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COMMUNICATIONS

A Background Level of Oxygen-Containing Aromatics for Synthetic Control of Carbon Nanotube Structure

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The addition of a background level (∼100−200 ppm) of water into the growth ambient has shown to dramatically improve the activity and lifetime of catalysts to synthesize vertically aligned single-walled carbon nanotube (SWNT) forests (“Super-growth”).[1−7] Based on the fundamental understanding that water reactivates catalysts by the removal of a carbon coating,[8] recent work showed that essentially any material containing oxygen could replace water as a “growth enhancer.”[9]

Besides the growth enhancer, another critically important factor is the catalyst. The general understanding is that the carbon nanotube (CNT) diameter matches the catalyst size as observed by Cheung et al.[10] In addition, larger diameter CNTs tend to possess increased wall numbers.[4,11−15] Therefore, the general approach to control the wall number is to adjust the catalyst size which is commonly done by adjusting the thickness of the thin film catalyst layer[4,11−14] or catalyst pretreatment.[15] These methods were all performed during or before the catalyst formation phase; therefore, prior to growth, the catalyst is tuned to synthesize the CNTs with the desired wall number and size.

In this communication, we report a completely different approach to tailor the CNT size and wall number by only introducing an oxygen-containing aromatic, constituting only ∼0.02% of the growth ambient, during the growth phase. By merely replacing water with oxygen-containing aromatics as growth enhancers, we could grow CNTs of different diameters and wall numbers under identical growth conditions and with the identical catalyst. Under conditions where water produced predominantly SWNTs (2.8 nm), we could synthesize double-walled carbon nanotubes (DWNTs) with populations as high as 84% with an average size of 5.4 nm with methyl-benzoate and few-walled CNTs with benzoaldehyde. This phenomenon is both surprising and differs from previous approaches to control wall numbers of CNTs.[4,11−15]

All CNT syntheses were performed using the same catalyst (Al_2O_3 (40 nm)/Fe (1 nm)) on silicon wafers. CNTs were synthesized with C_2H_4 (75 sccm) and various growth enhancers. Specifically, synthesis used He with H_2 as carrier gases (total flow 1 L per minute) at 1 atm with a controlled amount of growth enhancer (100−200 ppm) on a fully automated chemical vapor deposition (CVD) furnace with *in situ* telecentric height monitoring[16] and a syringe pump for precise injection of aqueous growth enhancers. It should be noted that every process prior to growth was identical, and therefore this profound difference can only be attributed to the growth phase. These growth conditions and catalyst were for water-assisted CVD “Super-growth” to grow SWNTs with a selectivity of ∼99%.

Different from water-assisted CVD for SWNTs, we found that mainly DWNTs or MWNTs could be synthesized by using different growth enhancers. Forests were grown with different growth enhancers (water, methyl-benzoate, and benzoaldehyde) from identical catalysts and growth conditions and characterized by Raman spectroscopy and transmission electron microscopy (TEM). First, macro-Raman spectroscopy (532 nm, $\tilde{\phi}100\ \mu$mshowed typical features for SWNTs using water, while the CNTs grown with methyl-benzoate and benzoaldehyde exhibited a decrease in graphitic band-to-disorder band ratio and the absence of radial breathing modes. This behavior is typical of MWNTs (Figure 2a). Second, TEM observations showed solely SWNTs grown with water and much larger nanotubes with an increased wall number for methyl-benzoate and benzoaldehyde (Figure 1a−c). Third, diameters and wall numbers were plotted in histograms from the TEM images (Figure 1d−f). With methyl-benzoate, DWNTs were predominant (84%) with a mean diameter of 5.4 nm (water, 100% SWNT; d_{ave}, 2.8 nm). With benzoaldehyde, the wall number (DW/3W/4W: 1.8:1:1) and size (5.7 nm) further increased. Unlike previous methods[4,11−15] where the catalyst size was tuned, this approach provides the easy and convenient growth of various kinds of nanotubes from the same catalyst and same growth conditions (Figure 2b).

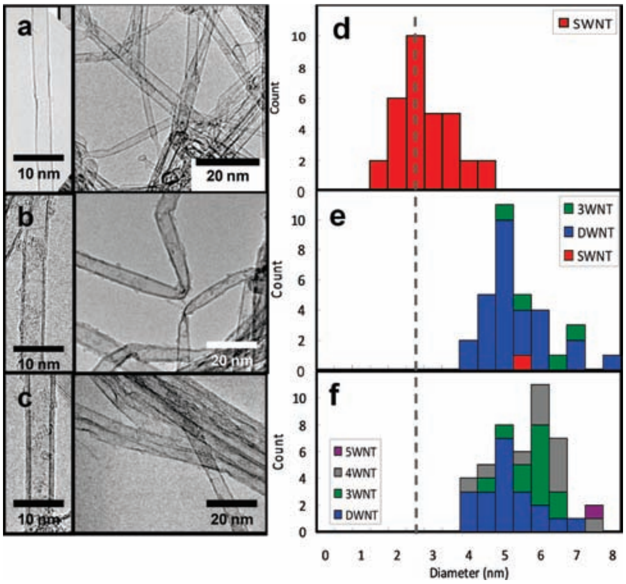

Figure 1. Structural change by growth enhancer. TEM images of CNTs using (a) water, (b) methyl-benzoate, and (c) benzoaldehyde growth enhancers. Histograms of the diameter and wall number for (d) water, (e) methyl-benzoate, and (f) benzoaldehyde growth enhancers.

The 84% DWNT selectivity was one of the highest reported without any additional selectivity improvement processes.[17,18] The selective DWNT synthesis using an Fe thin film catalyst was previously described by examining the relationship between the

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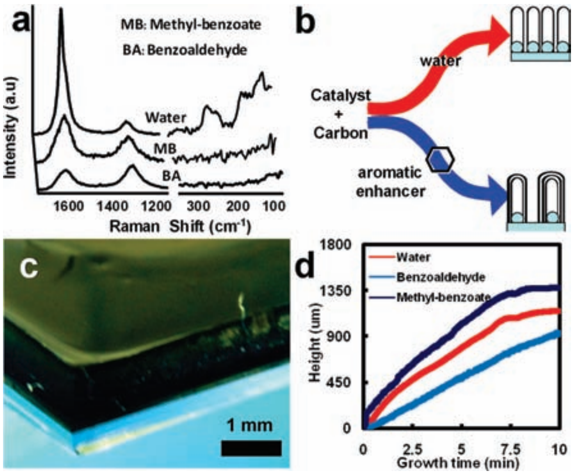

Figure 2. Growth of SWNTs to MWNTs. (a) Raman spectra of forest grown using water, methyl-benzoate, and benzoaldehyde. (b) Schematic of different CNT growth. (c) Photograph of the DWNT forest. (d) Growth curves for each growth enhancer.

nanotube diameter and wall number, with the diameter associated with the optimum DWNT population as 3.7 nm.[11] The 5.4 nm mean diameter found here differed significantly yet using a similar catalyst. Therefore the aromatic growth enhancers not only induced a shift in the CNT diameters but also changed the relationship between the CNT diameter and wall number.

Further growth characterization revealed that the methyl-benzoate and benzoaldehyde growth enhancers both influenced the CNT structure as well as increased the growth efficiency comparable to the case for water. As with water, increasing levels of methyl-benzoate or benzoaldehyde caused the growth yield to rise, then peak at some optimum level, and decrease. The optimum levels were ~200 ppm for both cases resulting in a C/O ratio of 375 and 750, respectively (ratio of carbon atoms in the carbon source to the oxygen atoms from the growth enhancer). Similar to water, the required amount of methyl-benzoate and benzoaldehyde was extremely small, but the influence on the growth was great. An image of a forest and their optimized growth curves (Figure 2c,d) showed forests could be grown to 1174, 1380, and 929 μm in a 10 min growth time with water, methyl-benzoate, and benzoaldehyde with extended lifetimes (7−10 min) and initial growth rates (~100 μm/min). Similar growth kinetics meant that DW and MWNT forests grown by benzoaldehyde and methyl-benzoate possessed the exceptional properties of supergrowth, such as high purity, surface area, long length, and alignment.

The most striking point is that this huge effect is caused by a minute level of growth enhancer. The catalyst could not have induced this phenomenon because their structures were identical at the onset of growth from their identical catalyst formation processes. In addition, as the optimized growth enhancer levels were only ~200 ppm, the carbon atoms in the growth enhancer could not have produced the additional layers or could not have reacted with the carbon source in the gas phase. As other growth enhancers (water, carbon dioxide, alcohol, acetone, etc.) could grow SWNTs,[9] we associate this effect to the phenyl groups. Adjusting the carbon concentration, to control dissociative adsorption of the carbon source at the catalyst surface, has been reported to modify CNT structure.[19] An extension of this model to include a background level (0.02%) change with a different carbon-containing species may partially explain our results. We preliminarily interpret that rigid π-stacking of the aromatic groups, from dissociated enhancer molecules, at the catalyst surface act as an oversized template to support growth of larger CNTs with increased walls. Theoretical studies should help to understand this effect at the atomic/molecular level.

In conclusion, we demonstrate a background level of oxygen-containing aromatics can control the structure of synthesized CNTs. This result opens up a new approach to control the CNT wall number and diameter simply by minutely changing the growth ambient. This approach holds advantages over tailoring the catalyst prior to growth.

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References

(1) Hata, K.; Futaba, D. N.; Mizuno, K.; Namai, T.; Yumura, M.; Iijima, S. *Science* **2004**, *306*, 1362–1364.
(2) Hart, A. J.; van Laake, L.; Slocum, A. H. *Small* **2007**, *3*, 772–777.
(3) Gong, K.; Chakrabarti, S.; Dai, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 5446–5450.
(4) Ci, L. J.; Vajtai, R.; Ajayan, P. M. *J. Phys. Chem. C* **2007**, *111*, 9077.
(5) Hayamizu, Y.; Yamada, T.; Mizuno, K.; Davis, R. C.; Futaba, D. N.; Yumura, M.; Hata, K. *Nat. Nanotechnol.* **2008**, *3*, 289–294.
(6) Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanaike, O.; Hatori, H.; Yumura, M.; Iijima, S. *Nat. Mater.* **2006**, *5*, 987–994.
(7) Amama, P. B.; Pint, C. L.; McJilton, L.; Kim, S. M.; Stach, E. A.; Murray, P. T.; Hauge, R. H.; Maruyama, B. *Nano Lett.* **2009**, *9*, 44–49.
(8) Yamada, T.; Maigne, A.; Yudasaka, M.; Mizuno, K.; Futaba, D. N.; Yumura, M.; Iijima, S.; Hata, K. *Nano Lett.* **2008**, *8*, 4288–4292.
(9) Futaba, D. N.; Gotou, J; Yasuda, S.; Yamada, T.; Yumura, M.; Hata, K. *Adv. Mater.* **2009**, *21*, 1–5.
(10) Cheung, C. L.; Kurtz, A.; Park, H.; Lieber, C. M. *J. Phys. Chem. B* **2002**, *106*, 2429–2433.
(11) Yamada, T.; Namai, T.; Hata, K.; Futaba, D. N.; Mizuno, K.; Fan, J.; Yudasaka, M.; Yumura, M.; Iijima, S. *Nat. Nanotechnol.* **2006**, *1*, 131–136.
(12) Bennett, R. D.; Hart, A. J.; Cohen, R. E. *Adv. Mater.* **2006**, *18*, 2274–2279.
(13) Kayastha, V. K.; Wu, S.; Moscatello, P.; Yap, Y. K. *J. Phys. Chem. C* **2007**, *111*, 10158–10161.
(14) Zhao, B.; Futaba, D. N.; Yasuda, S.; Akoshima, M.; Yamada, T; Hata, K. *ACS Nano* **2008**, *3*, 108–114.
(15) Nessim, G.D.; Hart, A. J.; Kim, J. S.; Acquaviva, D.; Oh, J.; Morgan, C. D.; Seita, M.; Leib, J. S.; Thonpson, C. V. *Nano Lett.* **2008**, *8*, 3587–3593.
(16) Yasuda, S.; Futaba, D. N.; Yumura, M.; Iijima, S.; Hata, K *Appl. Phys. Lett.* **2008**, *93*, 143115–18.
(17) Lyu, S. C.; Lee, T. J.; Yang, C. W.; Lee, C. J. *Chem. Commun.* **2003**, *373*, 1404–1405.
(18) Endo, M.; Muramatsu, H.; Hayamshi, T.; Kim, Y. A.; Terrones, M.; Dresselhaus, M. *Nature* **2005**, *433*, 476–476.
(19) Kayastha, V. K.; Yap, Y. K.; Dimovski, S.; Gogotsi, Y. *Appl. Phys. Lett.* **2004**, *85*, 3265–3267.

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