Production of Single-Wall Carbon Nanotubes at High Pressure†

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Using a graphite rod with a hole filled with the powder of a mixture of Y–Ni alloy and graphite as anode, single-wall carbon nanotubes (SWCNTs) with 50%–70% purity were produced in quantity of tens of grams a day under the arc conditions of 40–60 A d.c. and helium pressure of 2 atm. If calcium–nickel was used as catalyst instead of yttrium–nickel, high yields of SWCNTs can also be produced in large quantities, although the yield was slightly less than that of yttrium–nickel. The samples were characterized by SEM, HREM, and Raman spectroscopy. The results showed that the SWCNTs produced with yttrium–nickel as catalyst had the same structures as those obtained from laser-ablation with Co–Ni as catalyst. SWCNTs with smaller diameters were found when calcium–nickel was used as catalyst, proving that the diameter of SWCNTs is dependent on the properties of the metal catalysts. Furthermore, high helium pressure can lead to a high yield of SWCNTs. Our results suggested a formation mechanism of SWCNTs and the roles played by nickel and yttrium or calcium element.

Introduction

Single-wall carbon nanotubes (SWCNTs) have many potential applications including material as a good conductor,[1] quantum wires,[2] nano-devices,[2] and field-effect transistors,[3] etc. Scientists everywhere are eager to find a cheap way to produce large quantities of SWCNTs. Up to now, laser ablation[4,5] and d.c. arc-discharge method[6,7,8] are the most common ways to synthesize SWCNTs. Compared to the laser ablation method, the d.c. arc-discharge method can get more SWCNTs. Journet et al.[6] obtained a high yield of SWCNTs in the "collar" of the deposit with Y/Ni as catalyst. However, it is believed that a lot more products should be obtained in the soot. More recently, we synthesized SWCNTs in the cloth-like soot in quantity of grams with ~40% purity by the arc-discharge method with Y–Ni alloy as catalyst under 500 Torr helium atmosphere. It was found that high helium pressure seems to favor the formation of SWCNTs.[7] Although positive atmosphere was ever used,[8,9] a negative atmosphere pressure is generally used to synthesize fullerenes or carbon nanotubes in the arc-discharge method. In this report, we used a positive atmospheric pressure instead of negative pressure during the arc and 50% ~ 70% purity of SWCNTs was obtained in quantity of tens of grams. In addition, if calcium–nickel was instead of yttrium–nickel as catalyst, high yield SWCNTs can also be produced in large quantities although the yield is slightly less. The samples were characterized by SEM, HREM and Raman spectroscopy. The roles of nickel and yttrium or calcium element in the formation of SWCNTs are discussed.

Experimental Section

The SWCNTs were produced by the d.c. arc-discharge method similar to the one reported earlier.[7] The anode was a $\phi 6 \times 150$ mm graphite rod (spectroscopy pure) with a $\phi 4 \times 100$ mm hole drilled and then filled with a powder mixture of Y–Ni alloy or CaC_2/Ni (2 to 1 atomic ratio of Ni to Y or Ca) and graphite in metal/C atomic ratio of 3 to 10. The CaC_2/Ni composite anode was made in a glovebox to avoid the reaction between CaC_2 and water in air so as to ensure CaC_2 remaining intact in the preparing process of the rod. An arc was generated between the anode and a sharp-top graphite cathode at ~40 A in 2 atm of helium static atmosphere. The gap distance of the electrodes was maintained at ~10 mm by continuously translating the anode throughout the arc process. A cloth-like soot formed on the entire inner wall of the chamber afterward. In general, it took 2 h to spend a 10 cm anode rod and 5 g of soot can be obtained. If the composite rods were made directly from the mixture of graphite and catalyst powder, it was possible to obtain ~60 g of soot a day.

The raw soot was characterized by scanning electron microscope (SEM) (S-4200, Hitachi), high-resolution transmission electron microscope (HREM) (Topcon 002B, working at 200 kV) and Raman spectroscopy at room temperature (Renishaw System 1000, excited with 782 nm radiation).

Results and Discussion

Figure 1a shows a typical image for the case of Y–Ni alloy as catalyst, where many SWCNT bundles can be found together

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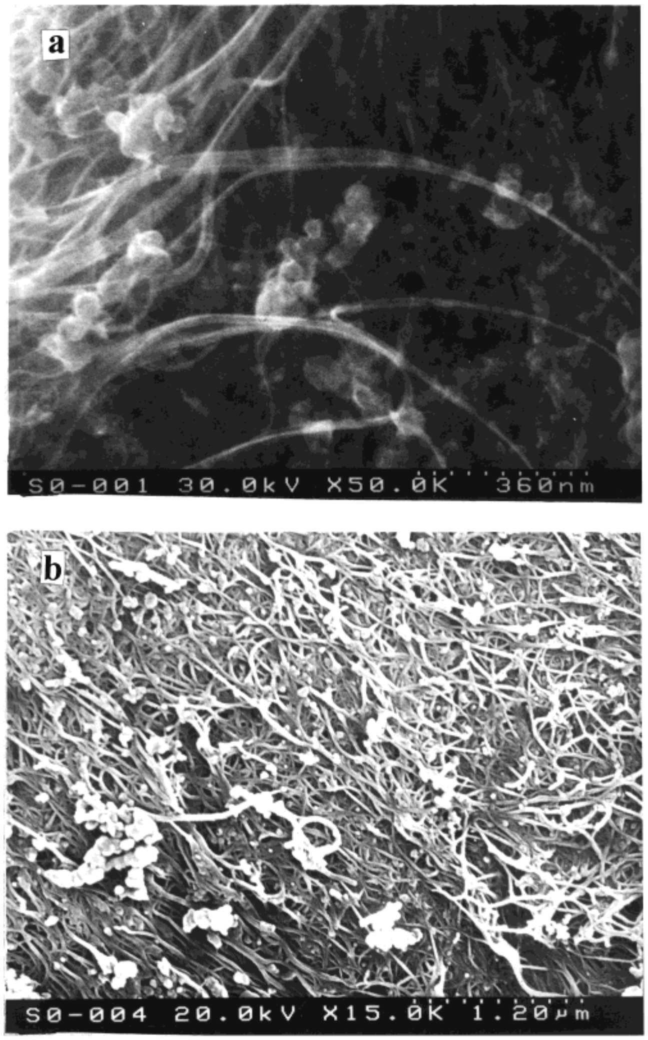

Figure 1. The surface SEM image of raw cloth-like soot produced with Y−Ni as catalyst, containing many SWCNTs, accompanied by other particles (a). Areas containing high density and purity of SWCNTs can also be easily found (b).

with other particles on most of the surface of the soot. The areas containing very pure SWCNT bundles with high density can also be easily observed as in Figure 1b. The bundles generally have diameters of 20−30 nm and lengths longer than 10 μm. The exact length cannot be measured because no bundle can be observed with both ends of the bundle at the same time.

By comparing the EM image and the Raman spectra with those from samples produced by laser ablation,[4] it is estimated that the cloth-like soot contains 50%−70% SWCNTs in samples produced with Y−Ni as catalyst. The yield of SWCNTs produced with CaC_2−Ni as catalyst under the same arc-discharge conditions, however, is slightly less.

The diameters of SWCNTs produced with the above two catalysts as seen from their TEM images are, surprisingly, very different. Those with Y−Ni as catalyst have a diameter range from 1.1 to 1.4 nm (as shown in Figure 2a), which is the same as those produced by the laser-ablation method. In contrast, those with CaC_2−Ni as catalyst have smaller diameters, ranging from 0.9 to 1.1 nm and containing very few SWCNTs with diameter of 1.3 nm, as shown in Figure 2b. This phenomena is similar to that reported earlier;[10] the diameters of SWCNTs are dependent on the catalyzed metals.

The diameter difference can also be characterized by the Raman spectra (Figure 3). Comparing the two spectra in Figure 3, it can be seen that the Raman features higher than 300 cm^{-1} are basically identical, but they are very different in the low wavenumber area. The low wavenumber region contains radial-breathing mode of SWCNTs. Note that the highest vibrational frequency is 207.5 cm^{-1}, corresponding to 1.13 nm diameter of SWCNTs according to the method proposed by Kurti et al.,[11] in SWCNTs produced with Y−Ni as catalyst but is 228.2 cm^{-1}, corresponding to 1.03 nm diameter of SWCNTs, in those produced with CaC_2−Ni as catalyst. The inset is the magnified figure in the low wavenumber area. Many previous studies have reported that the frequency of the radial-breathing mode depends strongly on the diameter of SWCNTs, with lower frequencies corresponding to SWCNTs with larger diameters.[11,12] Therefore, SWCNTs with small diameters exist in the sample produced with CaC_2−Ni as catalyst, a result consistent with TEM images.

In examining the conditions most favorable to producing higher yields, we found that the pressure of the helium atmosphere is a very important factor. No cloth-like soot was formed when the helium pressure was less than 300 Torr. Moreover, the viscosity of the soot increases with increasing helium pressure.[7] In general, the yield of SWCNTs is higher with more viscous soot. Therefore, the higher than atmospheric helium pressure used can obviously promote the yield of SWCNTs. High atmospheric pressure corresponds to a high temperature gradient from the center of the arc to the water-cooled oven wall. Our experimental results showed that high temperature gradient is a very important factor affecting the formation of SWCNTs. Furthermore, we found that lower current could prevent the formation of other kinds of carbon. Both contribute to the high yield of SWCNTs found in the soot.

We confirmed the results of a previous report[6] that no cloth-like soot can form if nickel and yttrium or calcium are absent in the anode, which means that both metal elements are necessary for the high-yield production of SWCNTs. We postulate that the metal elements, which can form acetylides, are playing the key role in the growth process of SWCNTs. These metals (yttrium and calcium) can form chemical bonds with both C_2^{2-} and other metal such as nickel, and also with the carbon nuclei of fullerenes which have conjugation π bonds. On the other hand, the encapsulation of C_{60} in the nanotube implies an open-end growth scheme, which allows mass transportation into the nanotubes.[13,14] So, in the growth process of nanotubes, the acetylide metal atom (or ion) will stay in the open cap end of the nanotube and at same time draw nickel atoms (or ions) to the open area of the nanotube. The latter catalyzes the growth of carbon nanotubes. As the growing nanotube moves out of the high-temperature area, which supports nanotube growth, the open cap closes and the metal atoms (or ions) leave the end of the nanotube. In this way, the nickel element plays the role of catalyst but the acetylide metal only plays a linkage role in the formation of carbon nanotubes. This conjecture can reasonably account for the fact that the yield of SWCNTs can be greatly improved with a mixture of two metals as catalyst. It can also be expected that alkali and alkaline-earth metal can be used as an effective catalyst in the production of SWCNTs and that the diameters of SWCNTs can be controlled with these different catalysts.

Conclusion

SWCNTs with 50%−70% purity were produced in tens of grams a day with Y−Ni alloy as catalyst in 2 atm helium atmosphere. In addition, high-yield SWCNTs can be produced in large quantities with calcium−nickel as catalyst. The SWCNTs produced with yttrium−nickel as catalyst have the

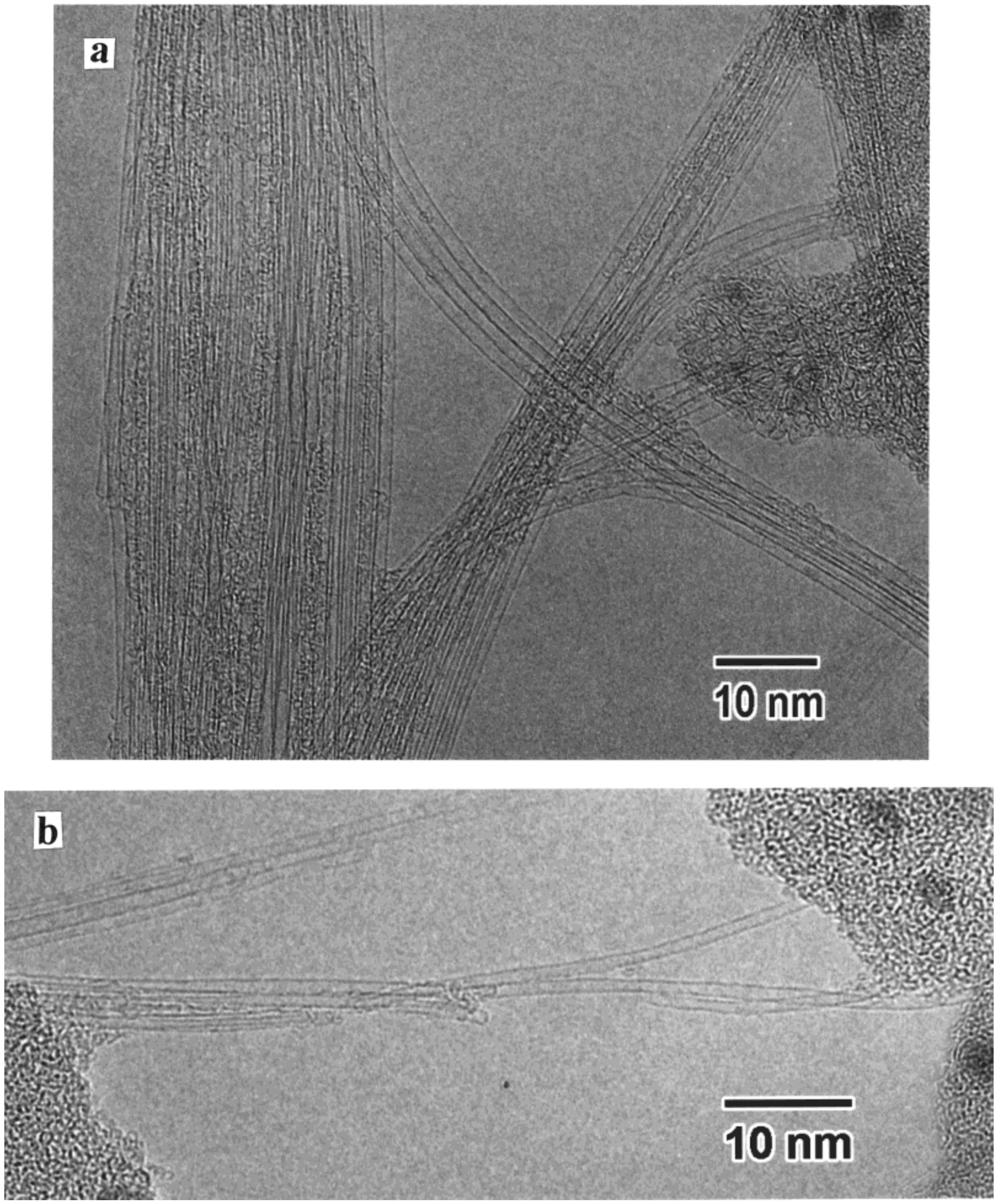

Figure 2. HREM images of SWCNTs produced with Y−Ni (a) and CaC_2−Ni (b) as catalyst, respectively. Note that the SWCNTs produced with Y−Ni as catalyst (a) have a larger diameter than those produced with CaC_2−Ni as catalyst (b).

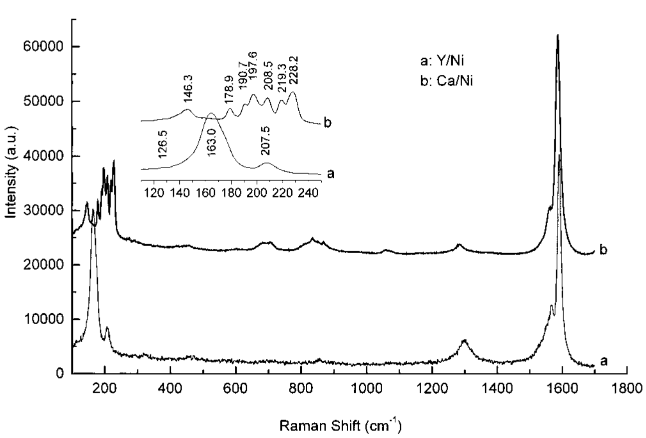

Figure 3. Room-temperature Raman spectra of SWCNTs, (a) produced with Y−Ni and (b) CaC_2−Ni as catalyst. Note that the vibrational frequencies of the radial-breathing mode of SWCNTs in (b) are obviously higher.

same structures as those obtained from laser-ablation with Co−Ni as catalyst, but the calcium−nickel catalyzed SWCNTs have a small diameter. This means that the diameter of SWCNTs depends on the properties of the metal catalysts. Furthermore, we confirm again that high helium pressure favors the high-yield formation of SWCNTs. The result suggested that the nickel element plays the role of catalyst but the acetylide metal only plays a linkage role in the formation of SWCNTs.

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References and Notes

(1) Tans, S. J.; Devoret, M. H.; Dai, H. J.; et al. *Nature* **1997**, *386*, 474.

(2) Collions, P. G.; Zettl, A.; Bando, H.; Thess, A.; Smalley, R. E. *Science* **1997**, *278*, 100.

(3) Martel, R.; Schmidt, T.; Shea, H. R.; Hertel, T.; Avouris, Ph. *Appl. Phys. Lett.* **1998**, *73*, 2447.

(4) Thess, A.; Lee, R.; Nikolaev, P.; et al. *Science* **1996**, *273*, 483.
(5) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; et al. *Appl. Phys. A* **1998**, *67*, 29.
(6) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; et al. *Nature* **1997**, *388*, 756.
(7) Shi, Z. J.; Lian, Y. F.; Zhou, X. H.; Gu, Z. N.; et al. *Carbon* **1999**, *37*, 1449.
(8) Saito, Y.; Tani, Y.; Miyagawa, N.; et al. *Chem. Phys. Lett.* **1998**, *294*, 593.
(9) Saito, Y.; Koyama, T.; Kawabata, K. *Z. Phys. D* **1999**, *40*, 421.
(10) Kasuya, A.; SaSaki, Y.; Saito, Y.; Tohji, K.; Nishina, Y. *Phys. Rev. Lett.* **1997**, *78*, 4434.
(11) Kurti, J.; Kresse, G.; Kuzmany, H. *Phys. Rev. B* **1998**, *58*, 8869.
(12) Rao, A. M.; Richter, E.; Bandow, S.; et al. *Science* **1997**, *275*, 187.
(13) Smith, B. W.; Monthioux, M.; Luzzi, D. E. *Nature* **1998**, *396*, 323.
(14) Zhang, Y.; Iijima, S.; Shi, Z. J.; Gu, Z. N. *Philos. Mag. Lett.* **1999**, *79*, 473.