Kinetics of Water-Assisted Single-Walled Carbon Nanotube Synthesis Revealed by a Time-Evolution Analysis

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Here we investigate the kinetics of water-assisted CVD (henceforth denoted as supergrowth CVD) by a quantitative time-evolution analysis based on a simple growth model. We found that the supergrowth can be well described by a model where the dynamics of the catalyst activity is treated similar to radioactive decay. An in-depth analysis based on this growth model revealed the kinetics of the supergrowth CVD, showing a scale relationship between the carbon source and water, and elucidated the role of water as a catalyst activity enhancer and preserver.

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The low efficiency of synthesis and the subsequent difficulty to produce long and pure high-quality single-walled carbon nanotubes (SWNTs) has always represented a major problem in the carbon nanotube field. The introduction of a small and controlled amount of water into the growth ambient of standard chemical vapor deposition (CVD) was reported to increase the synthesis efficiency of SWNTs to unprecedented heights [1]. From this water-stimulated catalytic activity dense, impurity-free, and vertically aligned SWNT forests with millimeter-scale heights could be grown and be patterned into scaled-up macroscopic organized structures with defined shape. These remarkable features make the supergrowth CVD quite unique from existing SWNT synthesis methods, such as arc discharge [2–4], laser ablation [5], and other methods of CVD [6–12].

This work was motivated to cultivate a general understanding of the kinetics of this new and promising synthetic method. Knowledge of the kinetics is critically important to understand the mechanism of the supergrowth CVD and to further improve SWNT synthesis to new levels. We have addressed this important issue by formulating a numerical growth model that describes the time evolution of the supergrowth. This growth model served as the key point to quantitatively analyze the kinetics of the supergrowth and to gain insight into the effect of water. Moreover, our growth model and subsequent analysis served as a guide in optimizing the growth conditions, a matter of significant importance for supergrowth CVD because the use of water adds an additional dimension of complexity.

Single-walled carbon nanotubes were synthesized in a one-inch diameter quartz tube furnace at a 750 °C growth temperature with ethylene as the carbon source. Water vapor was introduced into the growth environment by passing a small fraction of the He carrier gas through a water bubbler. The samples used in this experiment were Al_2O_3(10 nm)/Fe(1 nm) on Si wafers with a 600 nm SiO_2 layer. From our previous study [1] we have confirmed that the nanotubes were SWNTs. For this study, a fast-heating process was utilized to accommodate the large number of growths. While the furnace was maintained at 750 °C, samples were individually shuttled into the heating zone for catalyst formation and growth, then cooled, and exchanged.

We found it possible to evaluate the SWNT yield for a given growth condition simply by measuring the height of the SWNT forest. First, the height of the forest was remarkably consistent even for samples with size exceeding (2 cm × 2 cm), provided that the CVD was well controlled, thus making it possible to define the height of a forest. Second, the mass densities of the forests were consistently identical in value and did not depend on the height or growth conditions on the same batch of catalyst substrates [13]. Third, when these results were combined with the fact that the product of supergrowth is almost totally carbon nanotubes [1], the height of the forest could be converted to a meaningful number: the SWNT yield of the CVD at a given growth condition. Typically for a 2 × 2 cm sample, a 1 mm tall SWNT forest could be grown in a 10-minute growth time with >10 mg of SWNTs. For these conditions, the SWNT-to-catalyst mass ratio is approximately 590 (without including the weight of the Al_2O_3, this ratio exceeds 3000). To ensure consistency in the following analysis, all experiments in this work were performed on a single sputtering batch.

The time evolution of the forests' heights (yield) at a fixed growth condition (Fig. 1) showed that the growth rate was highest at the onset of growth, gradually decreased over the subsequent 20 min, and finally terminated with a height of 970 μm. Similar behavior with varying lifetimes and terminal heights was observed on a number of time-evolution experiments that covered a wide range of growth conditions (details mentioned later), and thus we regard this behavior as a general feature of supergrowth.

We modeled this time evolution by assuming that the catalysts lose their activity in a similar fashion to radio-

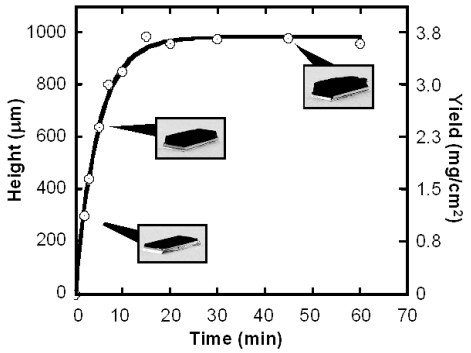

FIG. 1. Time evolution of SWNT forest growth. Plot of the SWNT forest height as a function of the growth time. The solid line indicates the excellent curve fitting of the growth equation to the experimental data. Inset photographs show the samples at various stages of growth.

active decay. Assumptions we made were the following: (1) the catalysts showed identical activity; (2) the increase in yield of SWNTs (and thus the height of forests) was directly proportional to the number of active catalysts; and (3) the number of catalysts that decay was proportional to the number of active catalysts. With these assumptions the growth rate could be expressed by the differential equation, $\partial H/\partial t \propto e^{-t/\tau_0}$, where H is the height of the forest, and τ_0 is a fitting parameter. Integration provided the growth equation for supergrowth, $H(t) = \beta\tau_0(1 - e^{-t/\tau_0})$. It is very important to note that within this model an important physical meaning can be assigned to the two fitting parameters: β is the initial growth rate (IGR) and τ_0 is the characteristic catalyst lifetime. Fitting our growth equation to the experimental time-evolution data yielded excellent agreement ($R^2 = 0.9940$) as demonstrated by the solid line in Fig. 1, supporting the soundness of our modeling. Other functional forms through nonlinear regression were ruled out due to lower R^2 values. The fitting parameters for this specific growth condition were IGR (β) of 207 μm/min and lifetime (τ_0) of 4.74 min, respectively. Interestingly, according to the growth equation, the product of the two fitting parameters, $\beta\tau_0$, gives the theoretical maximum height, $H_{\max}$, and for this specific growth condition $H_{\max}$ is calculated to be 980 μm, which matches very well with the experimentally obtained maximum height 970 μm.

This time-evolution analysis can be carried out on a variety of growth conditions to study the kinetics of the supergrowth. The major growth parameters in the supergrowth are the growth temperature, ethylene level, and water level. Ethylene is the carbon source for SWNT growth, while water acts as a catalyst enhancer and preserver, and in the following discussion we concentrate on how the kinetics of supergrowth depend on ethylene and water at a fixed growth temperature.

A family of time-evolution data of the supergrowth fitted with the growth equation taken at different ethylene flow rates spanning 25 to 300 cm^3 STP per minute (sccm) at a fixed water level (100 ppm) is shown in Fig. 2(a). The excellent fitting of the experimental time-evolution data to the growth equation demonstrates the generality of our modeling for arbitrary growth conditions. The family of growth equation curves exhibits a particularly complex behavior: as the ethylene level increases, not only does the maximum height raise then fall, but also many crossings among curves occur. The crossings mean that optimization of the yield cannot be achieved by maximizing the forest height at an arbitrary growth time.

The apparent complexity of the family curves hinders our ability to gain further insight into the kinetics of the supergrowth; however, we found that the analysis of the fitting parameters renders this complexity into a readily explainable phenomenon. From each growth equation curve, the initial growth rate β and the characteristic catalyst lifetime τ_0 was calculated and plotted as a function of the ethylene flow rate [Fig. 2(b)]. Overall, the lifetime and IGR followed divergent trends, i.e., the IGR monotonically increases while the lifetime decreases with the ethylene level. The existence of these crossings among growth equation curves is a direct result of this divergent trend: slower initial growth with long lifetimes achieves higher maximum heights than rapid initial growth but with short lifetimes. Furthermore, despite this divergent trend, the theoretical maximum height [Fig. 2(b) as a histogram], being the product of the two fitting parameters, $\beta\tau_0$,

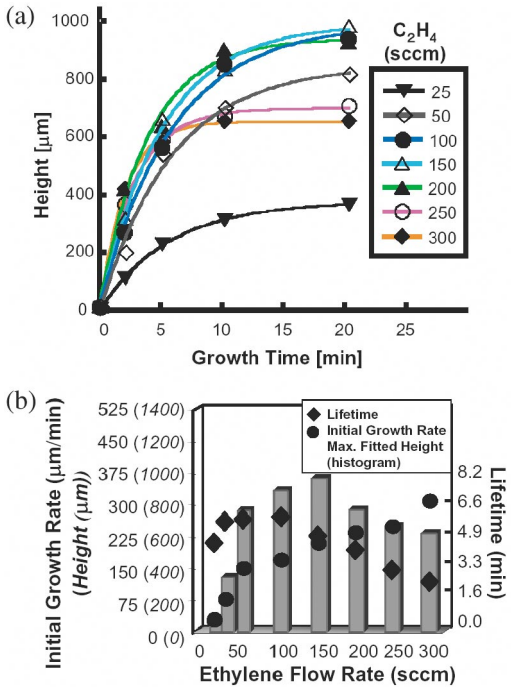

FIG. 2 (color). Ethylene dependence on SWNT forest growth. (a) Overlaid plots of the forest heights as a function of growth time for increasing levels of ethylene. The solid lines represent curve fits for each growth condition. (b) Overlaid plots of the lifetime, initial growth rate, and maximum height (histogram), as derived from each growth curve in (a) as a function of the ethylene level.

exhibits a peak representing the optimum ethylene flow rate for this water level. The divergent trends are easily explainable: (1) IGR monotonically increases with ethylene because the carbon source for SWNT growth increases; (2) lifetime decreases since the catalysts are poisoned faster by rapid accumulation of amorphous carbon coating, a factor known to kill catalyst activity [14]. A close examination of the trend at low ethylene levels shows that the lifetime increases until 100 sccm, and IGR shows a sharp increase up to about 50 sccm. This significantly different behavior from the overall trend is a result of the water-assisted increased growth efficiency, and reflects the ethylene level approaching the optimum growth condition for this water level.

A similar analysis was performed to study the water kinetics. A family of time-evolution data of the supergrowth fitted with the growth equation taken at different water levels spanning 50 to 290 ppm at a fixed ethylene flow rate (100 sccm) is shown in Fig. 3(a). The excellent fitting of the experimental time-evolution data to the growth equation again demonstrates the generality of our modeling. The family of growth equation curves exhibits a complex behavior: as the water concentration increases, the initial slope and maximum height increased until peaking at about 100 ppm, but with further increase both the initial slope and maximum height decreased. However, the behavior is different from Fig. 2(a) in that no crossings among the growth equation curves exist. Certainly this means that water plays a different role in SWNT synthesis.

Analyzing the fitting parameters again provided further insight into the kinetics. As shown in Fig. 3(b), in sharp contrast to that of ethylene, the two parameters, and thus also the theoretical maximum height changed in concert with each other, that is, they all increased with an increase in water level at the low water-level regime (<100 ppm), peaked at about 140 ppm, then beyond which they all decreased. The absence of crossings among the growth equation curves in Fig. 3(b) was a direct reflection of their similar dependence of the growth characteristics on water. This mutual increase in the lifetime and the initial growth rate with low water levels exemplifies the effect of water in enhancing and preserving catalyst activity, which is the principle characteristic feature of the supergrowth. Beyond the optimum water level, the growth characteristics dropped steadily, which is due to poisoning of the growth process from excess water that might be caused by oxidation of the catalysts or the carbon nanotubes. As demonstrated by these observations, the analysis of the lifetime and initial growth rate on the growth conditions can provide a profound understanding of the kinetics, thus illuminating the importance and appropriateness of our modeling. Furthermore, through this approach, we have quantitatively proved that water acts as a catalyst activity enhancer and preserver in supergrowth.

Further analysis was carried out by the two-dimensional mapping of the dependence of the lifetime, initial growth rate, and theoretical maximum height on water and ethylene. Overall, the lifetime and initial growth rate followed divergent trends in that the initial growth rate increased from lower water and ethylene levels to higher water and ethylene levels, while the lifetime did just the opposite. As such, the map for the theoretical maximum height (Fig. 4) proved to be quite complex, and neither provided further insight into the growth kinetics nor served as a useful guide to identify the optimum growth condition.

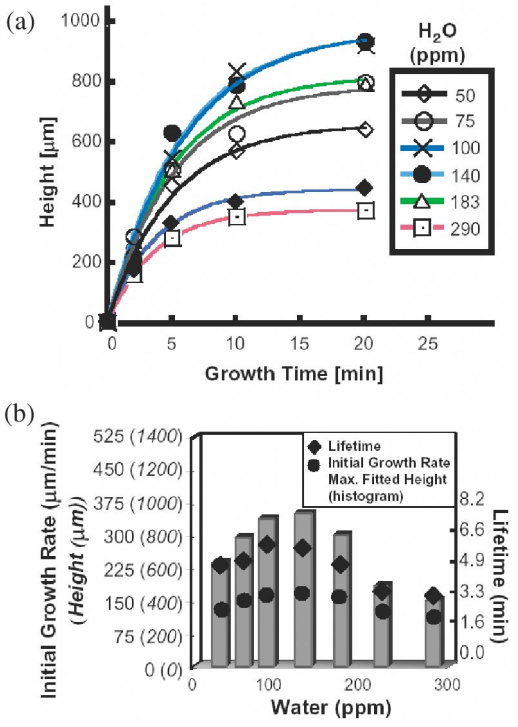

FIG. 3 (color). Water dependence on the SWNT forest growth. (a) Overlaid plots of the forest heights as a function of growth time for increasing levels of water. The solid lines represent curve fits for each growth condition. (b) Overlaid plots of the lifetime, initial growth rate, and maximum height (histogram) as a function of water level.

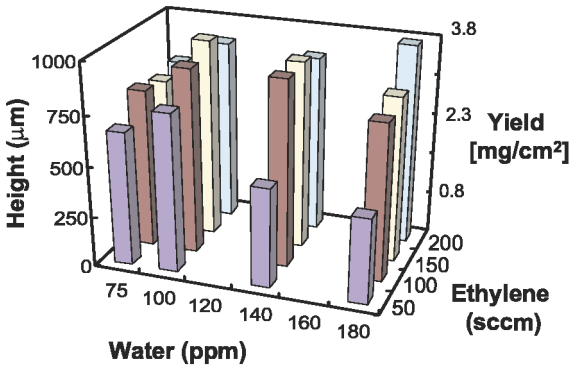

FIG. 4 (color). Two-dimensional mapping of the growth characteristics. Plot of the maximum forest height as a function of ethylene and water.

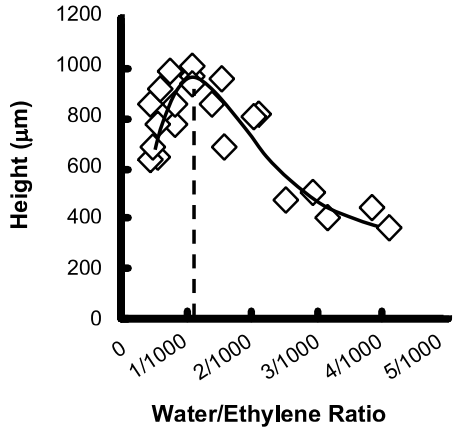

FIG. 5. Water/ethylene ratio. Plot of the maximum height as a function of the water/ethylene ratio, which illustrates the scaling relationship between the carbon source and water. The solid line is drawn to guide the eye.

However, we discovered that we could deepen our understanding by rearranging the data of Fig. 4 into a plot of the maximum height as a function of the water/ethylene ratio (Fig. 5). Interestingly, a clear trend emerged by this rearrangement, despite spanning a wide range of growth conditions (ethylene 10–300 sccm; water 50–290 ppm). The maximum height initially increased with the water/ethylene ratio, peaked at a value of about 1/1000, then decreased with a further increase of the water/ethylene ratio. The water-assisted enhanced growth efficiency is reflected in the initial increase of the maximum height, and the peak represents the optimum growth conditions of the supergrowth for this growth temperature and catalyst. In reexamining Fig. 4, the peak in Fig. 5 can be seen in a maximal height trend which traverses a diagonal path from the low water/low ethylene region toward the high water/high ethylene region. The existence of such a peak demonstrates that there exists a scaling relation between ethylene and water and that the balance of the ethylene and water is the most critical factor for the supergrowth. By this we mean that the same maximum height can be achieved by both a slow growth with a long lifetime and a fast growth with a short lifetime given that the water/ethylene ratio is the same. Furthermore, the existence of this scaling law suggests that the catalysts consume a specific number of ethylene and water molecules before they die, and this specific number is determined by the water/ethylene ratio. Moreover, it implies that each growth event in which a carbon atom is supplied from the gas phase, incorporated into a catalyst, and solidified as a SWNT can be considered as a Markov process, i.e., growth events are independent. This implies that the rate limiting process of the SWNT growth in this growth parameter's window is the supply of carbon to catalysts from the gas phase. We emphasize that any microscopic growth model of the supergrowth that might emerge in the future should be able to explain this interesting observation.

In conclusion, we have investigated the kinetics of the supergrowth through a quantitative time-evolution analysis based on a growth model where catalyst activity was treated similar to that of radioactive decay. A growth equation derived from the growth model was fitted to the time evolution of the height (yield) of the supergrowth forests for numerous growth conditions to investigate the kinetics. This quantitative analysis was made possible because of the high reliability and reproducibility of the supergrowth that enabled the precise control of the growth process, and represents the first analytical description of SWNT growth. We found that the complex behavior of the time evolution of supergrowth can be easily explained by analyzing the two fitting parameters of the growth model, i.e., initial growth rate and the characteristic catalyst lifetime. This analysis provided deep insight into the supergrowth mechanism and quantitatively demonstrated the effect of water acting to enhance and preserve catalyst activity. In addition, this study revealed that there exists a scaling relationship between the carbon source and water. We believe that this study represents the opening of a new era for carbon nanotube synthesis where the dependence of the yield on growth parameters is quantitatively analyzed and interpreted by numerical growth models. These analyses would guide the researcher to efficiently optimize the growth and provide a better understanding of the growth mechanism.

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