High-Speed in Situ X-ray Scattering of Carbon Nanotube Film Nucleation and Self-Organization

Eric R. Meshot,†,* Eric Verploegen,† Mostafa Bedewy,‡ Sameh Tawfick,† Arthur R. Woll,† Katherine S. Green,§ Marianne Hromalki,t Lucas J. Koerner,† Hugh T. Philipp,§ Mark W. Tate,‡ Sol M. Gruner,** and A. John Hart†,*

†Mechanosynthesis Group, Department of Mechanical Engineering, University of Michigan, 2350 Hayward Street, Ann Arbor, Michigan 48109, United States, ‡Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, California 94025, United States, §Department of Chemical Engineering, Stanford University, Stanford, California 94305, United States, **Cornell High Energy Synchrotron Source (CHESS), Cornell University, Route 366 & Pine Tree Road, Ithaca, New York 14853, United States, and †Laboratory of Atomic and Solid State Physics, Department of Physics, Cornell University, Ithaca, New York 14853, United States.

ABSTRACT

The production of high-performance carbon nanotube (CNT) materials demands understanding of the growth behavior of individual CNTs as well as collective effects among CNTs. We demonstrate the first use of grazing incidence small-angle X-ray scattering to monitor in real time the synthesis of CNT films by chemical vapor deposition. We use a custom-built cold-wall reactor along with a high-speed pixel array detector resulting in a time resolution of 10 msec. Quantitative models applied to time-resolved X-ray scattering patterns reveal that the Fe catalyst film first rapidly dewets into well-defined hemispherical particles during heating in a reducing atmosphere, and then the particles coarsen slowly upon continued annealing. After introduction of the carbon source, the initial CNT diameter distribution closely matches that of the catalyst particles. However, significant changes in CNT diameter can occur quickly during the subsequent CNT self-organization process. Correlation of time-resolved orientation data to X-ray scattering intensity and height kinetics suggests that the rate of self-organization is driven by both the CNT growth rate and density, and vertical CNT growth begins abruptly when CNT alignment reaches a critical threshold.

KEYWORDS: carbon nanotube · particle · catalyst · dewetting · X-ray scattering · kinetics · self-organization · chemical vapor deposition

The dynamics of catalyst formation and subsequent CNT nucleation and growth have profound effects on the final material properties, especially in the synthesis of CNT forests, where CNT growth and self-assembly occur in concert. Although ex situ characterization studies have led to many important insights about the complex morphology and growth kinetics of CNT forests,†‡24–31 dynamics of the nucleation and self-organization process can only be revealed by in situ methods. Researchers have previously applied in situ methods to study CNT synthesis, such as absorption spectroscopy,‡ environmental TEM,§33–36 XPS,36–38 and Raman spectroscopy.39 However, many of these require low pressures that are not typical for chemical vapor deposition (CVD) of CNTs and/or do not provide quantitative information (e.g., about size, shape, order) for statistically significant numbers of structures (i.e., catalyst nanoparticles or CNTs). AFM and TEM are typical methods for directly imaging and measuring particles. However, their incompatibility with the high temperatures (500–900 °C) used during synthesis limits their use to

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ex situ observations or requires special sample preparation and restricted operating conditions. Further, the morphology and chemistry of the catalyst may be altered during CNT growth or cooling, so ex situ imaging and scattering techniques may not provide an accurate interpretation of the growth process.

Previous studies have established that in situ small-angle X-ray scattering (SAXS) along with quantitative models can be applied to measure populations of nanostructures. For example, in situ SAXS has been used to probe the growth of substrate-bound nanoparticles and nanoparticles in solution as well as the pyrolytic formation of soot. In this paper, we present findings from the first use of grazing incidence small-angle X-ray scattering (GISAXS) to monitor CNT film growth in real time. Combining synchrotron radiation and the use of a high-speed pixel array detector, we resolve (1) the dynamics of catalyst particle formation from a metal thin film, (2) the evolution of catalyst morphology during annealing, (3) the nucleation of CNTs, and (4) the self-organization of CNTs into a vertically aligned forest. This nondestructive method interrogates statistically significant populations of nanostructures during thermal processing over a wide temperature range, at atmospheric pressure, and at a time resolution of 10 ms.

RESULTS AND DISCUSSION

Experimental Technique. To enable this study, a custom-built, cold-wall CVD reactor is mounted in a synchrotron beamline and configured such that the X-ray beam passes over the heated substrate (Figure 1). Resistive heating of a Si platform enables localized and rapid control of the substrate (catalyst) temperature. Thin polyimide (Kapton) windows that are highly X-ray transmissive (Figure 1b) allow incident and scattered X-rays to pass through the sealed reactor with minimal parasitic scattering. An X-ray energy of 10 ± 0.1 keV is selected with synthetic multilayer optics (W/B4C, 27 Å d-spacing), and we use a 2-D pixel array detector for X-ray imaging at a frame rate of 100 Hz. The incident collimated X-ray beam has a height of 100 μm as controlled by slits upstream of the CVD reactor. The substrate is tilted toward the X-ray beam at an angle of incidence αi = 0.15°, which is below the critical angle for total external reflection from the Si substrate. Operating this reactor at atmospheric pressure, we study the synthesis of CNT forests from C2H4/H2 precursors, which are first passed through a “pre-heater” (~1050 – 1070 °C) upstream of the reactor in order to thermally generate the suite of gas compounds necessary to achieve accelerated CNT growth to millimeter film thicknesses. All experiments shown here use a bilayer thin-film catalyst, 1 nm Fe film on top of a 10 nm Al2O3 support, which is sequentially deposited by electron-beam evaporation onto 300 nm of thermally grown SiO2 on (100) Si wafers.

Distinct stages of the synthesis process for CNT forests are schematically represented in Figure 2, along with corresponding in situ GISAXS images. This figure provides an overview of the dynamics and their relationship to the scattering patterns, and a more in-depth discussion of the dynamics follows later. The plots beneath each image show 1-D intensity profiles versus the inverse space parameter l(qy), which are extracted from the 2-D images and used for fitting of the mathematical scattering models described later. The GISAXS patterns are vertically symmetric about the X-ray beam because the form factor of the particles, CNTs, and their organization in the x–y plane (substrate) are all isotropic; therefore, only one-half of the GISAXS image is required for analysis. We hereafter refer to qy as q because we only consider this parallel scattering in this work.
First, the substrate is annealed in H$_2$/He by rapidly heating to 800 °C and holding at this temperature for 2 min. It is well-known that this step causes the Fe film to reduce and dewet to yield particles, which determines CNT diameter. However, to understand the dynamics of dewetting, it is necessary to observe the process in real time. During heating, we observe a distinct and rapid transition from diffuse scattering from the as-deposited Fe/Al$_2$O$_3$ film (Figure 2a) to coherent scattering from well-defined particles (Figure 2b), indicating that dewetting occurs over a short time frame. After the film dewets, the scattering pattern remains constant as the temperature is held, indicating that the particles do not undergo measurable coarsening during the 2 min time frame. This is discussed quantitatively later.

Next, C$_2$H$_4$ is introduced to initiate CNT nucleation and growth. Before detecting scattered X-rays from the transmission beam, we observe changes in the GISAXS pattern and a significant increase in the total scattered intensity (Figure 2c), which we attribute to the deposition of carbon at the substrate-bound nanoparticles. During the time delay (18 s) between when C$_2$H$_4$ is added and the onset of CNT scattering, the concentration of hydrocarbon is transient and surpasses a critical (yet precise) partial pressure for CNT nucleation. By real-time monitoring using a quadrupole mass spectrometer, we estimate the partial pressure of C$_2$H$_4$ is 0.01–0.05 atm, the CNTs self-organize and vertical growth is detected (Figure 6). It is not surprising that nucleation occurs before the steady-state partial pressure of C$_2$H$_4$ is reached because we have previously shown that only trace amounts (0.01 atm) of active alkyne precursors (in concert with C$_2$H$_4$) can induce efficient CNT growth.

Once CNTs begin growing, the specular beam contains scattering information for both Fe particles and CNTs; therefore, to monitor CNT growth we use a $q_z$ value corresponding to the transmitted beam, which includes only scattering from CNTs (Figure 2d). For a 100 μm X-ray beam impinging at $\alpha_i = 0.15^\circ$ on the bare 1 × 1 cm catalyst substrate (before CNT growth), we estimate that 75 μm of the beam passes over the downstream edge of the substrate without scattering. This portion of the beam is entirely blocked by the beamstop (a lead foil) and is not visible on the detector until the height of the CNT forest increases such that it scatters these X-rays onto a visible area of the detector below the GISAXS features. We use this transmission scattering to monitor and quantify prolonged, vertically aligned CNT growth. In situ X-ray scattering videos of both Fe particle formation and CNT nucleation are provided in the Supporting Information.

**GISAXS Modeling of Catalyst Nanoparticle Arrays.** We obtain quantitative measures of the particle size and spacing on the substrate by fitting the GISAXS data with a mathematical model. We adapt the approach of Renaud and co-workers to model the scattering cross section of an arrangement of truncated spheres (particles) on a flat substrate (schematic model in

![GISAXS images of four different stages of the CNT synthesis process: (a) as-deposited Fe/Al$_2$O$_3$ film before heating; (b) dewetting during rapid heating (Fe particles); (c) nucleation of CNTs (CNTs and Fe particles); and (d) CNT growth (only CNTs observed with transmitted beam). Each 2-D SANS image corresponds to the schematic of scattering geometry above and the plot of $I(q_y)$ along the dashed line in the SAXS image. According to the top row schematics, the blue-shaded portion of the scattered X-ray beam is used for analysis. For example in (d), the transmitted beam corresponds to the white dashed line at a lower position on the detector compared to when the grazing incidence scattering is analyzed.](image-url)
The GISAXS intensity collected from the catalyst particles is proportional to the modulus of the form factor squared, $|F(q)|^2$, multiplied by the interference function, $S(q)$,

$$I(q) = |F(q)|^2 S(q)$$  \hspace{1cm} (1)$$

$F(q)$ and $S(q)$ are the Fourier transforms of the catalyst shape and the particle–particle pair correlation function (i.e., spacing), respectively. The form factor is

$$|F(q)|^2 = A \int_0^\infty P(R_p)[f_p(q, R_p, H)]^2 dR_p \int_0^\infty P(R_p) dR_p$$  \hspace{1cm} (2)$$

where $A$ is an adjustable constant, $R_p$ is the radius of a sphere (particle) with variance $\sigma_{R_p}^2$, and $H$ (height) is the distance from the substrate to the top of a sphere. $P(R_p)$ is the probability density function for the population of particle radii, which accounts for the polydispersity in particle size; $f_p$ is the form factor of the individual scattering body (truncated sphere). There is precedence in the literature to suggest that the particles formed by dewetting a thin film on a flat substrate have a log-normal size distribution, analogous to the size distribution of grains within a solid. As a result, $P(R_p)$ is assigned a log-normal distribution, and we also find that the distribution of particle height, as measured by AFM, is log-normal (99% confidence). Accordingly,

$$P(R_p) = \frac{1}{R_p \sigma_{R_p} \sqrt{2\pi}} \exp \left[ -\frac{\ln R_p - (\langle R_p \rangle)^2}{2\sigma R_p^2} \right] \hspace{1cm} (3)$$

and

$$f_p(q, R_p, H) = \int_0^H 2\pi R_p^2 J_1(qR_p) dR_p$$  \hspace{1cm} (4)$$

In the latter equation $R_z = (R_p^2 - z^2)^{1/2}$, where $z$ is the vertical coordinate, and $J_1$ is a Bessel function of the first kind.

The structure factor represents particle–particle scattering, and we use the structure factor for a 1-D paracrystal, which is locally ordered but lacks long-range order. This is

$$S(q) = \frac{1}{1 + e^{-q^2 \sigma^2} - 2e^{-q^2 \sigma^2/2} \cos(q\delta)} \hspace{1cm} (5)$$

where $\delta$ is the mean particle spacing with variance $\sigma_\delta^2$.

According to this model, the spatial distribution of scattered intensity depends on the following independent parameters of the particles: diameter $D_p$ ($2 \times R_p$) and its variance ($\sigma_{D_p}^2$), spacing $\delta$ and its variance ($\sigma_\delta^2$), and height $H$. Thus, fitting eq 1 to line scans $I(q)$ from the GISAXS data enables us to extract quantitative, statistical information about the population of metal nanoparticles created by dewetting of the Fe film. Fitting is performed by least-squares error minimization using custom code and the MATLAB curve-fitting toolbox.

**Validation of GISAXS Model by AFM.** In order to validate the GISAXS measurement technique, we compare the fitting results to quantitative analysis of ex situ AFM images. For this, we prepared a series of reference samples by annealing Fe/Al2O3 films at different

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**Figure 3.** Validation of GISAXS model by quantitative analysis of AFM images. (a) Schematic of 1-D model of catalyst particle array as population of truncated spheres with polydispersity in both size and spacing. (b) Ex situ GISAXS data (red square) and model fitting (black line) of Fe particles formed by rapid heating and 2 min annealing in H2/He at 725 °C. The fit parameters are listed on the plot, and the corresponding 2-D image is the inset. (c) Isometric and top views of an AFM image of the same sample, with particle peaks (black circles) and Voronoi tessellation (black lines) indicated. (d) Comparison of GISAXS particle peaks (black circles) and Voronoi tessellation (black and top views of an AFM image of the same sample, with particle peaks (black circles) and Voronoi tessellation (black lines) indicated.
temperatures and durations (Figure S2), and we analyzed each sample using both GISAXS and AFM. After generic AFM image processing using WSxM software, we use custom processing to first identify the positions of all local maxima within each image and then decompose the image by a Voronoi tessellation. A 2-D Voronoi cell is a convex polygon whose segments are the points in the line that are equidistant to the two nearest maxima and whose vertices are the points equidistant to three maxima (Figure 3c). Thus, the Voronoi cell size, defined as the square root of the polygon’s area, is a measure of particle—particle nearest neighbor spacing δ (Figure 3d). This type of spatial decomposition is traditionally used to analyze paracrystals and applies to substrate-bound nanoparticles that exhibit only short-range order arising from excluded volume interactions and local coarsening. Further, the particle—particle spacing in the GISAXS model has previously been associated with a distribution of Voronoi cell sizes.

Using AFM images, we determine the height (H) of each particle by subtracting its maximum from the mean roughness of the Al2O3, which ranges from 3 to 5 nm depending on annealing conditions (Supporting Information, Figure S2). The shape and diameter of a particle are affected by the tip geometry (which can change with time due to wear) and the tip—sample convolution, so we consider peak height to be a reliable metric from AFM imaging. As a result, the peak height of each particle most accurately captures the distribution of sizes, as opposed to measuring the curvature of the peaks or tallying every pixel. In the latter case, larger particles would be disproportionately weighted because they occupy more pixels than smaller particles.

The summarized results in Figure 3d show that both AFM and GISAXS provide consistent quantitative measures of the mean particle height (H) and spacing δ, for a variety of annealing conditions that result in different film morphologies. We attribute the discrepancy of δ to the decoupling approximation (DA) used in the model, which states that the size of the scattering bodies and their relative positions are not correlated. While DA is typically used only for diffuse systems because it allows for overlapping of the structures, incorporating size-space correlations is challenging for large numbers of images. The GISAXS model also assumes the particles are supported on a flat substrate, whereas the Al2O3 support in fact has a finite roughness (Figure S3), which contributes to the disparity in H. Despite these simplifying assumptions, our approach yields good agreement with AFM, thus enabling in situ measurement of the catalyst morphology using GISAXS.

SAXS Modeling of CNTs. To relate particle dynamics to CNT growth dynamics, we also adopt a quantitative model of CNT scattering. CNTs are described as a population of hollow cylinders with log-normally distributed outer diameters, as in our previous work.

The mathematical equations are also reproduced in the Supporting Information for reference. The fitting parameters of the CNT form factor are the outer diameter (Dc) and its variance (σDc2) and the inner diameter (Di). The CNT—CNT spacing is ~100 nm (q ≈ 10−2 nm−1) and therefore above the resolution limit of our setup.

This allows us to simplify the expression I(q) for CNTs by setting the structure factor S(q) = 1.

Shortly after the hydrocarbon source is added to the reactor, the CNTs comprise a thin, tangled film (Supporting Information, Figure S4), such that GISAXS carries information both from pure Fe particles (without CNTs) and from short CNTs emerging from the Fe particles. By separately fitting the GISAXS scattering during heating and annealing (before CNT nucleation) and the transmission scattering after CNT nucleation, we quantify the dynamics of both catalyst particle formation and CNT growth for a series of thermal and chemical conditions. This enables direct measurement of the CNT size distribution in comparison to the catalyst size distribution. In the next section, we discuss implementation of this analysis methodology to canonical CNT forest growth experiments.

For this work, we collected scattered X-rays at q ≈ 0.1—1.6 nm−1, which enables measurement of particles and CNTs in the range of ~3—30 nm. The measurement range depends on the area of the detector and the sample-to-detector distance. Smaller nanostructures (i.e., single-wall CNTs) can be measured by collecting X-rays at larger q values, but samples should be sufficiently monodisperse to produce defined scattering peaks, which can be practically fitted by mathematical models.

**Dynamics of Particle Formation and CNT Nucleation.** First, we study the dynamics when the substrate is rapidly heated (100 °C s−1) to 800 °C in H2/He (Figure 4a). The film rapidly dewets to form particles, starting when the substrate reaches 350 °C (11 s after heating begins). At this instant, D0 and σDc both increase rapidly, and they saturate at 17 s. The particle size distribution then remains constant at D0 = 11.7 ± 2.1 nm for the rest of the 2 min annealing step. The diameter of CNTs at the start of growth (Dc = 12.0 ± 4.3 nm) is very close to the measured average particle diameter, although the variance is approximately doubled. However, within 10 s after nucleation, the CNT diameter distribution rapidly shifts downward, and the distribution (σDc) focuses, reaching σDc = 2.6 nm. High-resolution SEM imaging of the top of the forest, representing the beginning of growth, gives Dc = 10.6 ± 1.8 nm. This confirms that SAXS accurately measures the CNTs present at the start of the growth process. This value is shown as the black data point superimposed in Figure 4a, and more details are in the Supporting Information (Figure S5).

The subsequent downward shifts in Dc and σDc suggest that newly nucleating CNTs overwhelm the
existing population with time. The shift in mean CNT diameter is not due to the diameters of individual CNTs changing with time. Indeed, previous studies of isolated, millimeter-long CNTs have shown that diameter and chirality changes typically do not occur during growth unless a process variable such as temperature is modulated. Our explanation of the early shift in mean diameter is also consistent with our recent observations that CNT number density increases up to 10 times during the initial stages of CNT forest growth. This initial density increase is corroborated by increased X-ray scattering intensity measured in situ, which is discussed later (Figure 6c). For reference, additional data and fit parameters from this experiment are reported in the Supporting Information (Figure S5).

While rapid heating and annealing is an attractive approach for high-rate continuous manufacturing of CNTs, slower heating is typical in most laboratory processes that are limited by the thermal mass of hot-wall systems (e.g., tube furnaces). Under relatively slow heating (10 °C s⁻¹) in H₂/He, the film dewets at approximately 550 °C (60 s after heating begins), and compared to the rapid heating experiment, the subsequent increase of particle diameter (Figure 4b) is more gradual and is slower to reach a steady value (~100 s). The particle diameter continues to change in the presence of increasing C₂H₄ partial pressure until CNTs nucleate (past which accurate quantification of particles is difficult). While the mean CNT diameter for this case is also dynamic during early growth, σDC remains comparatively more stable and smaller overall. Thus, the heating rate influences the size and monodispersity of the nanoparticles, and in these experiments a slower heating rate in H₂/He results in smaller diameter CNTs with lower variance.

While we find that the film dewets very rapidly in H₂/He, previous studies have suggested that continued
annealing in H\textsubscript{2}/He causes coarsening of the particles.\textsuperscript{34,76} As a result, an increasingly common practice for CNT synthesis is to rapidly heat the catalyst film in the presence of both hydrocarbon and H\textsubscript{2} precursors, aiming also to achieve smaller diameter CNTs and further reduce the process time.\textsuperscript{71,72} Figure 5a shows results where the substrate was heated rapidly (100 °C s\textsuperscript{-1}) in C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2}/He. In this case, the film begins to dewet at approximately 350 °C, and the particle diameter (\(D_{p} = 10.4 \pm 2.7\) nm) is close to the value obtained by rapid heating in H\textsubscript{2}/He. However, the first CNTs observed in transmission scattering are much smaller (\(D_{c} = 5.7 \pm 1.5\) nm) than after pretreating in H\textsubscript{2}/He and, interestingly, are the particles that are detected immediately upon dewetting. This suggests that heating the catalyst film in the presence of active carbon precursors creates and/or activates a subpopulation of catalysts of smaller average diameter. However, as time proceeds, the CNT population evolves to \(D_{c} = 9.2 \pm 2.1\) nm, which is closer to the initial size of the catalysts. Thus, the smaller subpopulation either is not stable to support prolonged CNT growth or is overwhelmed by the main population of larger particles and corresponding larger CNTs. This experiment also demonstrates the time resolution of our technique. For instance, Figure 5b shows that we quantify changes in the catalyst film morphology with time steps of 60 ms, but in principle the limit is 10 ms, given the frame rate of the pixel array detector. Here, we clearly resolve the particle scattering signature before CNT scattering appears, thus confirming that dewetting of the film into approximately hemispherical islands is a distinct step of the process, even in the presence of hydrocarbons.

During the initial heating, the Fe film, which is oxidized when exposed to ambient, reduces to its metallic state,\textsuperscript{36} dewets, and forms stable islands (particles). When the substrate is heated in an inert atmosphere (i.e., He) we do not observe dewetting. Thus, a reducing atmosphere, which evidently affects the mobility of the Fe atoms, is important for transforming a thin film into particles. Overall, the dewetting of the Fe film is driven by instability induced by surface tension and thermal stress, which arises from mismatch in coefficients of thermal expansion between the film and its support.\textsuperscript{73–77} There is a net decrease in free energy when the film restructures into hemispherical particles by surface diffusion of Fe. After dewetting, the subsequent rate of particle coarsening is expected to decay exponentially\textsuperscript{74,76} as the system tends toward equilibrium. The equilibrium size and shape (contact angle) of the catalyst particles are related to the free energy balance of the lower energy surface of the Al\textsubscript{2}O\textsubscript{3} support with that of the Fe,\textsuperscript{78} and herein we show that the heating rate also influences the resultant particle geometry.

In all of our experiments, we find that rapid dewetting is followed by relatively slow coarsening of the particles. Although we observe that the Fe particles remain relatively stable over the 2 min annealing step in H\textsubscript{2}/He, our AFM data in Figure 3d and additional \textit{in situ} GISAXS studies (Supporting Information, Figure S7) clearly show that particle size and spacing increase gradually over a longer duration. This complements recent studies that show populations of Fe nanoparticles on Al\textsubscript{2}O\textsubscript{3} can coarsen significantly during annealing.\textsuperscript{34,35} However, the particles in these recent studies are smaller than those found in our work, and we expect smaller particles to coarsen more quickly. Combining all these insights, it is apparent that the dynamic behavior of CNT catalyst populations is related to their size, the surface properties of the substrate, and the processing conditions.

**Dynamics of CNT Self-Organization.** Finally, we demonstrate that GISAXS enables quantification of the dynamics of CNT self-organization into a vertically aligned forest. The CNT alignment is quantified by integrating the scattered intensity along the azimuthal
angle $\phi$ (about the beam’s axis), as shown in Figure 6a. The intensity distribution is an indication of the average CNT orientation within the beam path. As in our previous work,$^{21,24,79}$ we quantify orientation using the parameter

$$f = \frac{1}{2}(3(\cos^2\phi) - 1)$$

where

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

Values of $f$ equal to $0.5$, $0$, and $1$, correspond to perfectly horizontal, random (disordered), and perfectly vertical orientations, respectively. Therefore, by calculating $f$ for each sequential scattering image we quantify the evolution of alignment as CNT growth proceeds with time. Note that the azimuthal scan is performed at $q \approx 0.8$ nm$^{-1}$, which is the location of the CNT signature peak. This is important so as not to confuse the catalyst scattering with that of the CNTs, since for a period there are contributions from both nanostructures in the GISAXS images (Figure 2c). Also, there is inherent anisotropy in GISAXS patterns because of the multiple scattering effects along the horizon that arise from the substrate.$^{40}$ Nevertheless, we can still definitively identify and quantitatively monitor alignment using this approach.

We show that CNT alignment increases and then saturates; we associate this increase during early growth with a transition from the ubiquitous tangled "crust" at the top of CNT forests (i.e., beginning of growth)$^{21,27,28}$ to the vertically aligned morphology (Figure 6b). Note that in order to directly compare data from different experiments, time equals zero in Figure 6c,d corresponds to the point at which CNT growth is initiated, either by introducing C$_2$H$_4$ to the heated catalyst or by heating the catalyst in an environment of C$_2$H$_4$. We expect that this increase of alignment is due to an increasing number density of CNTs,$^{22}$ which is corroborated by an increase in total scattering intensity (Figure 6c). The increase of alignment is influenced by increased van der Waals forces between CNTs as the existing CNTs grow longer; thus, in combination with increasing number density of CNTs, self-alignment is a cooperative effect. The transient increase in alignment is sublinear with growth time, and the saturation of $f$ is concomitant with the beginning of upward forest growth. Thus, we show there is a critical threshold of alignment necessary for CNTs to self-organize into a
forest (i.e., to "lift off" from the substrate; Figure S8). We expect that, depending on the diameter and straightness of the CNTs, there is a density at which the transition occurs. This critical density for self-organization is analogous to the density decay that suddenly interrupts the self-aligned morphology and leads to abrupt termination of CNT forest growth. We previously measured this critical density to be ~1 × 10^5 CNTs cm^{-2}.21,22

When the substrate is heated rapidly in the presence of thermally treated C_2H_2 (with H_2/He), we observe accelerated self-organization (3 x) and a higher final value of the orientation parameter compared to annealing in H_2/He alone. It is also interesting that the rate at which the transition occurs correlates with the average growth rate v of the forest with v = 1.7, 3.1, and 5.6 μm s^{-1} for forests shown in Figure 4a,b and Figure 5, respectively. Namely, steeper height kinetics corresponds to a faster transition to the vertically aligned morphology. This suggests that the transition is at least in part governed by the lengthening rate of constituent CNTs, in conjunction with increasing density. While we believe this is the first study to quantify this transition in situ during CNT synthesis, we are reminded of the isotropic–nematic (aligned) phase changes previously observed both experimentally in CNT solutions81–83 and DNA84 and in numerical models of rod-shaped molecules (for study of liquid crystals).85–87 The latter body of work has built upon excluded volume interactions (i.e., length) and/or packing density of the rods can induce the transition from disordered to higher order phases based on excluded volume interactions (i.e., van der Waals).88 Combining these insights with additional analysis and modeling may allow us to relate the dynamics and mechanics of self-organization to the CNT diameter and attractive forces. The forces that evolve between adjacent CNTs during this stage are implicitly essential to the morphology of the film and also may influence the maximum density of CNTs.

CONCLUSIONS

We show that in situ X-ray scattering enables nondestructive interrogation of the dynamics of collective CNT growth, including catalyst film dewetting and particle coarsening, CNT nucleation, and CNT self-organization into vertically aligned forests. Mathematical models of time-resolved scattering patterns are used to quantify the evolution of catalyst and CNT populations. The size and monodispersity of the catalyst particles are influenced by the heating rate, and while the CNT diameters that nucleate are similar to those of the catalysts initially, the CNT population typically evolves rapidly during nucleation. Further, vertically aligned growth begins abruptly once the average CNT orientation reaches a critical threshold, which depends on the process conditions. Our use of synchrotron radiation and a high-speed detector is a powerful high-speed diagnostic tool for nanomaterials production and will be useful to devise feedback control schemes to optimize synthesis conditions in situ. The technique may also be useful to engineer nanoparticle arrays for in situ catalytic studies and to explore the growth and self-assembly of other one-dimensional nanostructures.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Mathematical model for SAXS of CNTs, mass spectrometry data, AFM images of annealed catalyst films, SEM of CNTs, additional data and fitting parameters for in situ experiments, as well as videos of real-time X-ray images during catalyst annealing, CNT nucleation, and CNT self-organization. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES
