

Millimeter-Tall Single-Walled Carbon Nanotubes Rapidly Grown with and without Water

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Synthesis of single-walled carbon nanotubes (SWCNTs) has been extensively studied, and recent progress in chemical vapor deposition (CVD) using nanoparticle catalysts supported on substrates has enabled the growth of vertically aligned SWCNTs (VA-SWCNTs).^{1–11} This achievement shows the potential of CVD processes on substrates for practical applications in the direct synthesis of SWCNT device layers on a substrate and also in mass production. Among them, a water-assisted CVD method designated super growth realized a remarkably rapid growth of millimeter-tall VA-SWCNTs in 10 min.² In this process water is added to a C₂H₄ feedstock at a water/C₂H₄ ratio as small as 1/1000.¹⁰ It is reported that water retains the catalytic activity by removing the carbon byproduct from the Fe catalyst surface supported on the Al₂O₃ underlayer.¹² Reports about the production of millimeter-tall CNTs obtained without using water do exist but many of them yield multiwalled CNTs (MWCNTs)^{13–15} instead of SWCNTs, and others yield millimeter-tall SWCNTs in several hours.¹⁶ Most of the methods that yield millimeter-tall SWCNTs in several tens of minutes required water^{2,7,8} or oxygen-containing molecules.¹¹ Our previous work⁸ was the first to report the production of millimeter-tall SWCNTs in 10 min without water- or oxygen-containing species.

Extensive efforts have been directed toward the reproduction of super growth and to determine the role of water. One paper reported that ultrahigh-yield growth of SWCNTs was not achieved by water addition but was achieved by O₂ addition to the plasma CVD process.⁵ Another paper reported that super growth was achieved by water addition and attributed the role of water to suppressing Ostwald ripening causing catalyst deactivation.¹⁷ However, the SWCNT growth reported using their

ABSTRACT Millimeter-tall vertically aligned single-walled carbon nanotubes (SWCNTs) were grown in 10–15 min by chemical vapor deposition from C₂H₂/Ar with or without water addition using Fe catalyst supported on an Al–Si–O underlayer. Using combinatorial catalyst libraries coupled with the real-time monitoring of SWCNT growth, the catalyst and chemical vapor deposition conditions were systematically examined, and millimeter-tall SWCNTs were obtained even without water addition. The key for millimeter-scale growth of SWCNTs is to limit the C₂H₂ supply to below a certain partial pressure to retain an active catalyst. Water prolongs the catalyst lifetime under excess C₂H₂ supply, whereas it deactivates small catalyst particles and degrades the quality of SWCNTs at the same time. We also observed a gradual increase in the diameter of SWCNTs with growth because of the coarsening of catalyst particles and found that water had no effect on this phenomenon. We demonstrate millimeter-tall SWCNTs grown by simply using C₂H₂/Ar gas without water addition, which revealed the mysterious role of water, and we show a practical route for the large-scale production of SWCNTs.

KEYWORDS: single-walled carbon nanotubes · catalytic chemical vapor deposition · water · real-time monitoring · combinatorial catalyst screening · growth and termination mechanisms · coarsening of catalyst particles

methods^{5,17} (10 μm per 10 min⁵ and 220 μm per 120 min,¹⁷ respectively) was 2 orders of magnitude slower than those reported by the original² and reproduced^{7,8} super growth (over 1 mm per 10 min) methods. The rapid growth of millimeter-tall SWCNTs using water is still uncommon, and that without water is even more uncommon, although six years have passed since it was first reported.²

In addition to the difficulty and the unclear mechanism of water-assisted growth, we need to consider how to feed water at such low levels (typically 1/1000 of the carbon feedstock)¹⁰ uniformly over large-scale reactors for this method to be used in practical material/device fabrication. The millimeter-scale growth of SWCNTs without additives, such as water, will be of practical use and will enable a clear discussion of the growth mechanism. The catalyst and the underlayer are another key for the millimeter-scale growth of SWCNTs. Both the original² and reproduced⁷ super growth

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used an Fe catalyst supported on an Al_2O_3 underlayer. We have developed the Al–Si–O underlayer by annealing Al/SiO_2 , which is effective to activate thin catalytic layers of Fe,⁸ Co,^{11,18} and Ni.¹⁸ Among them, the combination of Fe/Al–Si–O is the most efficient to grow taller SWCNTs from a C_2H_4 feedstock.¹⁸ The effect of the gas-phase reaction is also the key for SWCNT growth. The effect of the gas-phase conversion of the carbon source has also been studied,^{11,19–21} and C_2H_2 generated in the gas phase is supposedly one of the main species.^{11,20} We have previously developed the “cold-gas CVD” method in which the gas is preheated, cooled down, and then fed to the substrate, which is electrically heated while the gas is kept at a low temperature. Using this method, we found that C_2H_2 generation by the gas-phase decomposition of the carbon feedstock is necessary for rapid SWCNT growth from both C_2H_4 ²² and $\text{C}_2\text{H}_5\text{OH}$.²³ In this work, we used C_2H_2 as the carbon feedstock and diluted it with Ar as a balance gas with or without water addition so that we could ignore the gas-phase reaction and discuss the effect of gas composition on SWCNT growth. The self-decomposition of C_2H_2 is negligibly slow under our CVD conditions (temperature of 1073 K and gas residence time of a few s) (see Supporting Information, Figure S1).

The growth window of millimeter-tall SWCNTs without the addition of water is expectedly limited for both the catalyst and CVD conditions. We previously developed a combinatorial masked deposition (CMD) method and applied this method to screen and optimize the catalyst conditions for SWCNT growth.^{24,25} Briefly, a gradient thickness profile is formed in the catalyst layer by sputter depositing the catalyst on a substrate through a physical filter. The catalyst layer is transformed into catalyst particles of various sizes, depending on the initial catalyst thickness by annealing in a CVD reactor.^{26,27} Using this method, we clarified the CVD condition for the rapid growth of millimeter-tall SWCNTs⁸ and discussed a growth enhancement mechanism for millimeter-tall SWCNT growth by Fe/Al–Si–O catalyzed C_2H_4 –CVD.^{8,18} The optimum catalyst condition (nominal thickness and/or composition) changes with other conditions, such as underlayers,⁸ feedstock pressures,¹⁹ and reaction temperature.¹⁹ There is no universal optimum condition for catalysts, and therefore the combinatorial catalyst library realizing a series of catalyst conditions on a single substrate is effective to study various CVD conditions. Also, we developed a simple real-time monitoring (RTM) method for SWCNT growth, and the growth rate and the lifetime for a series of catalyst conditions were easily and systematically obtained by coupling RTM with CMD.²⁸ In this work, we used our CMD-RTM method to discover the window, reveal the role of water, and examine the effects of catalyst and CVD conditions for the millimeter-scale growth of SWCNTs.

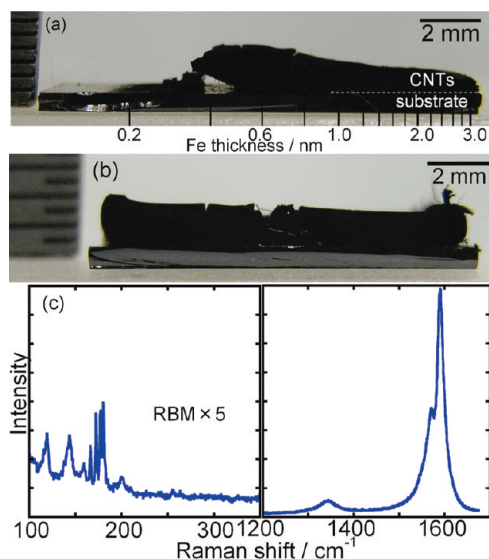


Figure 1. Side-view photographs of SWCNT forests grown from: (a) a combinatorial catalyst library and (b) a uniform 0.7 nm thick Fe catalyst. CVD was carried out at 1073 K with 0.30 vol % $\text{C}_2\text{H}_2/\text{Ar}$ balance at ambient pressure. (c) Raman spectra of the sample shown in (b) from top of forest using a wavelength of 488.0 nm for excitation.

RESULTS AND DISCUSSION

Rapid Growth of Millimeter-Tall SWCNTs without Water Addition. Fe/Al–Si–O catalysts were prepared by sequentially sputter-depositing Al and Fe on silicon wafers with a thermal oxide layer and by annealing under 10 vol % H_2/Ar at ambient pressure and 1073 K for 5 min in a tubular CVD reactor. The Al had a uniform thickness of 15 nm, and the Fe had a gradient thickness profile of 0.1–3 nm when formed by the CMD method²⁵ (the combinatorial catalyst library) or a uniform nominal thickness of 0.7 nm. CVD was then carried out by switching the gas to 0.10–0.60 vol % $\text{C}_2\text{H}_2/\text{Ar}$ containing 0–300 ppmv H_2O at ambient pressure.

Figure 1a shows a photograph of a CNT sample grown in 20 min without water addition. The Fe catalyst thickness increased from 0.1 nm on the left to 3 nm on the right. The CVD conditions were 1073 K, 0.30 vol % $\text{C}_2\text{H}_2/\text{Ar}$ balance, and ambient pressure. The direction of gas flow is perpendicular to that of the catalyst's thickness gradient so as to uniformly feed the reactant gases to catalysts of different thicknesses. The height of the VA-CNTs was largely dependent on the Fe thickness; VA-CNTs were 1.4 mm tall at an Fe thickness of 0.6 nm, became shorter for the thicker Fe (>0.8 nm), and hardly grew for the thinner Fe (<0.3 nm). The VA-CNTs growing on an Fe thickness of 0.4–0.5 nm sometimes peeled off from the substrate because of the tension caused by the CNTs growing faster or longer at an Fe thickness of 0.6 nm. To grow SWCNTs of smaller diameters, thinner catalyst layers are preferable because they yield smaller catalyst particles.^{8,18} On the other hand, the growth of SWCNTs becomes

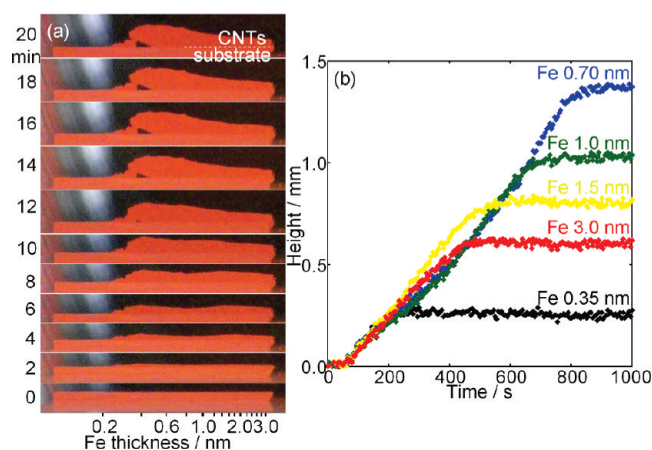


Figure 2. (a) Photographs of the SWCNT forests during growth at 2 min intervals. (b) Time profiles of CNT heights for different Fe thicknesses: 0.35 (black), 0.70 (blue), 1.0 (green), 1.5 (yellow), and 3.0 nm (red). Sample is the same as that shown in Figure 1a.

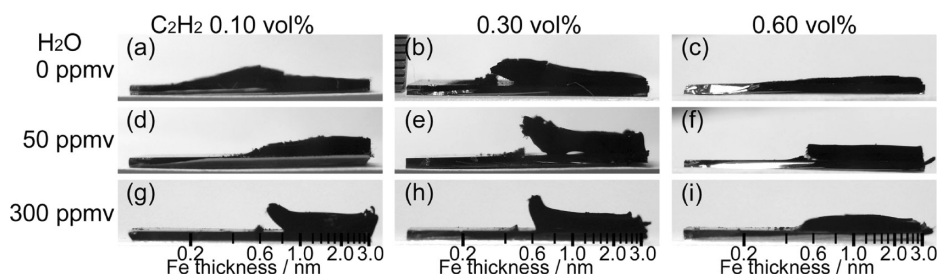


Figure 3. Side-view photographs of the CNT forests grown at 1073 K and different C₂H₂ and H₂O concentrations from the combinatorial catalyst libraries.

unstable for too thin catalyst layers (see also Figure 3). Therefore, we chose 0.7 nm thick Fe as the standard hereafter. Figure 1b shows a photograph of a CNT sample grown on a uniform 0.7 nm thick Fe without the addition of water. The CVD condition was the same as for Figure 1a. VA-CNTs grew most uniformly to 1.0 mm, whereas they grew to 1.4 mm at the edge of substrate. At the inner region of the substrate, the millimeter-tall SWCNT forest becomes the diffusion barrier for C₂H₂ to the catalyst particles staying on the substrate. Whereas at the edge of the substrate, C₂H₂ can diffuse to the catalyst particles more easily from the side of the SWCNT forests.⁸ The small width (3 mm) of the substrate used for the combinatorial catalyst library enables clear investigation of the effect of the catalyst condition on SWCNT growth by supplying C₂H₂ uniformly from the side of the SWCNT forest. Figure 1c shows a Raman spectrum of the same sample shown in Figure 1b, which was taken from the top of the forest using a wavelength of 488.0 nm for excitation. The G-band peak at ≈ 1590 cm⁻¹ was branched, and radial breathing modes (RBMs) were clearly observed at 100–200 cm⁻¹. A small D-band peak at ≈ 1360 cm⁻¹ was also observed. These features suggest the formation of SWCNTs. Figure 1a–c show that millimeter-tall SWCNTs actually grow rapidly from C₂H₂/Ar without water addition.

We monitored the growth of the CNTs on real-time using a digital camera. Figure 2a shows photographs of the same CNT sample as that shown in Figure 1a during its growth at 2 min intervals. A movie is available as Supporting Information (Movie S2). The CNTs are red at the elevated CVD temperature of 1073 K. Figure 2b shows the time profiles of the CNT forest height at various Fe thicknesses for the same sample. Regardless of Fe thickness, the initial growth rate was 1.5 $\mu\text{m/s}$. CNT growth continued at a constant growth rate and then abruptly terminated after about 10 min, which is similar to our previous report using a C₂H₄ feedstock²⁸ instead of C₂H₂. The growth lifetime largely depended on the Fe thickness. The maximum growth lifetime was 800 s for 0.7 nm thick Fe and was shorter for thinner and thicker Fe. Thus, careful optimization of the catalyst is essential for the rapid growth of millimeter-tall SWCNTs without water addition.

Effect of Water on the Rapid Growth of Millimeter-Tall SWCNTs. The effects of the Fe catalyst thickness, the concentration of carbon feedstock, and the water addition on SWCNT growth were also examined. Figure 3 shows photographs of the SWCNT samples grown using the combinatorial catalyst libraries under various CVD conditions. Without water addition (a–c), the SWCNT height largely depended on Fe thickness and C₂H₂ concentration. The SWCNTs were tallest at an optimum Fe thickness and were shorter outside of this

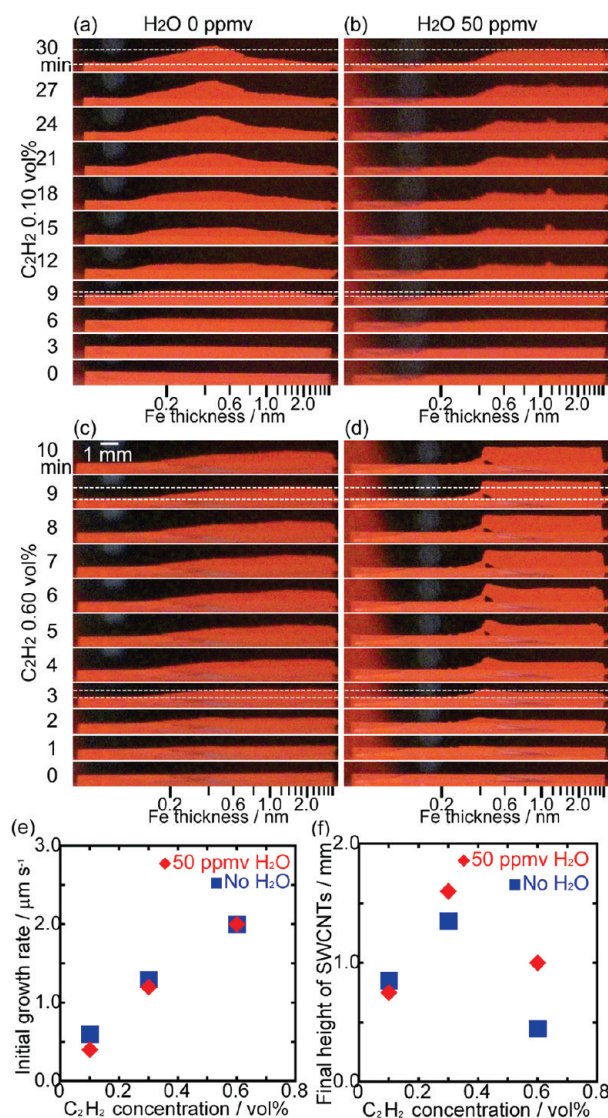


Figure 4. Photographs of CNT forests during growth at 3 min intervals. The samples are the same as those shown in: (a) Figure 3a and (b) Figure 3d, respectively. Photographs of CNT forests during growth at 1 min intervals, and the samples are the same as those shown in: (c) Figure 3c and (d) Figure 3f, respectively. Effects of C₂H₂ and H₂O concentrations on: (e) the initial growth rate and (f) the final height of the SWCNTs grown using the combinatorial catalyst libraries at an Fe thickness of 0.7 nm.

optimum at moderate C₂H₂ concentrations of 0.10–0.30 vol %. The SWCNTs were much shorter at a higher C₂H₂ concentration of 0.60 vol %. When water was added (d–i), the height distribution of the CNTs drastically changed. A clear threshold appeared for an Fe thickness of 0.5–0.6 nm, below which the CNTs hardly grew and above which the CNTs grew uniformly to around 0.8 mm in height. The CNTs were tall even for a higher C₂H₂ concentration of 0.60 vol %. The difference in SWCNT height was larger between the CNTs grown with H₂O concentrations of 0 and 50 ppmv than those grown with H₂O concentrations of 50 and 300 ppmv. These results show that the catalyst and the CVD conditions for millimeter-tall SWCNTs are limited without water addition and that water addition stabilizes their growth for a wider variety of conditions. On the other hand, SWCNT growth from a thinner catalyst layer and thus smaller catalyst particles was disturbed by water addition.

The effect of water is discussed in detail next using CMD-RTM data for each CVD condition. Figure 4a–d shows photographs of the SWCNT samples grown on the combinatorial catalyst library shown in Figure 3a, d, c, and f over 3 or 1 min intervals. Initially during SWCNT growth, the difference between the samples is small (see the white broken lines at 9 min for (a) and (b) and at 3 min for (c) and (d)). At a later stage, the difference becomes more prominent. The CNTs grow uniformly and became taller with water addition for thick Fe (>0.8 nm) at a low C₂H₂ concentration (0.10 vol %) (see the white broken lines at 30 min for (a) and (b)), and the CNTs continue to grow longer with water addition at a high C₂H₂ concentration (0.60 vol %) (see white broken lines at 9 min for (c) and (d)). Figure 4e and f shows the initial growth rate and the final height of the SWCNTs, respectively, when they were grown from a uniform 0.7 nm thick Fe catalyst at different C₂H₂ concentrations. The growth rate was not influenced by water addition and

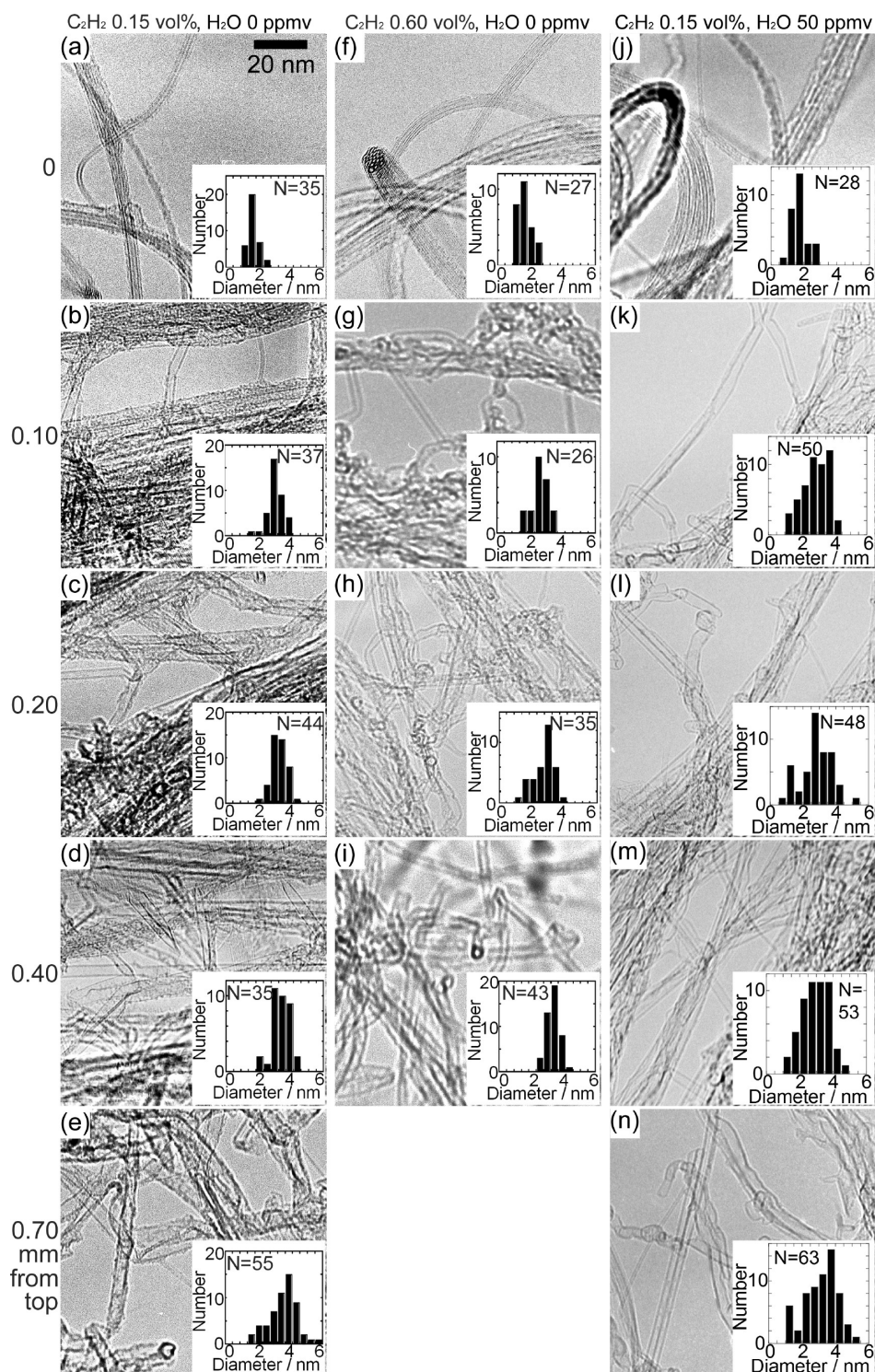


Figure 5. TEM images and diameter distributions of SWCNTs at different depths from the top of the forests. CVD was carried out at 1073 K using a uniform 0.7 nm thick Fe catalyst with: (a–e) 0.15 vol % C_2H_2 without water addition, (f–i) 0.60 vol % C_2H_2 without water addition, and (j–n) with 0.15 vol % C_2H_2 and 50 ppmv H_2O . The scale bar in (a) applies for all images.

was linearly proportional to the C_2H_2 concentration. These results show that water addition prolongs the growth lifetime of the SWCNTs only when the C_2H_2 concentration is high or the Fe thickness is not optimal.

Effects of Water and C_2H_2 Concentration on the Structure of SWCNTs. We previously found a diameter increase in the

0.8 mm tall SWCNTs from 1.7 to 3.7 nm during their rapid growth and attributed it to the coarsening of catalyst particles.²⁹ The coarsening of catalyst particles is a reason for the termination of SWCNT growth, and structural changes in the SWCNTs during their growth is a major problem for their practical application.

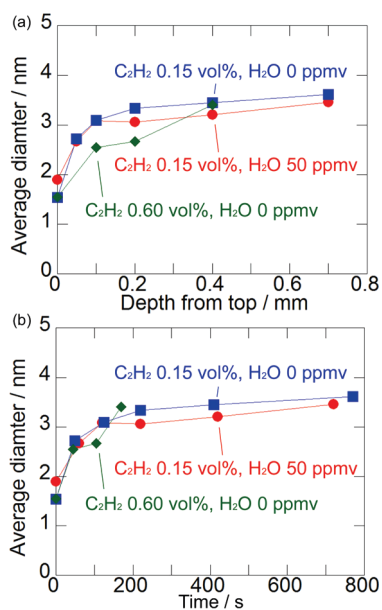


Figure 6. Average diameters of SWCNTs: (a) at different depths from the top of the forests and (b) at different times when the corresponding SWCNT parts were grown. The samples are the same as those shown in Figure 5.

Therefore, we studied the effect of water addition and C_2H_2 concentration on structural changes in SWCNTs.

Figure 5 shows transmission electron microscope (TEM) images of the SWCNTs at different depths of the forests, which were grown on a uniform 0.7 nm thick Fe catalyst until the growth termination. All CNTs were single-walled, and no MWCNTs were observed at any depth. The insets show histograms of the SWCNT diameter distributions. For each condition, the average SWCNT diameter gradually increased from 1.5 to over 3 nm. SWCNTs near the top of the forest were straight and bundled (Figure 5a, f, and j), whereas the SWCNTs at a specific distance from the top were bent and isolated and had collapsed in some cases (Figure 5b–e, g–i, and k–n), as previously reported.²⁹

Figure 6 shows average diameters of SWCNTs at different depths from the top of the forests (a) and at different times when the corresponding SWCNT parts were grown (b). When we compare the SWCNTs grown with 0.15 vol % C_2H_2 without water addition and those with 0.60 vol % C_2H_2 without water addition, the latter had the smaller average diameters than the former when plotted against depth (Figure 6a), whereas they had similar diameters when plotted against time (Figure 6b). Therefore, it proves that the diameter of SWCNTs (and that of catalyst Fe particles) increases with the CVD time rather than the SWCNT length and that the rate of diameter increase did not depend on the C_2H_2 concentration. Next, we compare the SWCNTs grown with 0.15 vol % C_2H_2 without and with water addition. These SWCNTs had similar diameters in both cases, *i.e.*, when plotted against the depth (Figure 6a)

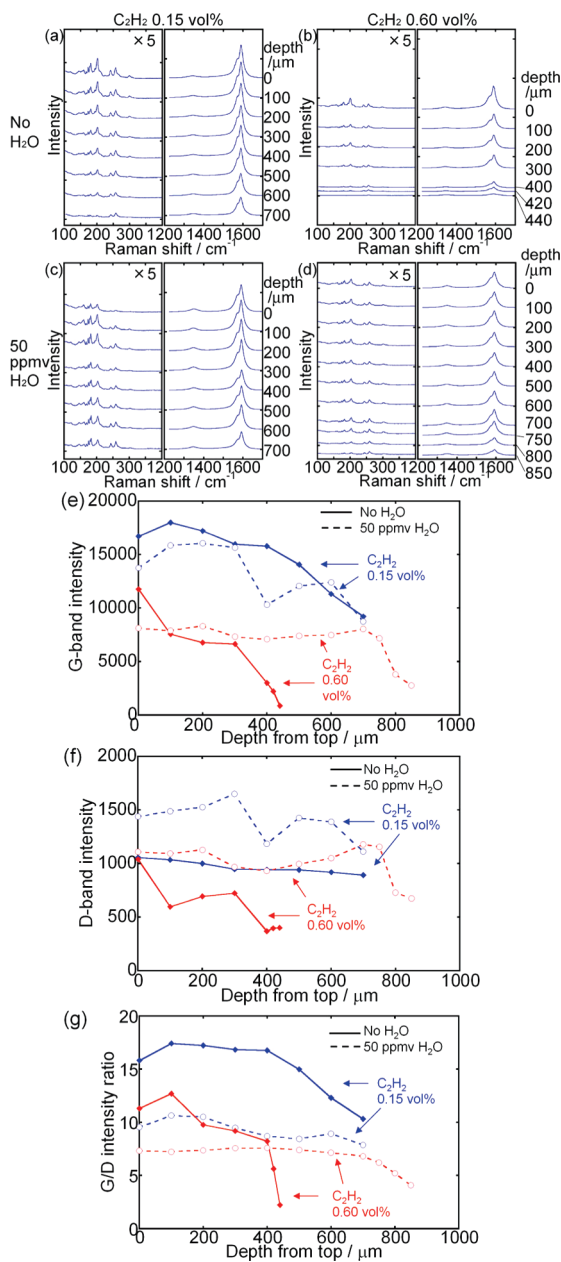


Figure 7. Raman spectra of SWCNTs taken from a cross-section at different depths from the top to the bottom using an excitation wavelength of 488 nm. CVD was carried out using uniform 0.7 nm thick Fe catalysts at 1073 K. Concentrations of C_2H_2/H_2O were: (a) 0.15/0, (b) 0.60/0, (c) 0.15/50, and (d) 0.60 vol %/50 ppmv. Peak intensities of: (e) G-band, (f) D-band, and (g) G/D peak intensity ratios at different depths from the top of the forest grown under different CVD conditions.

and when plotted against the time (Figure 6b). Because the SWCNT growth rate is the same regardless of water addition, this result is consistent with the result above, that the diameter of SWCNTs increases with the CVD time. Considering that the diameter of SWCNTs is correlated with that of catalyst particles, it proves that water addition does not affect the catalyst particle size and their coarsening rate under these conditions.

Figure 7a–d shows Raman spectra of the SWCNT forests grown using uniform 0.7 nm thick Fe catalysts at

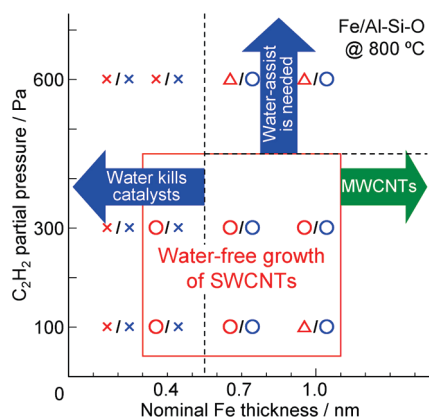


Figure 8. The window for the rapid millimeter-scale growth of SWCNTs. Figure 3 is used to determine the degree of growth from three categories: (O) millimeter-scale growth, (Δ) submillimeter-scale growth, and (\times) poor growth. Red symbols on the left represent the growth without water, and blue symbols on the right represent the growth with water.

different H_2O and C_2H_2 concentrations. The Raman spectra were obtained from the cross-section of the forests at different depths from the top using a 488.0 nm excitation wavelength. Under each condition, the intensities of the G-band and the RBM peaks decreased as the distance from the top increased. At a high C_2H_2 concentration of 0.60 vol %, the G-band peak significantly decreased, and the RBM peak disappeared at the bottom of the forest. Figure 7e–g shows: (e) the G-band peak intensities, (f) D-band peak intensities, and (g) G/D intensity ratio at different depths from the top of the forests. At 0.15 vol % C_2H_2 , the G-band intensity profile was similar for the SWCNTs grown using 0 and 50 ppmv H_2O . On the other hand, the D-band intensity was higher for the forest grown at 50 ppmv H_2O than that without water addition. As a result, the G/D peak ratio decreased for all depths when 50 ppmv H_2O was added during CVD. For 0.60 vol %, the G-band intensity was similar for the two conditions, and the D-band intensity was higher with water addition. At the bottom of the forest, the G-band intensities showed a large decrease for both conditions, and the G/D ratio was less than 5. This decrease in G-band and RBM peak intensity from the top to the bottom of the forest was also observed in our previous work.²⁹ This result indicates a decrease in the content of small diameter SWCNTs from the top to the bottom of the forest, which is in agreement with the TEM results (Figures 5 and 6). The larger D-band intensity for the SWCNTs grown with water than those without water shows that water introduces defects into the SWCNTs.

DISCUSSION

As shown above, a window for the rapid growth of millimeter-tall SWCNTs without water addition has been found. Because the partial pressures of C_2H_2

and water rather than their concentrations govern the SWCNT growth, we discuss based on their partial pressures hereafter. The window for the rapid millimeter-scale growth of VA-SWCNTs is summarized in Figure 8. At a low C_2H_2 partial pressure, the millimeter-scale growth is possible for a wide catalyst window without water. Whereas at high C_2H_2 partial pressures, SWCNT growth is suppressed without water; SWCNTs grow to submillimeter scale from relatively thick catalysts and hardly grow from thin catalysts. Water addition promotes the growth from relatively thick catalysts at high C_2H_2 partial pressures whereas inhibits the growth from thin catalysts. It should be noted that Figure 8 is qualitatively valid for different growth temperatures, but the quantitative values change depending on the growth temperature.

To grow millimeter-tall SWCNTs rapidly in 10 min, the prevention of catalyst deactivation is the most important factor. As shown in Figures 2 and 4, the SWCNTs did not grow to millimeter height when their growth stopped too early. As shown in Figure 4, a higher C_2H_2 partial pressure increased the growth rate but decreased the catalyst lifetime as well. The high carbon source feed rate caused catalyst deactivation possibly by forming a carbon byproduct on the catalyst's surface. The reaction of CNT growth is first-order, as shown in Figure 4e, whereas the reaction of carbon byproduct formation should be higher-order, resulting in the significant reduction of growth lifetime, and thus the short final height at the high C_2H_2 partial pressure. In other words, the higher-order reaction is significant only when the C_2H_2 partial pressure is high, and water prolonged the catalyst's lifetime possibly by oxidizing and removing the carbon byproduct on the catalyst's surface, as previously reported by Yamada *et al.*¹² Thus, the carbon source feeding rate should be low enough to allow for the rapid growth of millimeter-tall SWCNTs without water addition. On the other hand, water addition inhibited SWCNT growth from the thin Fe catalyst (thinner than 0.5–0.6 nm). Water may oxidize and deactivate small catalyst particles and/or oxidize small diameter SWCNTs,³⁰ but further study is needed to clarify the underlying mechanism.

The effects of water and C_2H_2 partial pressure on the structures of SWCNTs and catalyst nanoparticles are discussed next. As shown in Figures 5 and 6, the diameters of the SWCNTs increased during growth because of the coarsening of the catalyst nanoparticles. The rate of SWCNT diameter increase did not depend on water addition or C_2H_2 partial pressure. This finding conflicts with the previous report.¹⁷ Amama *et al.* reported that water prolonged SWCNT super growth by preventing the coarsening of catalyst particles through Ostwald ripening.¹⁷ They added a much higher concentration of H_2O (0.5 vol %) to 0.5 vol % C_2H_2 than we did (50 ppmv), and this large difference may have caused the difference in coarsening behavior

for the catalyst particles. It should be noted that their super growth (0.22 mm in 120 min) is much slower than that found in this work (1.4 mm in 13 min). On the other hand, the SWCNT quality was influenced by water addition. The increased D-band intensity with water addition shown in Figure 7 indicates that water introduced some defects into the SWCNTs. Water can oxidize and remove carbon byproduct on the catalyst surface and prolong SWCNT growth but can oxidize and damage the walls of SWCNTs at the same time.

Here we propose the general picture for the sustainable catalytic growth of SWCNTs. Let us think of the situation where a CNT is growing from a catalyst particle. Carbon sources decompose on the catalyst particle, and carbon atoms diffuse through/over the catalyst particle and precipitate at/bind to the edge of the CNT. Carbon atoms will attach to the regular sites of the CNT edge to grow CNTs but sometimes attach to irregular sites of the CNT edge to yield disordered structures or attach together to yield carbon byproduct. If only the forward reaction (*i.e.*, precipitation/attachment of carbon) exists, then the CNT will quickly lose its ordered structure and stop growing (note that the attachment of carbon for 10^7 times yields a millimeter-long SWCNT). If the reverse reaction (*i.e.*, dissolution/detachment of carbon) coexists, then the disordered carbon (*i.e.*, defects in CNTs and carbon byproduct) with lower stability is preferentially removed, while the ordered carbon with higher stability is preferentially formed, resulting in the growth of the CNT with the ordered structure. When we increase the feed of the carbon source (C_2H_2 in this study) to fasten the CNT growth, the forward reaction is promoted, while the reverse reaction is preserved, resulting in the disordering and/or the growth termination. Water assists the reverse reaction by oxidizing the disordered carbon but at the same time oxidizes the wall of the CNT which cannot be repaired by the catalyst. The essential requirement for the sustainable CNT growth should be the coexistence of the forward and reverse reactions, with a slightly larger rate for the former than the latter (note that their difference is the growth rate).

The next step for the better understanding and control of the SWCNT growth should be the quantification of the kinetics of both growth and termination. The former is rather simple, first order to the C_2H_2 partial pressure in our reaction system (Figure 4e). But the latter is complicated. First, the formation of “carbon by-products” needs to be quantified. We can learn from the extensive research

made in the catalyst research field.³¹ Second, the coarsening of catalyst particles possibly by Ostwald ripening^{17,19} needs to be quantified. Again, we can learn from the extensive research made in the catalyst research field.^{32,33} But, there is a big difference between the usual gas–solid catalytic reaction and the CNT growth. The main product is typically the gas for the former while the solid for the latter. Moreover, CNTs strongly bundle and aggregate with each other, which will cause some cooperative phenomena. Actually, CNT growth often terminates abruptly (Figure 2b and refs 14 and 28), which can be hardly explained just by the gradual changes in the catalyst particles due to coking and coarsening. We still need to know better what is occurring during catalytic growth of CNTs.

CONCLUSIONS

In summary, we achieved the rapid growth of millimeter-tall SWCNTs in 10–15 min using only C_2H_2/Ar without water addition. The window for this growth is determined, and the key is keeping the C_2H_2 partial pressure at a moderate level so as not to kill the catalyst. As the C_2H_2 partial pressure increases, the growth rate of SWCNTs increases linearly, whereas the growth lifetime decreases more rapidly, resulting in shorter SWCNTs. In this situation, water as low as 5 Pa effectively suppressed catalyst deactivation but damaged SWCNTs and inhibited the growth of SWCNTs with small diameters at the same time. Another important mechanism for the growth termination is the catalyst coarsening such by Ostwald ripening,^{17,19} and the average diameters of the SWCNTs actually increased during their growth. Contrarily to the previous report,¹⁷ water had no effect on this phenomenon. The next step is how to quantify the rate process of the growth termination, and we can learn from the extensive research made in the catalyst research field for coking³¹ and Ostwald ripening.^{32,33} But explaining the abrupt growth termination of CNTs^{14,28} based on the gradual coking and/or coarsening of the catalysts is still challenging.

For the large-scale production of SWCNTs, water addition would be beneficial because it widens the window for the rapid growth of millimeter-tall SWCNTs especially at high C_2H_2 partial pressures, but it does cause difficulty in the control of water at low levels (~ 5 Pa). Thus, the rapid growth of SWCNTs using a simple C_2H_2/Ar gas mixture without water addition is promising for the practical, large-scale production of SWCNTs.

METHODS

The SWCNT growth process has been described in detail elsewhere.^{8,18} Briefly, the catalysts were prepared on silicon wafers containing a thermal oxide layer. Substrate surfaces were pretreated by dipping them into a H_2SO_4/H_2O_2 solution. A 15 nm thick Al layer was sputter deposited onto the substrate and partially oxidized by exposure to air. An Fe layer was then

sputter deposited onto the Al layer. A gradient thickness profile of 0.2–3 nm was formed in the Fe layer using our previously described CMD method in which the deposition flux distribution was formed by a physical filter during sputter deposition.²⁵ The substrate was set in a tubular CVD reactor (34 mm inner diameter and 300 mm heating zone length), which had a quartz glass tube with one end closed.¹⁹ It was then heated to 1073 K

and kept at that temperature for 5 min while being exposed to a 26 vol % H₂/Ar balance mixture at a flow rate of 500 sccm at ambient pressure. During this heat treatment, the partially oxidized Al layer transforms into a disordered Al–Si–O mixed oxide via a redox reaction with SiO₂, and Fe forms nanoparticles of a certain diameter and areal density depending on the initial Fe thickness. After heat treatment, CVD was carried out by switching the gas to a 0.10–0.60 vol % C₂H₂/Ar balance mixture containing 0–300 ppmv H₂O at ambient pressure. The samples were monitored during CVD using a digital camera to obtain side-view images every 5 s through a window on one side of the reaction tube. The spacial resolution was 0.03 mm per pixel. After CVD the samples were analyzed using micro-Raman scattering spectroscopy (Horiba HR800) and TEM (JEOL 2000EX). The TEM sample was prepared by picking up a portion of the VA-SWCNTs (several μm in radial thickness and 0.8 mm in length) and laying it on a TEM grid using tweezers.²⁹

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Supporting Information Available: The composition change of the reactant gas with the residence time simulated by CHEMKIN^{34,35} and a movie of growing CNTs on the combinatorial catalyst library. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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