Vertically Aligned ^{13}C Single-Walled Carbon Nanotubes from No-flow Alcohol Chemical Vapor Deposition and their Root Growth Mechanism

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Abstract

We present the successful synthesis of aligned ^{13}C labeled single-walled carbon nanotube (SWNT) arrays from alcohol by a modified no-flow chemical vapor deposition (CVD) method which makes possible efficient growth using a small amount of carbon source. Synthesis of high-quality SWNTs by this alternate method was confirmed by Resonance Raman spectroscopy, which also showed the quality is uniform during the growth. The synthesis of ^{13}C labeled SWNTs provides clear and solid evidence for the root growth mechanism in alcohol CVD, which agrees well with the TEM observations.

KEYWORDS: SWNT, ACCVD, no-flow, isotope, ^{13}C, Raman, root growth

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1. Introduction

A single walled carbon nanotube (SWNT)[1, 2] is a novel one-dimensional material possessing attractive electric, mechanical, and thermal properties.[3] Driven by the potential applications of SWNTs, many methods have been proposed to synthesize SWNTs.[4-12] Among these, alcohol catalytic chemical vapor deposition (ACCVD) can yield high-quality SWNTs at moderate temperatures.[8] It is also the first method by which vertically aligned SWNT arrays were obtained.[9] However, the incomplete understanding of the growth mechanism in this process, e.g. insufficient information about the catalyst status and position during growth, hinders full control over the final product.

Isotope labeling is a strong technique to identify the reaction pathway in chemical reactions. It has been used to identify the catalyst location, i.e. so-called root growth or tip growth,[13] in the synthesis of multi-walled carbon nanotubes (MWNTs), and also the growth sequence of graphene layers in MWNTs.[14, 15] One challenge in applying this isotope method to ACCVD is that, due to the high ethanol flow rate, the percentage of supplied ethanol converted into the final SWNT product is typically less than 0.04%. This low efficiency makes the use of an isotope-labeled carbon source prohibitively expensive. Therefore, an improvement in the ethanol efficiency of the current ACCVD method is necessary.

For other considerations, isotope-labeled aligned SWNTs are also useful to identify the different vibration modes in Raman spectroscopy studies, as the presence of isotopes would change the phonon energy while keeping the electron structure unaltered.[16, 17] A bulk material with controlled isotope concentration, or a sequenced nanotube junction might also be interesting regarding thermal conductivity in SWNTs.[18]

Here, we present the synthesis of aligned SWNT arrays from a no-flow CVD condition,[19] in which as much as 40% of the supplied ethanol was converted into the final product. The high efficiency of this process enables us to grow ^{13}C SWNT arrays from a small amount of isotope labeled ethanol. The ^{12}C-^{13}C junction from sequential feeding of two different carbon sources confirmed the SWNT array forms by the root growth model.

2. Experimental

SWNT arrays were grown on quartz at temperatures from 750 to 850ºC using ethanol as a carbon source and Co/Mo bimetal as catalyst. The catalyst was prepared through the previously reported dip-coat process[9] and the 0.5 gram ^{13}C ethanol carbon source was purchased from Cambridge Isotope Inc. In principle, ^{13}C SWNT arrays can be easily obtained from typical ACCVD process as long as the carbon source, normal ^{12}C ethanol, is replaced by ^{13}C labeled ethanol. However, as the ethanol flow rate is typically 300-500 sccm, 0.5 grams of ^{13}C ethanol would be consumed in just a few minutes. Therefore, instead of passing ethanol throughout the growth time, we only fed ethanol only until reaching the desired pressure, from 0.3 to 2.0 kPa in the current study, and then sealed the chamber and waited for the SWNTs to grow from that limited amount of ethanol. When growing ^{12}C -^{13}C SWNT junctions, ^{12}C ethanol was first fed into the growth chamber until reaching the desired

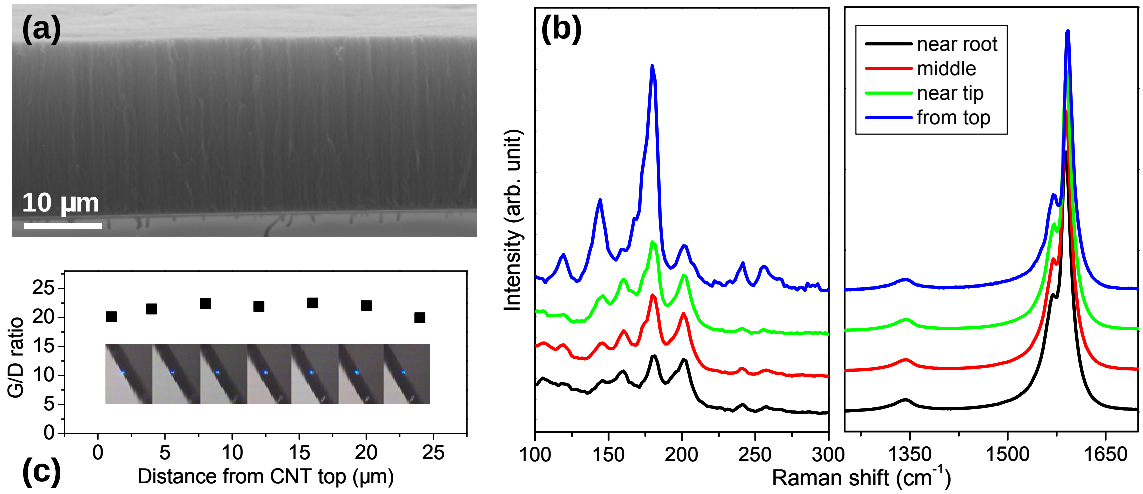

Fig. 1: (a) SEM image of the as-grown aligned SWNTs from no-flow CVD, (b) Raman spectra at different positions along the height of an SWNT array, (c) ratio of G/D peak intensities at different position along the SWNT arrays, with inset optical microscope images showing the corresponding incident laser positions.

pressure. After 1 minute of growth, the chamber was evacuated (within 1 min), and then ^{13}C ethanol was introduced at the same pressure for the second stage of growth. The film thickness in all experiments was measured *in situ* by a 488nm laser, and the as-grown SWNTs were characterized using SEM, Raman spectroscopy, and optical absorption spectroscopy.

3. Results and Discussion

3.1. No-flow ACCVD

Figure 1(a) presents a typical SEM image of 25 µm aligned SWNT arrays from a 10 min no-flow CVD. One significant difference between the no-flow condition and our normal CVD is that, as there is no gas refreshment inside the chamber, the gas composition continually changes during growth. Accordingly, the quality of the SWNTs at different height in the array might also be different. Additionally, the SWNT growth byproduct, e.g. H_2O, might also have a more significant impact than in the normal CVD. Therefore, the as-grown arrays were characterized using micro-Raman spectroscopy, which allowed us to obtain spectra from several small regions (a few square micrometers) along the height of the array. In the spectra obtained from different locations on the film, as shown in Fig. 1(b), the G/D intensity ratio varied only from 20 to 23 (Fig. 1(c)), which suggests the SWNT quality is uniform from the top to the root. TEM observation also confirmed that the arrays are comprised of SWNTs, with little amorphous carbon; no MWNTs were found. Notably, the absence of constant ethanol refreshment in the chamber resulted in some difference in the growth curves (not shown), but the reason for this is still being investigated.

3.2. ^{13}C vertically aligned SWNT arrays

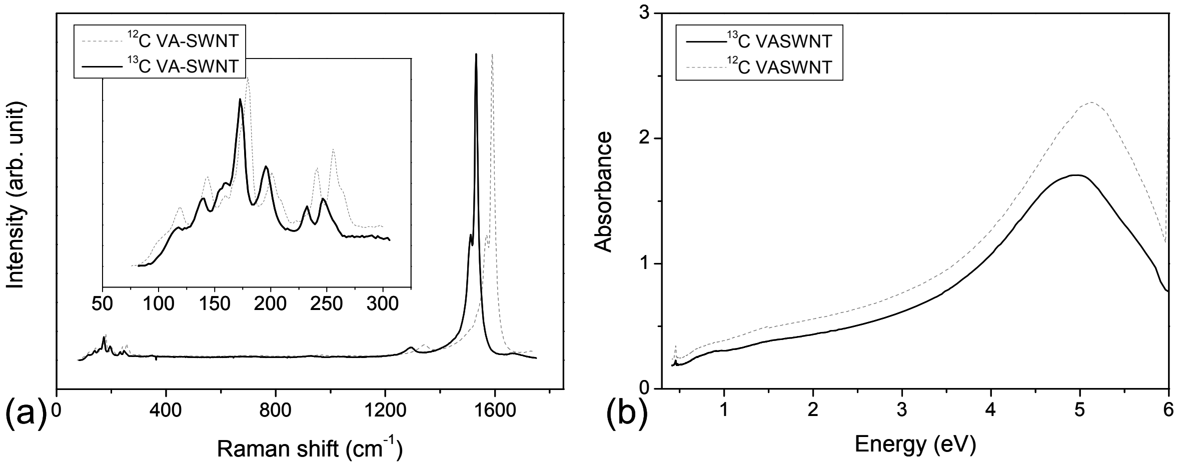

Fig. 2: (a) Raman and (b) optical absorption spectra of the ^{13}C (solid line) and ^{12}C (dashed line) aligned SWNT arrays, showing (a) the shifted phonon energy and (b) similar electronic structure.

In this work, the most attractive feature of the no-flow condition is that the conversion rate of ethanol to SWNTs is much higher than in the conventional CVD method. After weighing both the ethanol fed into the chamber and the nanotubes produced, the conversion rate was found to be as high as 40%. Thus, no-flow CVD enables us to grow SWNTs from small amounts of ethanol, which is critical for the successful synthesis of aligned ^{13}CNT arrays from our 0.5 gram of ^{13}C ethanol and also for the cost-performance of future advances in SWNT mass production.

Figure 2(a) shows a typical Raman spectrum of a 4 μm aligned SWNT film obtained in 1 min using 0.02 gram of ^{13}C ethanol. As only 0.02 gram of ethanol is needed for one CVD run, more than 20 samples of ^{13}C aligned SWNTs can be reproduced with 0.5 grams of ethanol. The G band, D band, and RBM peaks in Raman spectra are all shifted to $\sqrt{12/13}$ of the ^{12}C position (dashed line), confirming the apparent isotope effect. This shift is due to the larger atomic mass of ^{13}C, and thereby a different phonon energy. As the electron structure of the isotope does not change, the optical absorption in Fig. 2(c) shows little difference in peak positions. One exception is a shift of the plasmon peak to lower energy, which may be caused by poor alignment.20) It was also noted that the catalyst lifetime in the ^{13}C case is usually shorter than when using normal ^{12}C ethanol, and is thereby thinner in film thickness. Incubation time to initiate the CNT growth was also observed sometimes. These differences might be caused by the lower purity of the ^{13}C ethanol, as isotope-labeled molecules were not supposed to very different chemically in reactions.

3.3 ^{12}C-^{13}C SWNT junctions and their root growth model

Besides the pure ^{13}C carbon nanotubes, we also grew ^{12}C-^{13}C SWNT junctions, which is interesting in understanding the SWNT growth mechanism or studying thermal conductivity of SWNT. Figure 3(a) gives an example of the ^{12}C-^{13}C junction, synthesized by first feeding ^{12}C ethanol, followed by evacuating the chamber and then feeding of ^{13}C ethanol. From the *in situ* optical absorption in Fig. 3(b), the entire array contains 8 μm of ^{12}C and 1 μm of ^{13}C nanotubes. As the ^{12}C is fed before the ^{13}C, the location of this 1 μm ^{13}C can be used to clarify if the SWNTs are grown from the root of the array or the tip. Figure 3(c) shows a change in Raman spectra along the array. It is clearly shown that the ^{13}C can only be detected near the root of the SWNT array; this is solid evidence for the root growth mechanism, shown by the schematic in the inset of 3b.

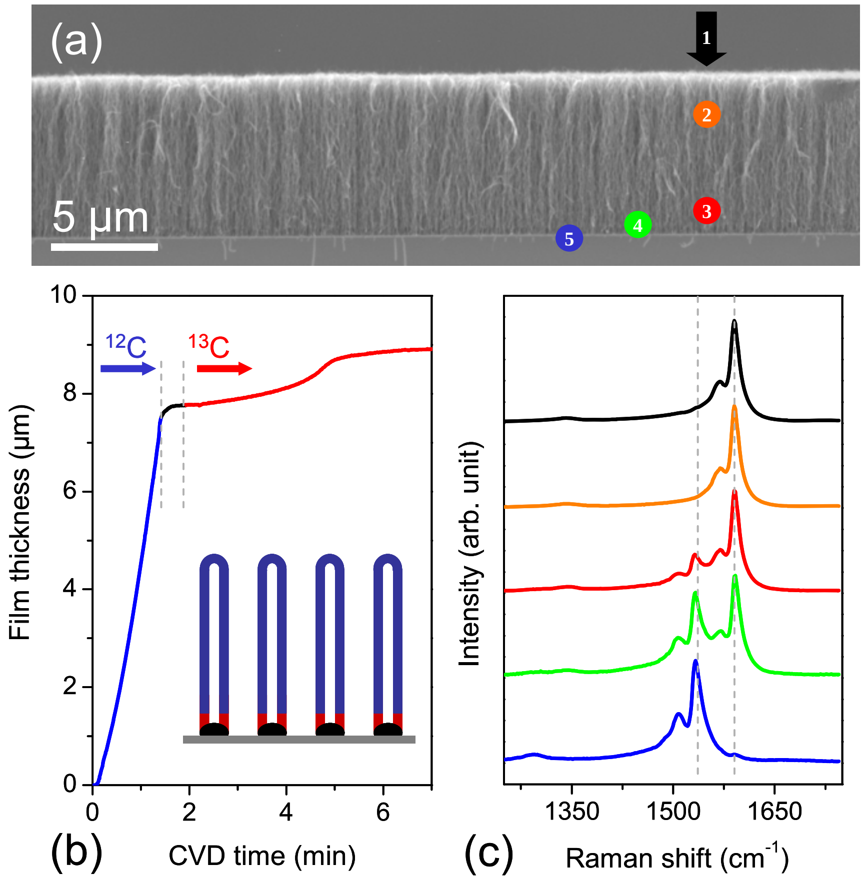

Fig. 3: (a) SEM image, (b) growth curve from *in situ* optical absorption, and (c) cross-sectional Raman spectra across a ^{12}C-^{13}C junction. The arrow and spots in (a) represents the direction and position of the incident light. The inset schematic in (b) illustrates the junction structure in case of root growth.

We also compared the above findings with our previous TEM observation. Under TEM, most of the catalyst particles were usually found at one edge of the array, which should be identified as root region from this study. The other edge, i.e. the tip region, was usually clean and metal species were seldom observed. The reason why the root model were usually found to be dominant in the case of vertical growth, as also confirmed in other CVD methods,[14, 15, 21-24)] might need further investigation.

4. Conclusions

We report the growth of ^{13}C enriched, aligned SWNT arrays using a no-flow CVD, where the carbon conversion efficiency from ethanol to SWNTs can be as high as 40%. The sequential feeding to two types of isotope-labeled ethanol resulted in ^{12}C-^{13}C SWNT junctions, which provided concrete evidence for the root growth mechanism of SWNTs synthesized by ACCVD. Clarification on the root growth model is critical in understanding the growth and catalyst deactivation mechanisms in ACCVD. It also affords better control over producing aligned SWNT arrays with tailored morphologies. More work in this area is in progress.

References

1. S. Iijima, T. Ichihashi: Nature **363** (1993) 603.
2. D. S. Bethune, C. H. Kiang, M. S. Devries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers: Nature **363** (1993) 605.
3. R. Saito, G. Dresselhaus, M. S. Dresselhaus: *Physical Properties of Carbon Nanotubes*. (Imperial College Press, London, 1998).
4. A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, R. E. Smalley: Science **273** (1996) 483.
5. C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. L. de la Chapelle, S. Lefrant, P. Deniard, R. Lee, J. E. Fischer: Nature **388** (1997) 756.
6. H. J. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley: Chem. Phys. Lett. **260** (1996) 471.
7. P. Nikolaev, M. J. Bronikowski, R. K. Bradley, F. Rohmund, D. T. Colbert, K. A. Smith, R. E. Smalley: Chem. Phys. Lett. **313** (1999) 91.
8. S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, M. Kohno: Chem. Phys. Lett. **360** (2002) 229.
9. Y. Murakami, S. Chiashi, Y. Miyauchi, M. H. Hu, M. Ogura, T. Okubo, S. Maruyama: Chem. Phys. Lett. **385** (2004) 298.
10. K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima: Science **306** (2004) 1362.
11. G. Y. Zhang, D. Mann, L. Zhang, A. Javey, Y. M. Li, E. Yenilmez, Q. Wang, J. P. McVittie, Y. Nishi, J. Gibbons, H. J. Dai: Proc. Natl. Acad. Sci. U.S.A. **102** (2005) 16141.
12. G. F. Zhong, T. Iwasaki, K. Honda, Y. Furukawa, I. Ohdomari, H. Kawarada: Chem. Vap. Deposition **11** (2005) 127.
13. S. B. Sinnott, R. Andrews, D. Qian, A. M. Rao, Z. Mao, E. C. Dickey, F. Derbyshire: Chem. Phys. Lett. **315** (1999) 25.
14. L. Liu, S. S. Fan: J. Am. Chem. Soc. **123** (2001) 11502.
15. M. Pinault, V. Pichot, H. Khodja, P. Launois, C. Reynaud, M. Mayne-L'Hermite: Nano Lett. **5** (2005) 2394.
16. F. Simon, C. Kramberger, R. Pfeiffer, H. Kuzmany, V. Zolyomi, J. Kurti, P. M. Singer, H. Alloul: Phys. Rev. Lett. **95** (2005) 017401.
17. Y. Miyauchi, S. Maruyama: Phys. Rev. B **74** (2006) 35415.
18. J. Shiomi, S. Maruyama: Phys. Rev. B **74** (2006) 155401.
19. H. Oshima, Y. Suzuki, T. Shimazu, S. Maruyama: Japanese Journal of Applied Physics **submitted** (2007).
20. Y. Murakami, E. Einarsson, T. Edamura, S. Maruyama: Phys. Rev. Lett. **94** (2005) 087402.
21. X. Li, A. Y. Cao, Y. J. Jung, R. Vjatai, P. M. Ajayan: Nano Lett. **5** (2005) 1997.

22. L. B. Zhu, Y. H. Xiu, D. W. Hess, C. P. Wong: Nano Lett. **5** (2005) 2641.
23. T. Iwasaki, G. F. Zhong, T. Aikawa, T. Yoshida, H. Kawarada: J. Phys. Chem. B **109** (2005) 19556.
24. R. Xiang, G. H. Luo, W. Z. Qian, Q. Zhang, Y. Wang, F. Wei, Q. Li, A. Y. Cao: Adv. Mater. **19** (2007) 2360.

Figure Captions

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