffusion of Fe to the near subsurface Al2O3 layer,
although we hypothesize that Fe could also diffuse to
the SiO2 layer.

On the basis of population analysis enabled by high-
resolution X-ray mapping and the observation of cat-
alyst migration into the substrate, we present a unified
picture of the successive stages of CNT forest growth in
Figure 8. This picture begins with the catalyst prepara-
tion stage by dewetting of a thin Fe film (1 nm thick) to
form nanoparticles. In separate work where we have
studied the dewetting process using in situ grazing
incidence X-ray scattering,87 we observe that the ki-
netics of particle formation is very fast; that is, the Fe
film dewets almost immediately when the tempera-
ture reaches a certain value during rapid heating. After
this, the particle size and shape are fairly stable by the
time the hydrocarbon gas is introduced.87 Hence, the
crowding of CNTs during and after self-organization
occurs over a much longer time scale than particle
formation. Also, as can be seen in Figure 3, the CNT
diameter distribution does not change during crowd-
ing, indicating that catalyst size evolution is an even
longer time scale process. The finding that activation of
the catalyst population occurs at an increasing rate
evokes thoughts of popcorn (CNTs) popping from a
defined population of kernels (particles).91 The nuclea-
tion kinetics of the CNT population is likely dependent
on the hydrocarbon gas decomposition, surface
carotolysis, and other processes and may reflect an autocatalytic behavior.

After the brief steady growth stage that follows crowding, the CNT density decays gradually and for a long duration, resulting in at least an order of magnitude decrease in active population of CNT-bearing catalyst particles. The density decay is accompanied by a decrease in the average CNT diameter and a focusing of the diameter distribution. Finally, the collective termination stage is represented by a rapid loss of alignment and a widening in the CNT diameter distribution as discussed earlier. Collective termination occurs when the forest is no longer sufficiently dense to maintain a self-supporting structure, although it is likely that some CNTs continue to grow and push upward into the tangled base layer.59

In situ87 and ex situ84,92 studies showed that the average size of catalyst nanoparticles increases with successive exposure to a hydrogen atmosphere, presumably due to Ostwald ripening. Hence, there is a discrepancy between the evolution of catalyst size (increases) and the evolution of CNT size (decreases). We have also noticed in repeated growth experiments (i.e., growth, delamination, growth) from the same catalyst-coated substrate that the CNT forests have larger diameter and lower mass density in subsequent growth cycles. A possible explanation for the decreasing average CNT diameter within a single growth cycle is that larger diameter CNTs stop growing first; that is, smaller CNTs have a longer catalyst lifetime. A further important point is that not all catalyst particles grow CNTs, and in fact, only a small fraction of the catalyst particles may be active depending on the annealing and growth conditions. The catalyst activity measurements shown in Figures 6 indicate that the maximum CNT number density is ≈11% of the catalyst particle number density (Figure S10).

Hence, we must consider that the size evolution of catalyst particles that bear CNTs may be considerably different than particles that do not bear CNTs. It is plausible that the presence of a CNT constrains particle migration and atomic diffusion of Fe, and therefore particles with CNTs could have a more stable size distribution than particles without CNTs. Therefore, the ripening of the overall particle population could be dominated by the large subpopulation of particles that do not bear CNTs. In the limiting case that CNT growth rate does not depend on diameter (which is unlikely based on our recent results), and that CNT-bearing particles do not evolve by Ostwald ripening, the decrease of average CNT diameter with continued growth could be driven solely by a decrease in catalyst size caused by diffusion of Fe atoms into the substrate. While it is widely accepted that the catalyst nanoparticle size determines the CNT diameter,62,93,94 there is no consensus on how an already nucleated CNT responds to size changes in the catalyst nanoparticle at its root, or how the presence of the CNT affects how the catalyst size changes. Indeed, the catalyst particle is highly dynamic under the thermal and mechanical conditions imposed by CNT growth,60,95 and further study is required to understand how to stabilize catalyst particles for longer durations and overcome the several competing mechanisms of CNT growth deactivation. Also, the distribution of growth behaviors presented by our complete CNT population implies that a particular set of time-invariant growth process parameters may be optimal for only a small subpopulation, whereas the collective growth behavior is dominated by the response of the remainder of the population to the resulting suboptimal process parameters.

CONCLUSION

Understanding the population growth dynamics of individual nanostructures such as CNTs is vital to engineer materials comprising assemblies of nanostructures and to develop accurate models of their scale-dependent properties. We presented a comprehensive methodology for studying the population growth dynamics of vertically aligned CNT forests, utilizing high-resolution spatial mapping of synchrotron X-ray scattering and attenuation, along with real-time height kinetics. This methodology enables non-destructive calculation of the spatiotemporal evolution of absolute CNT mass and number density as well as CNT dimensions (diameter and number of walls). After the CNT forest self-organizes, the density increases during a crowding stage, and then the density decays almost an order of magnitude before self-termination occurs. The S-shaped mass kinetics is accurately fitted with the asymmetric Gompertz model of population growth; hence, CNT synthesis is governed by competing rates of activation and deactivation and is eventually limited by competing effects of gas-phase chemistry and catalyst evolution. This comprehensive picture of CNT population growth combines both chemical and mechanical cooperation throughout five distinct stages: self-organization, crowding, steady growth, decay, and collective termination.

Although all of the X-ray data in this paper were obtained ex situ, the same technique can be applied in situ to enable real-time monitoring of population behavior, enabling the control of the outcome by tuning the process parameters in situ either in an open loop or a feedback closed loop system. Such dynamic growth recipes will enable synthesis of CNT forests with highly uniform density or prescribed density gradients and possibly overcome collective termination to enable growth of indefinitely long CNTs. The population-based picture of CNT synthesis can be extended to bulk CNT growth processes from powder catalysts that also represent nanoparticle populations and is vital for manufacturing uniform CNT
materials by postprocessing, such as spinning,\textsuperscript{20} rolling,\textsuperscript{12} and transfer printing,\textsuperscript{96} which are essential to integration of CNTs into functional materials and devices. Finally, our methodology and insights into the collective growth behavior of filaments can be generalized to study other systems of filamentary nanostructures including inorganic nanowires or biological filaments such as actin.\textsuperscript{97}

METHODS

Forests of vertically aligned CNTs are grown using either a hot-wall reactor (tube furnace) or a substrate-heated cold-wall reactor that is equipped with real-time height monitoring (see Figure S1 in Supporting Information). In both cases, custom labVIEW interfaces were used to control process variable, such as temperature and gas flow rates. For the cold-wall reactor, the substrate temperature was measured by an infrared sensor (Exergen 2ACF-K-HIE). Digital mass flow controllers (Aalborg GFC 17, response time = 2 s) were used to control and measure gas flow rates. Real-time forest height is measured using a noncontact laser displacement sensor (LK-G152, Keyence) which is mounted above the cold-wall reactor as described earlier.\textsuperscript{25,26} The substrate is a multilayer catalyst thin film (1 nm Fe/10 nm Al\textsubscript{2}O\textsubscript{3}/300 nm SiO\textsubscript{2}) deposited by e-beam evaporation at room temperature on the substrate-bound catalyst for diameter distribution as well as for the ratio of each scan and determine an approximate location of the peak, as described in Figure S7. The peak, as described in Figure S7. The peak based on the locations of the inflection points above the peak, as described in Figure S7. The fitting code used an iterative approach in searching for the best fit within this selected fitting range. By including the low q part of the data, a good fit was achieved that selects a probability density function (PDF) for diameter distribution as well as for the ratio \( l = ID/OD\), where \( ID\) is the inner diameter of the multiwalled CNT and \( OD\) is the outer diameter of the multilwalled CNT (see Figure S8).

X-ray photoelectron spectroscopy (XPS) was carried out at room temperature on the substrate-bound catalyst for \( \approx 5 \times 5 \) mm samples. In all cases, samples were exposed to the atmosphere before putting them in the high-vacuum XPS chamber. A Kratos Axis Ultra X-ray photoelectron spectrometer was used with a monochromatic X-ray source (Al K\( \alpha\) X-ray radiation). The pass energy of the analyzer is 160 eV for the survey scans and 20 eV for the core scans. An anode voltage was set to 15 kV, and emission current to 6 mA (X-ray power \( \approx 90 \) W). CasaXPS software (version 2.3.14) was used to process the spectra. All samples were placed together on the same sample holder, and spectra were collected back-to-back during the same run for comparative purposes (Figure S12). The carbon 1s peak is used to obtain an offset correction factor of \( \approx 3.2 \) eV, based on the commonly used value of 285 eV for the carbon peak (Figure S13).

AFM imaging was done using MultiMode AFM, Nanoscope IIIa controller in tapping mode, and WSxM 3.0 Beta 12.1 software was used to view results.\textsuperscript{99} A Matlab code was developed to further process AFM images in order to count the particle number density based on an algorithm that finds the local maxima of the intensity map representing the AFM image (Figure S10).

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Supporting Information Available: Details of the CVD reactors (hot-wall and cold-wall) used for CNT synthesis with respective schematics and growth recipes; the X-ray mass attenuation measurements and local density calculations; SEM images of the forest showing the flatness of the top surface and CNT morphology at different parts of the forest (top, middle, and bottom); sample alignment procedure; TGA of the same sample that was grown in the cold-wall reactor and was used for the analysis in the paper; the schematic and mathematical model used for fitting the linescans obtained from SAXS images by a log-normally distributed hollow cylinders (Figure S6). These linescans are obtained by integration of intensities within \( \pm 10\%\) from the reference direction (y-axis) of the inverse space parameter q (chosen to be the direction of maximum intensity). In order to automate the process of fitting for hundreds of scattering images, an algorithm was developed to select the fitting range of each scan and determine an approximate location of the peak based on the locations of the inflection points above the peak, as described in Figure S7. The fitting code used an iterative approach in searching for the best fit within this selected fitting range. By including the low q part of the data, a good fit was achieved that selects a probability density function (PDF) for diameter distribution as well as for the ratio \( l = ID/OD\), where \( ID\) is the inner diameter of the multiwalled CNT and \( OD\) is the outer diameter of the multilwalled CNT (see Figure S8).

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Unpublished data.


SUPPORTING INFORMATION for

Population Growth Dynamics of Carbon Nanotubes

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

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CNT growth methods

Figures S1 shows the schematics and time-temperature-flow sequences for the two different reactors that were used for carbon nanotube (CNT) forest synthesis by chemical vapor deposition (CVD). Source gases of He (99.999%, PurityPlus), H$_2$ (99.999%, PurityPlus), and C$_2$H$_4$ (99.999%, PurityPlus) were used.

During growth in the cold-wall reactor, the heated substrate is operated at $T_s$, while the thermal decomposition of the incoming gas mixture is determined by preheating upstream of the reactor at temperature $T_p$. First, a five-minute purging step is carried out to purge out air from the tube as a preparation step for introducing H$_2$; during this step, the preheater is ramped to the setpoint $T_p$ = 1050°C. Then, a three-minute gas-mixing step is carried out to stabilize the gas atmosphere before heating. After that, the temperature is rapidly increased to $T_s$ = 775°C in a period of approximately ten seconds.
Figure S1. Details of CNT synthesis: Schematics of the (A) hot-wall reactor (tube furnace) and (B) cold-wall reactor; Process sequence for growth of CNTs forests in the (C) hot-walled reactor and the (D) cold-walled reactor for growth time (t).
Density measurement procedure

Figure S2 shows the intensity readings from the X-ray sensors placed upstream and downstream to the CNT forest placed in the beampath of synchrotron X-rays, as well as the local mass density calculated from X-ray intensity attenuation according to Beer-Lambert-Bouguer law (Eq.1). The downstream X-ray intensity measurements are normalized to the upstream measurements in order to eliminate the effect of the drift in intensity with time.

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**Figure S2.** X-ray attenuation results for the sample grown in the cold-wall reactor: (A) Schematic of the sample configuration showing that the focused X-ray beam passes through the middle portion of the forest (away from the sample corners); (B) Evolution of the X-ray intensity measured downstream of the CNT forest sample (using the beam-stop diode shown in Figure 1A), as a function of distance from the bottom substrate. The 50 µm span for intensity increase as the beam crosses the top-edge of the Si-substrate results from two main sources: angular misalignment of the sample (about y-axis) and beam divergence; (C) Evolution of the X-ray intensity measured upstream of the CNT forest sample (using the fluorescence detector shown in Figure 1A), as a function of distance from the bottom substrate; (D) Evolution of the mass density of each slice in our CNT sample, as a function of distance from the bottom substrate.
Figure S3. SEM images of the sample grown in the cold-wall reactor: (A) forest sidewall, showing flatness of top-surface in the middle if the forest; (B) forest corner, showing uniformity of the top surface; forest morphology near the top (C); the middle (D); and the bottom (E) of the sidewall of the forest, showing the evolution of alignment and qualitative trends of CNT number density.
Sample alignment procedure

In order to align the samples, a bare Si substrate is placed on a metal holder having a ground top surface, as shown in Figure S4A. The motorizes sample stage is then used to scan the vertical direction (z-axis) to find the edge by recording the respective intensity reading at each position and selecting the middle point (Figure S4B). Then, the tilt angle $\theta$ (around y-axis) is scanned to find the position of maximum intensity, which corresponds to the surface orientation that is parallel to the direction of the X-ray beam (Figure S4C). As a result, the error in tilt angle is expected to be less than 0.01°.

Figure S4. Sample alignment procedure: (A) Schematic of the alignment procedure; (B) Scan of X-ray intensity versus vertical position; (C) Scan of X-ray intensity versus tilt angle $\theta$. 
Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA) of the CNT forest grown in the cold walled reactor according to the growth recipe in Figure S1 is shown in Figure S5. As shown, contributions to amorphous carbon and other low evaporation temperature contaminants are limited to about 10% of the total mass. The vertical drop after 800 is due to the setpoint hold, which was preprogrammed for 825 °C.

**Figure S5.** TGA of CNTs from the sample grown in the cold-wall reactor, which is used for all the analysis in the paper.
### Fitting of SAXS linescans

Scattering patterns (Figure S6) are used to calculate the integrated intensity of line scans between +/- 10° of the maximum intensity direction of the inverse space parameter $q$, 

$$I(q) = \int_{-\pi/18}^{\pi/18} I(q, \theta) d\theta$$

The mathematical model used considers the scattering intensity of hollow cylinders (Figure S6) having the same inner radius ($R_i$) and outer radius ($R_o$) as a CNT, with the ratio $c = R_i / R_o$. The probability density function (PDF) used is for a log-normal distribution of diameters.

The scattering intensity is modeled as $I(q) = A F(q) S(q)$, where $F(q)$ is the intraparticle form factor, $S(q)$ is the interparticle structure factor, and $A$ is an adjustable constant that accounts for instrumental and other experimental factors. We set $S(q) = 1$ because particle-particle scattering occurs at far lower $q$ values than of interest for determining the CNT diameter. The CNT forest is therefore modeled as a population of non-interacting hollow cylinders. The form factor for a rod-like particle can be expressed as $F(q) = \frac{L\pi}{q} I_C(q)$, where $L$ is the length of a CNT, $I_C(q)$ is the cross-section scattering function of a cylinder, and $q$ is the scattering vector. $I_C(q)$ is

$$I_C(q) = \frac{\int_0^{\infty} P(R) f^2(q, R) dR}{\int_0^{\infty} P(R) dR},$$

where $P(R)$ is the distribution function of cylinder radii. For a hollow cylinder,

$$f(q, R, c) = \Delta \rho R_o \frac{2J_1(Rq) - c J_1(cRq))}{qR^2(1-c^2)}.$$
$J_1$ is the spherical Bessel function of the first kind, $\Delta \rho$ is the difference in scattering density distribution between the CNT and the surrounding medium (air), and $R$ is the CNT radius. We choose a lognormal distribution to account for polydispersity in CNT radii, such that:

$$P(R) = \frac{1}{R \sigma \sqrt{2\pi}} \exp\left(-\frac{(\ln R - \mu)^2}{2\sigma^2}\right)$$

The parameters $\mu$ and $\sigma$ are related to the mean ($\bar{R}$) and variance ($\sigma_R$) of the CNT radius as

$$\mu = \ln \bar{R} - \frac{1}{2} \ln \left(1 + \frac{\sigma_R^2}{\bar{R}^2}\right)$$

$$\sigma^2 = \ln \left(1 + \frac{\sigma_R^2}{\bar{R}^2}\right)$$

**Figure S6.** Typical SAXS image used to in the diameter fitting: the model of hollow cylinders having the same inner radius ($R_i$) and outer radius ($R_o$) as a CNT, with the ratio $c = R_i / R_o$. 
Algorithm for finding the fitting limits and peak

An algorithm is developed for automating the selection process for the fitting range and determining an approximate location of the peak. As shown in Figure S7, the experimental data points of a linescan within a predetermined range ($q = 0.45 – 1.6$) are first fitted with a $9^{th}$ order polynomial equation that matches the data almost exactly. This fitted polynomial equation is then differentiated twice to identify a local maximum, as well as the two inflection points that typically straddle the peak point. Then either the local maximum is used as the peak location if it is present, and in case that there is no well-defined peak, the arithmetic mean of the two $q$ locations of the inflection points is used instead. The starting and end points for the selected fitting range are then selected based on a predetermined factor that entails how much of the (maximum intensity – peak intensity) is included in the fitting range in case of the start point, and how much of the (peak intensity – minimum intensity) is included in the fitting range in case of the end point (see the two horizontal dashed red lines). The start and end of fitting range are then selected based on the intersection of those two horizontal red lines with the data. For all the fits in this paper the factors used for determining the start and the end points were 0.8 and 0.7, respectively.
Figure S7. (A) Range- / peak-finding algorithm; (B) Semi-log plot of the experimentally-obtained linescans, along with the peak and fitting limits obtained from the algorithm.
Effect of $c$ on SAXS model-fits

Effect of the diametral ratio ($c$) on the fit of intensity curve in the low $q$ range. As can be seen in Figure S8, the correct choice of $c$ results in a better fit of the slope of the low $q$ part of the linescans. The slope is generally steeper for smaller values of $c$.

Figure S8. SAXS model fits for linescans of three forest slices along forest height with fixing value of the fitting parameter $c$ to (A) 0.5, (B) 0.6, and (C) 0.7.
Analysis of repeatability of CNT mass output

Figure S9 shows the mass density vs. forest height for a number of CNT forest samples that were grown in a hot-wall reactor (tube furnace) according to the growth recipe in Figure S1, but for a growth time of 15 minutes (almost half of the time needed for self-termination). Results show considerable non-repeatability in height and mass density, but incidentally show a much narrower variation in their total areal density (mass per unit substrate area), indicating the CNT mass output is essentially conserved for the same growth conditions, even if forest height varies considerably.

Figure S9. Forest mass density vs. height of samples grown in the hot-wall reactor for 15 min. Red line represents a line of constant areal density of 0.011 mg/mm². The table summarizes the results and presents the mean, standard deviation, and coefficient of variation for height and mass per unit area.
Figure S10. Activity of catalyst nanoparticles: (A) AFM image of a sample annealed in the cold-wall reactor according to the recipe in Figure S1; (B) applying an algorithm that counts the particles by identifying local maxima in an intensity map from the AFM image; (C) plot of the catalyst nanoparticle activity as a function of time for the same sample by relating the calculated CNT number density to the number density of particles obtained from AFM.
Population growth models

As can be seen in Figure S10, the Gompertz model gives the best fit compared to the other two models (Monomolecular and Autocatalytic models). The monomolecular model does not have an inflection point, so it fails to fit the initial accelerating part of the kinetics. Although the autocatalytic model has an inflection point, the s-curve is symmetric about that point, so it fails to fit the asymmetric accelerating and decelerating parts of the mass kinetics data.

Figure S11. Time evolution of the areal mass density (mass per unit substrate area) with fits from three different models: monomolecular model, autocatalytic model, Gompertz model. Equations are modified to include a y-intercept term added to them in order to find better fits. This is justified by the large SNR that we have, which might mean that our choice of zero is not accurate.
Figure S12. XPS survey spectra for three samples collected together in the same run. The three samples were substrates for CNT forest growth. The first sample is the as-deposited multi-layer thin film catalyst (1 nm Fe/10 nm Al₂O₃/300 nm SiO₂/500 µm Si); the second sample was annealed according to the recipe in the inset; the third sample was after growth according to the recipe in the inset, and then the forest was delaminated.
Figure S13. XPS core spectra for C 1s peaks for different samples (as deposited, after annealing, after growth). Peak position at ≈ 281.8 eV, is used to calibrate the binding energy value by using the commonly used value of 285 eV, i.e. a shift of +3.2 eV is applied to the spectra in Figure 7.