Growth window and possible mechanism of millimeter-thick single-walled carbon nanotube forests

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Our group recently reproduced the water-assisted growth method, so-called "super growth", of millimeter-thick single-walled carbon nanotube (SWNT) forests by using $C_2H_4/H_2/H_2O/Ar$ reactant gas and Fe/Al₂O₃ catalyst. In this current work, a parametric study was carried out on both reaction and catalyst conditions. Results revealed that a thin Fe catalyst layer (about 0.5 nm) yielded rapid growth of SWNTs only when supported on Al₂O₃, and that Al₂O₃ support enhanced the activity of Fe, Co, and Ni catalysts. The growth window for the rapid SWNT growth was narrow, however. Optimum amount of added H₂O increased the SWNT growth rate but further addition of H₂O degraded both the SWNT growth rate and quality. Addition of H₂ was also essential for rapid SWNT growth, but again, further addition decreased both the SWNT growth rate and quality. Because Al₂O₃ catalyzes hydrocarbon reforming, Al₂O₃ support possibly enhances the SWNT growth rate by supplying the carbon source to the catalyst nanoparticles. The origin of the narrow window for rapid SWNT growth will also be discussed.

Keywords: Single-Walled Carbon Nanotubes, Vertically Aligned Nanotubes, Combinatorial Method, Growth Mechanism, Growth Window

1. INTRODUCTION

Single-walled carbon nanotubes (SWNTs) have unique mechanical and electrical properties, and many applications for them have been proposed and researched. To realize practical applications, mass production of SWNTs is essential, and various catalytic chemical vapor deposition (CCVD) methods have been developed to achieve this mass production. There are two types of CCVD; one involving nanoparticle catalysts suspended in the gas phase and the other involving nanoparticle catalysts supported on substrates. A gas-phase production process, the so-called "HiPco process", is the first process to be used in the mass production of SWNTs.¹ Recently, remarkable progress has been made in CCVD processes using supported catalysts. Submicrometer-thick films of randomly-oriented SWNTs have been the typical product when supported catalysts are used. In 2003, vertically aligned single-walled carbon nanotubes (VA-SWNTs) were realized² by using alcohol catalytic CCVD (ACCVD).³ VA-SWNTs have now been achieved using several CVD methods and conditions.⁴⁻⁷ As a result, CCVD from substrates now has potential as a process in the mass production of SWNTs.

Among those growth methods, the water-assisted method, so-called "super growth",⁴ realized an outstanding growth rate of a few micrometers per second, leading to millimeter-thick VA-SWNTs forests. However, many research groups have failed in reproducing "super growth", and the underlying mechanism of the growth rate enhancement by water remained unclear. By using our combinatorial method for catalvst optimization,^{8,9} we recently reproduced the "super growth" method and showed the important role of catalyst supports.¹⁰ In this current work, by doing a parametric study, we report in detail the effect of the catalyst and reaction conditions determined, and discuss the novel mechanism essential for rapid growth VA-SWNTs.

2. EXPERIMENTAL

Catalysts were prepared on SiO_2 substrates by sputter-deposition. An Al_2O_3 layer was formed by depositing 15-nm-thick Al on a substrate and then exposing the layer to ambient air. Fe was deposited

on Al₂O₃ layers or directly on SiO₂ substrates. For a separate experiment, gradient-thickness profiles of Fe were formed by using combinatorial masked deposition (CMD) method previously described.⁹ The catalysts were set in a tubular CVD reactor (22 mm in diameter and 300 mm in length), heated to a target temperature (typically 1093 K), and kept at that temperature for 10 min while being exposed to 27 kPa H₂/75 kPa Ar at a flow rate of 500 sccm, to which H₂O vapor was added at the same partial pressure as for the CVD condition (i.e., 0 to 0.03 kPa). During this heat treatment, Fe forms nanoparticles of a certain diameter and areal density depending on the initial Fe thickness.⁸ After the heat treatment, CVD was carried out by switching the gas to $C_2H_4/H_2/H_2O/Ar$. The standard condition was 8.0 kPa C₂H₄/ 27 kPa H₂/ 0.01 kPa H₂O/ 67 kPa Ar at 500 sccm at 1093 K for 10 min. The samples after CCVD were analyzed by using transmission electron microscopy (TEM) (JEOL JEM-2000EX), field emission scanning electron microscopy (FE-SEM) (Hitachi S-900), and micro-Raman scattering spectroscopy (Seki Technotron, STR-250) with an excitation wavelength at 488 nm.

3. RESULTS AND DISCUSSION

3.1. Standard condition of "super growth"

Figure 1a shows a photograph of CNT samples grown by a combinatorial catalyst library under the standard condition. Millimeter-thick vertically aligned CNTs (VA-CNTs) were grown at regions where the Fe thickness was 0.4 nm or more. The maximum thickness of VA-CNTs was 1.2 mm at a Fe thickness of 0.5 nm. The thickness of VA-CNTs decreased when Fe thickness exceeded 0.5 nm.

Figure 1b shows TEM images of CNTs grown under the same condition as Fig. 1a on substrates with uniform Fe thicknesses of 0.5 and 1.0 nm. SWNTs with a diameter around 4 nm mainly grew for 0.5-nm-thick Fe catalyst, whereas thicker CNTs grew for 1.0-nm-thick Fe catalyst. This difference in CNTs is because a thicker initial Fe layer yields larger Fe nanoparticles,⁸ indicating a narrow VA-SWNTs growth window for the initial Fe thickness.

Figure 1c shows Raman spectra of the same CNT sample as Fig. 1a taken at Fe thicknesses of 0.5, 0.8, and 1.0 nm. Sharp, branched G-bands with a small D-band and peaks of radial breathing mode (RBM) were detected, indicating the existence of SWNTs. The G/D peak area ratios were smaller for thicker Fe layers (≥ 1 nm), because multi-walled CNTs (MWNTs) became the main product when a



Fig. 1 CNTs grown on the Fe/Al₂O₃ catalyst library under the standard condition (8.0 kPa $C_2H_4/27$ kPa $H_2/0.010$ kPa $H_2O/67$ kPa Ar at 1093 K for 10 min)

. (a) Side view photograph of CNTs grown on the combinatorial catalyst library. (b) Raman spectra of the same sample at Fe thickness of 0.5, 0.8 and 1.0 nm. Intensity at the low wavenumber region (< 300 cm⁻¹) was 10x magnified. (c) TEM images of CNTs grown on substrates with uniform Fe thickness of 0.5 nm (left) and 1.0 (right) nm.

thicker Fe layer was used as catalyst.

These figures show that "super growth" was achieved in this work. The growth temperature of the standard condition of this work is higher than that of the original "super growth" ⁴ because both the CNT thickness and the G/D ratio increased with increasing growth temperature.

3.2. Effects of catalyst metals and supports

Effects of catalyst metals and their supports were investigated next. Figure 2a shows top-view photographs of CNT samples grown on the Fe/Al_2O_3 , Co/Al_2O_3 , and Ni/Al_2O_3 combinatorial catalyst libraries under the standard condition. The

surfaces of both Fe/Al₂O₃ and Co/Al₂O₃ libraries became black at regions where the Fe thickness was 0.4 nm or more. On the other hand, the surface of Ni/Al₂O₃ was somewhat darkened only at the relatively thin Fe region around 0.5 nm. Figure 2b shows cross-sectional SEM images of these samples. About 200- μ m-thick VA-CNTs grew for 0.5-nm-thick Co and about 0.4- μ m-thick VA-CNTs grew for 0.5-nm-thick Ni..

Figure 2c shows top-view photographs of combinatorial catalyst libraries of Fe/SiO₂, Co/SiO₂, and Ni/SiO₂ after CVD under the standard condition. The results were completely different from those libraries with Al₂O₃ support layer (i.e., Fe/Al₂O₃, Co/Al₂O₃, and Ni/Al₂O₃); VA-CNTs did not form on any library and only part of the surface of Fe/SiO₂ for the thickness range from 0.4 to 0.6 nm darkened slightly compared with the library before CVD. As for Co/SiO₂ and Ni/SiO₂, negligible change appeared in color. Figure 2d shows the Raman spectra for the Fe/ SiO₂ sample in Fig. 2b at Fe thickness of 0.5 nm, indicating growth of SWNTs. Fe catalyst supported on SiO₂ can actually grow CNTs, including SWNTs, although the CNT yield is much smaller (submicrometer thickness or less) than that grown using catalysts supported on Al₂O₃ (up to millimeter thickness), regardless of the thickness of the catalyst.

Next, we examined if an Al₂O₃ catalyst support layer actually acts as Al₂O₃ rather than metallic Al. Another catalyst library was prepared by first depositing 15-nm-thick Al on SiO₂, then exposing the layer to ambient air, then oxidizing the layer under air at 973 K for 5 min, and finally depositing a gradient thickness profile of Fe on the layer at ambient temperature. Figure 3a shows photographs of the Fe/ Al₂O₃ catalyst libraries before CVD. In the thick Fe region (≥ 2 nm), both libraries were metallic silver in color. In the thinner region (< 2 nm), the Al layer only exposed to air was gray metallic in color, indicating the existence of metallic Al, whereas the Al layer oxidized at 973 K was completely transparent, indicating the complete oxidation of the Al layer. Then, CVD was carried out on these libraries. Figure 3b shows the photograph after CVD of the library with the Al layer oxidized at high temperature. The growth of the VA-CNT films was similar to that without high-temperature oxidation of the Al layer (Fig. 1a), indicating that the surface of the Al layer was oxidized by just being exposed to air, and that the layer acted as an Al₂O₃ support.

Fe nanoparticles can grow SWNTs on either SiO_2 or Al_2O_3 supports, but they need to be



Fig. 2 Effects of catalyst metals and supports on CNT growth under the standard condition. (a,c) Top-view photographs of CNTs samples grown by combinatorial catalyst libraries prepared on Al_2O_3 (a) and SiO_2 (c). All of the catalyst metals (i.e. Fe, Co, Ni) had the same thickness profiles between 0.2 nm (left) and 3 nm (right). (b) Cross-sectional FE-SEM images of the CNTs samples grown by 0.5-nm-thick Co and Ni catalysts prepared on Al_2O_3 . (d) Raman spectrum of the CNTs samples grown by 0.5-nm-thick Fe catalyst prepared on SiO_2 supports. Intensity at the low wavenumber region (<300 cm⁻¹) was 10x magnified.



Fig. 3 Effect of the preparation process of Al_2O_3 layer. (a) Photographs of Fe/Al₂O₃ catalyst libraries before CVD. Al₂O₃ layer was formed by oxidizing 15-nm-thick Al layer only by exposure to ambient air (top) and then by oxidizing in air at 973 K (bottom). (b) Photograph of CNT grown on the Fe/Al₂O₃ library with Al₂O₃ layer oxidized at 973 K (same library as Fig. 3a, bottom).

supported on Al_2O_3 to achieve rapid growth of VA-CNTs at a rate of micrometers per second. In addition, Al_2O_3 support enhances the CNT growth by other catalysts (i.e., Co and Ni). Al_2O_3 support layer should have an essential role in growing CNTs.

3.3. Effects of H₂O and H₂

Figure 4a shows the thickness profiles of CNTs grown on Fe/Al₂O₃ catalyst libraries under the standard condition, except that the amount of added H₂O (i.e. partial pressure) was varied. Without H₂O, CNTs grew only at the relatively thin Fe region (0.3-1.0 nm) and the maximum thickness of VA-CNTs was 0.7 mm at the 0.5 nm-thick Fe region. Addition of 0.010 kPa H₂O enhanced the growth, especially at the thick Fe region (> 0.7 nm), and the maximum VA-CNT thickness increased to 1.0 mm at the 0.5-nm-thick Fe region. Further H₂O addition (0.030 kPa) inhibited CNT growth at the thin Fe region (0.3- 0.6 nm) where SWNTs grew at the lower H_2O partial pressures (≤ 0.010 kPa). Figure 4b shows the G/D ratios for each CVD condition at Fe thickness of 0.5, 0.8, and 1.0 nm. Slight addition of H₂O (0.010 kPa) did not affect the G/D ratio at the thin Fe region (0.5 nm), but decreased the G/D ratio at the thicker regions (0.8 and 1.0 nm). Further addition of H₂O (0.030 kPa) significantly decreased the G/D ratio at all regions. These results show that proper amount of



Fig. 4 Effect of H_2O on CNT growth. CVD was carried out by using Fe/Al₂O₃ combinatorial catalyst libraries under the standard condition except the amount of added H_2O (partial pressure) was varied. (a) Relationship between thickness of VA-CNTs and Fe thickness at different H_2O pressures. (b) Relationship between G/D ratio of Raman spectra and Fe thickness at different H_2O pressures.

 H_2O enhances the growth rate of CNTs, but excessive H_2O decreases the growth rate of CNTs from small nanoparticles (i.e. small Fe thickness) and degrades the quality of CNTs possibly by oxidation. In conclusion, excess H_2O totally inhibits "super growth" of SWNTs.

Figure 5a shows thickness profiles of CNTs grown under the standard condition except that the amount of added H_2 (i.e. partial pressure) was varied. When a lower amount of H_2 was added (2.7 kPa), VA-CNTs became much thinner at Fe thickness of 0.7 nm or less. When a large amount of H_2 was added (54 kPa), CNTs grew at any Fe thickness at a reduced VA-CNT thickness (around 0.4 mm). Figure 5b shows the G/D ratios for each CVD condition at Fe thickness of 0.5, 0.8, and 1.0



Fig. 5 Effect of H_2 on CNT growth. CVD was carried out by using Fe/Al₂O₃ combinatorial catalyst libraries under the standard condition except the amount of added H_2 (partial pressure) was varied. (a) Relationship between thickness of VA-CNTs and Fe thickness at different H_2 pressures. (b) Relationship between G/D ratio of Raman spectra and Fe thickness at different H_2 pressures.

nm. The G/D ratios decreased in either case of lower (2.7 kPa) and higher (54 kPa) H_2 was added. These results indicate that an optimum amount of H_2 is needed for rapid growth of VA-SWNTs of relatively good quality.

3.4. Possible mechanism of rapid growth of VA-SWNTs

Based on the results discussed above, we propose three necessary conditions for "super growth" of SWNTs. The first condition is that the Fe catalyst needs to be thin enough, about 0.5 nm, so that the catalyst nanoparticles are small enough to grow SWNTs with small diameters. The second condition is that the catalyst nanoparticles need to be supported on Al_2O_3 . The third is that the partial



Fig. 6 Schematic of enhancement mechanism of SWNT catalytic growth by Al₂O₃ support.

pressures of both H_2O and H_2 need to be carefully adjusted; these gases are essential but excessive amounts degrade the growth rate and/or the quality of SWNTs.

Al₂O₃ and its related materials have long been used as catalysts for decomposition and dehydrogenation of hydrocarbons.^{11,12} Figure 6 shows a schematic of our proposed mechanism explaining the enhancement effect of Al₂O₃ on CNT growth. In this mechanism, C₂H₄ or its derivatives adsorb on Al2O3, diffuse over Al2O3 surface to catalyst nanoparticles, and then are incorporated in Fe nanoparticles. In contrast, when Fe is deposited directly on SiO₂, C₂H₄ can be decomposed only on Fe nanoparticles whose surface is largely covered with growing CNTs. As a result, the growth rate of CNTs on Al_2O_3 is much faster than that on SiO_2 . In addition, the catalytic activity of Al2O3 strongly depends on its crystalline structure.¹¹ α -Al₂O₃, the most stable phase, has low activity,¹¹ and thus, rapid CNT growth does not occur when catalysts are supported on sapphire (i.e. monocrystalline α -Al₂O₃).

Next, we discuss why the window of "super growth" for SWNTs is narrow. One reason might be due to the catalyst deactivation mechanism, i.e. coking of either Al₂O₃ surface or Fe nanoparticles. In the dehydrogenation process of hydrocarbons,¹¹ Al₂O₃ easily loses its catalytic activity due to carbon deposition, and thus, H₂O vapor has long been used to remove carbon byproducts. H₂ also keeps the Al₂O₃ surface reactive by controlling the balance between dehydrogenation and hydrogenation of carbon surface species, as is known in the hydrocracking process.¹³ In contrast, excessive H₂ inhibits the growth of SWNTs by hydrogenating C₂H₄-derivatives adsorbed on Al₂O₃. Concerning Fe nanoparticles, when the incoming flux of carbon into Fe nanoparticles increases, carbon in Fe nanoparticles will be highly supersaturated, resulting not only in increased SWNT growth rate but also in graphite formation on the surface of the nanoparticles. The fewer walls and larger free energy of SWNTs than MWNTs may

make the degree of supersaturation larger for nanoparticles growing SWNTs than those growing MWNTs. This may be the reason why the "super growth" window for SWNTs is such narrow compared with MWNTs. (Note that MWNTs grow rapidly under a wide window of reaction conditions if catalyst nanoparticles are supported on Al_2O_3). In conclusive, two conditions are needed to sustain the rapid growth of SWNTs: first, the partial pressures of C_2H_4 , H_2 , and H_2O need to be balanced to suppress coking of Al_2O_3 , and second, the incoming flux of carbon into Fe nanoparticles must not be too large, that means nanotubes must not grow too rapid, to prevent carbonization of Fe nanoparticles.

4. CONCLUSION

Rapid growth of VA-SWNTs, namely, a few micrometers per second, or so-called "super growth", was reproduced in this study, and the growth window was clarified. The standard condition of this work was 8.0 kPa C₂H₄/ 27 kPa H₂/ 0.01 kPa $H_2O/67$ kPa Ar at 500 sccm at 1093 K for 10 min using a tubular CVD reactor (22 mm in diameter and 300 mm in length). Results showed that for the rapid growth of SWNTs, small nanoparticles formed from a thin Fe layer (about 0.5 nm) need to be supported on Al₂O₃ and that only the optimal amounts of H₂O and H₂ should be used. We proposed a novel mechanism by which Al₂O₃ enhances the growth rate of SWNTs, and offered a simple explanation of the effect of H₂O and H₂ on the growth rate. Namely, Al₂O₃ supports supply a carbon source to Fe nanoparticles, and H₂O and H₂ prevent catalyst deactivation by keeping the Al₂O₃ surface reactive and by balancing the carbon fluxes among the gas-phase, Al_2O_3 support, Fe nanoparticles, and growing SWNTs.

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