Selective Production of Single-Wall Carbon Nanohorn Aggregates and Their Formation Mechanism

Daisuke Kasuya,*,† Masako Yudasaka,‡ Kunimitsu Takahashi,§ Fumio Kokai,§ and Sumio Iijima†,‡,||

Department of Material Science and Engineering, Faculty of Science and Technology, Meijo University, 1-501 Shiogamaguchi, Tenpaku-ku, Nagoya, Aichi 468-8502, Japan, "Nanotubulites" Project, Japan Science and Technology, c/o NEC, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan, Institute of Research and Innovation, 1201 Takada, Kashiwa, Chiba 277-0861, Japan, and NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan

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Single-wall carbon nanohorn (SWNH) aggregates can be produced by CO_2 laser vaporization of carbon, and a single aggregate can take either a "dahlia-like" or "bud-like" form. We found that "dahlia-like" SWNH aggregates were produced with a yield of 95% when Ar at 760 Torr was used as the buffer gas, while "bud-like" SWNH aggregates were formed with a yield of 70 or 80% when either He or N_2 at 760 Torr was used. The internal structures of both aggregates were studied by partially burning them in an O_2 atmosphere. We were then able to examine the mechanism for the formation of SWNH aggregates.

1. Introduction

Since the discovery of novel carbon nanometer-sized materials such as fullerenes,[1] carbon nanotubes,[2] and single-wall carbon nanohorn (SWNH) aggregates,[3] controlling their structure and size has been one of the most intriguing challenges in the material science field. The aggregates can be produced with a yield of about 95% by CO_2 laser ablation of graphite at room temperature. An SWNH is a horn-shaped sheath composed of single-wall graphene sheets, 2 to 3 nm in diameter, that form an aggregate with a diameter of about 80 nm. These SWNHs protrude from the surface of the aggregate like the petals of a dahlia; we therefore call them "dahlia-like" SWNH aggregates. The ethanol adsorption capacity of these aggregates is considerably larger than that of commercially obtainable activated carbon.[4] An oxidation treatment can produce pores in the aggregates, and their specific surface area increases with the oxidized temperature.[5]

Another type of SWNH aggregate is known as a "bud-like" aggregate. This new type of aggregate is also composed of SWNHs, but they do not protrude from the surface of the aggregate. Although this aggregate can be formed using a high-intensity CO_2 laser,[3] the yield is too low to enable properties such as adsorption capacity to be studied.

In this article, we discuss how it is possible to selectively produce SWNH aggregates by choosing the type of buffer gas used and its pressure. To understand the formation mechanism of SWNH aggregates, their structures were studied by partially burning them in O_2.

2. Experimental Section

We used a CO_2 laser vaporization technique to produce SWNH aggregates. As the experimental apparatus used has previously been reported in detail,[3] only a brief account is given here. A graphite target rod (50-mm length, 30-mm external diameter, 99.99% purity) was set in the middle of a plastic-resin chamber ($30 \times 30 \times 25$ cm^3). After the chamber was evacuated, it was filled and buffer gas was run through; the gas pressure was kept constant. The buffer gas used was either He, Ar, or N_2. The gas pressure was 150, 300, 450, 600, or 760 Torr. Laser vaporization was done by focusing a CO_2 laser beam

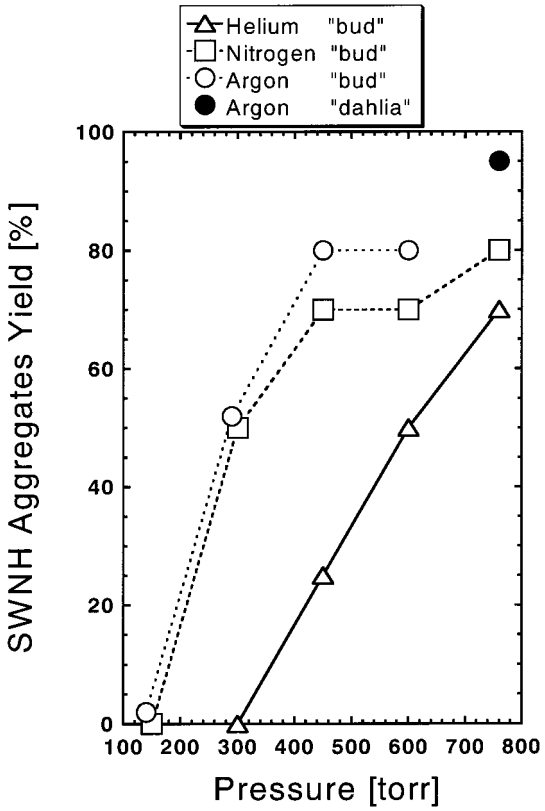

Figure 1. Yield of SWNH aggregates against buffer gas pressure.

* Corresponding author. Fax: +81-298-50-1366. E-mail: kasuya@nlp.jst.go.jp.
† Meijo University.
‡ "Nanotubulites" Project, Japan Science and Technology, c/o NEC.
§ Institute of Research and Innovation.
|| NEC Corporation.

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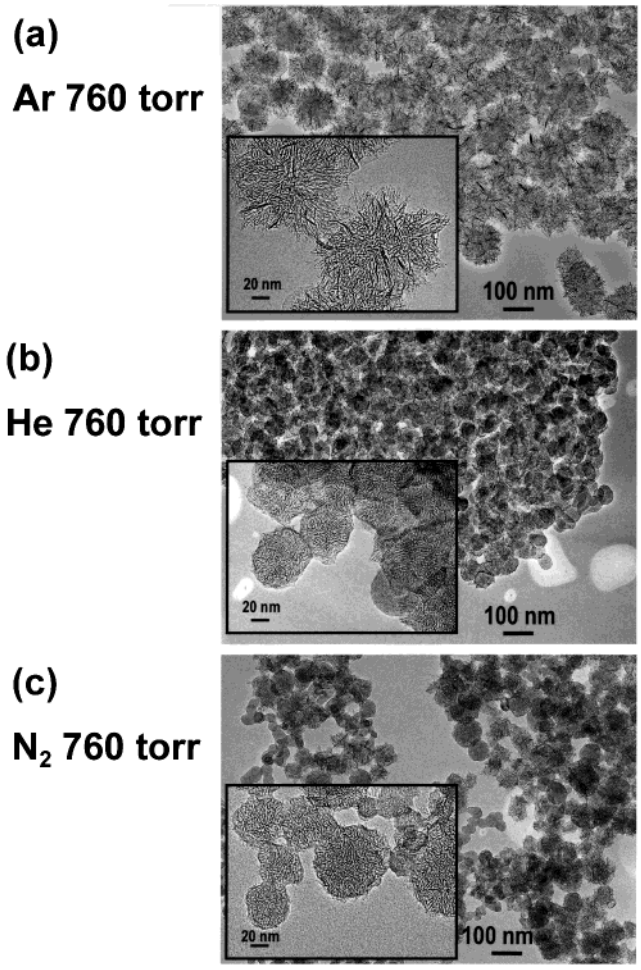

Figure 2. TEM images of soot produced in Ar, He, and N_2 at 760 Torr. Each insert is a highly magnified TEM image.

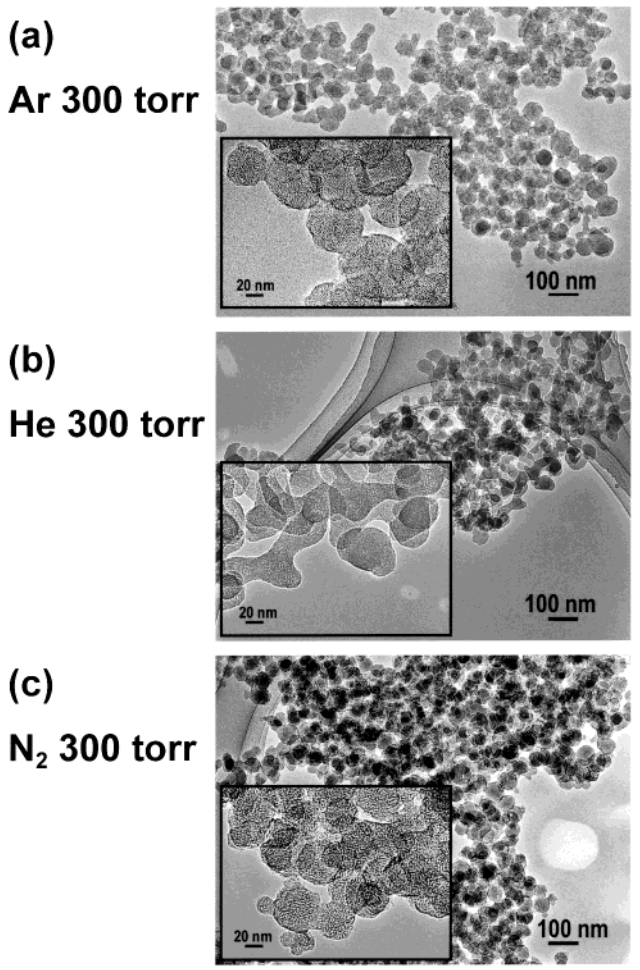

Figure 3. TEM images of soot produced in Ar, He, and N_2 at 300 Torr. Each insert is a highly magnified TEM image.

(wavelength 10.6 μm, power density ~20 kW/cm^2, pulse width 500 ms, frequency 1 Hz) on the graphite target rod. All laser vaporization experiments were performed at room temperature. The resultant SWNH aggregates were collected and their structures were studied using a transmission electron microscope (TEM).

The aggregates were burned in O_2 at 760 Torr for 10 min at temperatures varying from 300 to 600 °C. The structural changes resulting from the burning were studied by examining the Raman spectra and TEM images.

3. Results

The yields of the "dahlia-like" and "bud-like" SWNH aggregates were estimated using the TEM images of the CO_2-laser-vaporization products formed under pressures ranging from 150 to 760 Torr for all three buffer gases (Figure 1). When Ar at 760 Torr was used, many TEM images (Figure 2a, for example) indicated that the yield of "dahlia-like" SWNH aggregates was about 95% and that the 5% impurity materials consisted of "bud-like" SWNH aggregates and amorphous carbon (a-C). This result agrees with findings from a previous report.[3] High-yield production of "dahlia-like" SWNH aggregates is only possible under these conditions.

In the cases of He and N_2 at 760 Torr, "bud-like" SWNH aggregates were formed with yields of about 70 and 80%, respectively, and the impurities consisted only of a-C particles (Figures 2b and c). The TEM images of soot produced from Ar

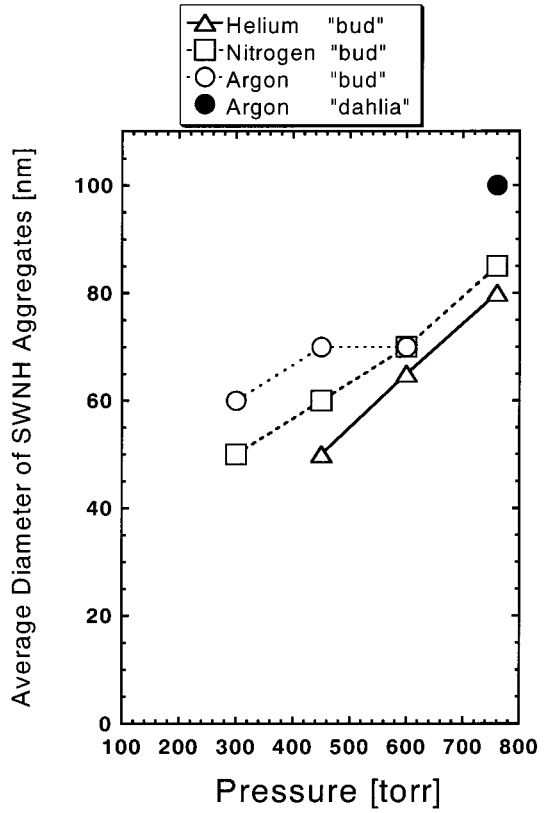

Figure 4. Average diameter of SWNH aggregates against pressure of buffer gas.

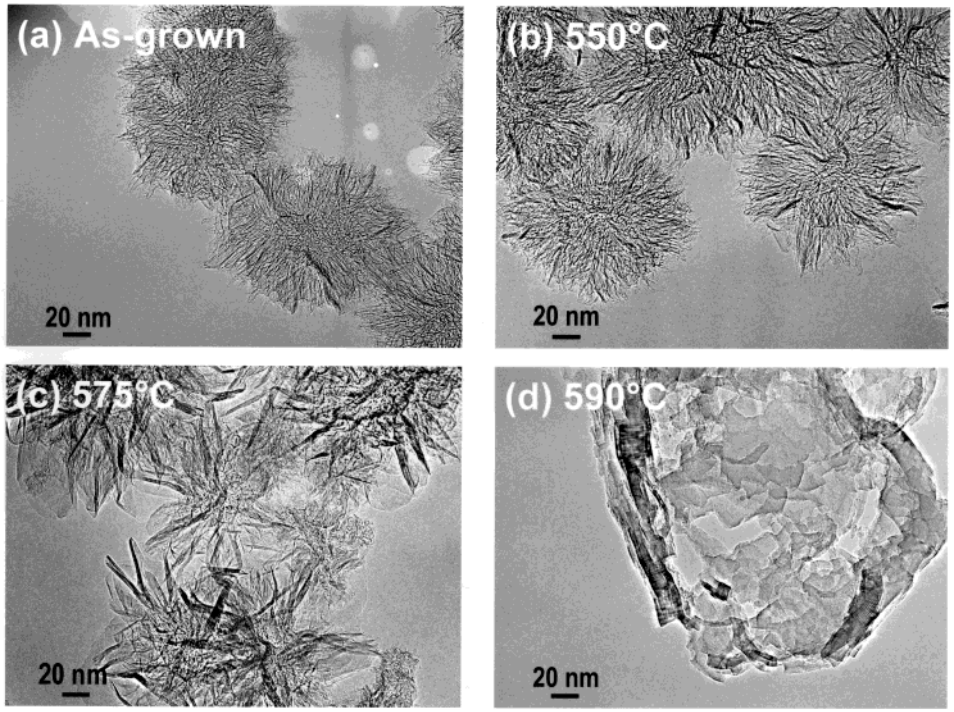

Figure 5. TEM images of (a) as-grown and (b−d) heat-treated "dahlia-like" SWNH aggregates.

and N_2 at 300 Torr (Figures 3a and c) indicated that the yield of the "bud-like" SWNH aggregates was about 50%. When He at 300 Torr was used, "bud-like" aggregates were not present, only a-C particles (Figure 3b). The soot formed from Ar, He, and N_2 at 150 Torr consisted of a-C.

When the buffer-gas pressure was decreased, the "bud-like" SWNH aggregates became smaller (Figure 4), for example, the aggregates formed in N_2 at 760 Torr had diameters of 70 to 100 nm (Figure 2c), which decreased to about 50 nm when the pressure was decreased to 300 Torr (Figure 3c). Similar trends were observed in Ar and He atmospheres. From Figure 4, we can see that the type of gas also influenced the diameters of the "bud-like" SWNH aggregates, that is, the diameters decreased in the order of $Ar > N_2 > He$.

To understand the formation mechanism of "dahlia-like" and "bud-like" SWNH aggregates, we studied the structures of the aggregates. The internal structures of the aggregates have not previously been revealed because they were too large to study using the TEM. However, we were able to study the structures by partially burning the aggregates. Our results are described below.

As previously reported,[5] the size and structure of "dahlia-like" SWNH aggregates did not change greatly when they were exposed to temperatures below 550 °C (Figures 5a and b). The only change that occurred was that pores of about 0.5 nm were formed. The pores were not visible using the TEM. When the temperature was 575 °C, most of the SWNHs burned, 80% of the "dahlia-like" SWNH aggregates disappeared, and only thin graphene sheets remained, some of which looked like petals (Figure 5c). After being exposed to a temperature of 590 °C, the thin graphene sheets disappeared and only small quantities of rugged graphite particles remained (Figure 5d). These structural changes were reflected in the Raman spectra (Figure 6).

The Raman spectra of the as-grown "dahlia-like" SWNH aggregates show two peaks that are characteristics of SWNHs (Figure 6a). When the burning temperature was below 300 °C, the Raman spectra showed little change (Figures 6b and 6c).

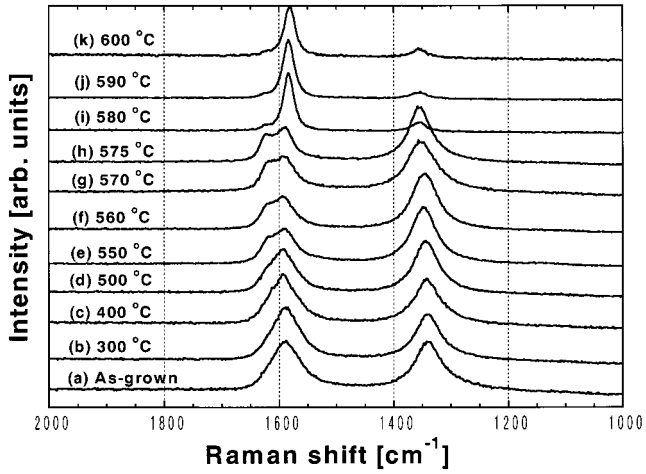

Figure 6. Raman spectra of (a) as-grown and (b−k; 300−600 °C) heat-treated "dahlia-like" SWNH aggregates.

When the burning temperature was between 400 and 575 °C, peaks appeared at 1620 cm^{-1} and became stronger as the temperature increased. At the same time, the intensity of the peak at about 1350 cm^{-1} increased. These changes showed that the defects in the SWNHs increased and the size of the graphene sheets forming the SWNH decreased as the burning temperature increased.[6,7] When the burning temperature was above 580 °C, the Raman spectra had a peak at about 1580 cm^{-1} (Figures 6i to 6k), which indicated that the majority of the material remaining after burning at 580 °C was graphite.

The structural change in the "bud-like" SWNH aggregates due to burning indicated that the "bud-like" SWNH aggregates formed in N_2 were different from those formed in He. To distinguish between these two types of aggregates, we refer to them as "bud-like(N_2)" SWNH aggregates and "bud-like(He)" SWNH aggregates.

The "bud-like(N_2)" SWNH aggregates (Figure 7a) decreased in diameter and 40% of the aggregates disappeared during partial burning at 500 °C. After being exposed to temperatures of 525

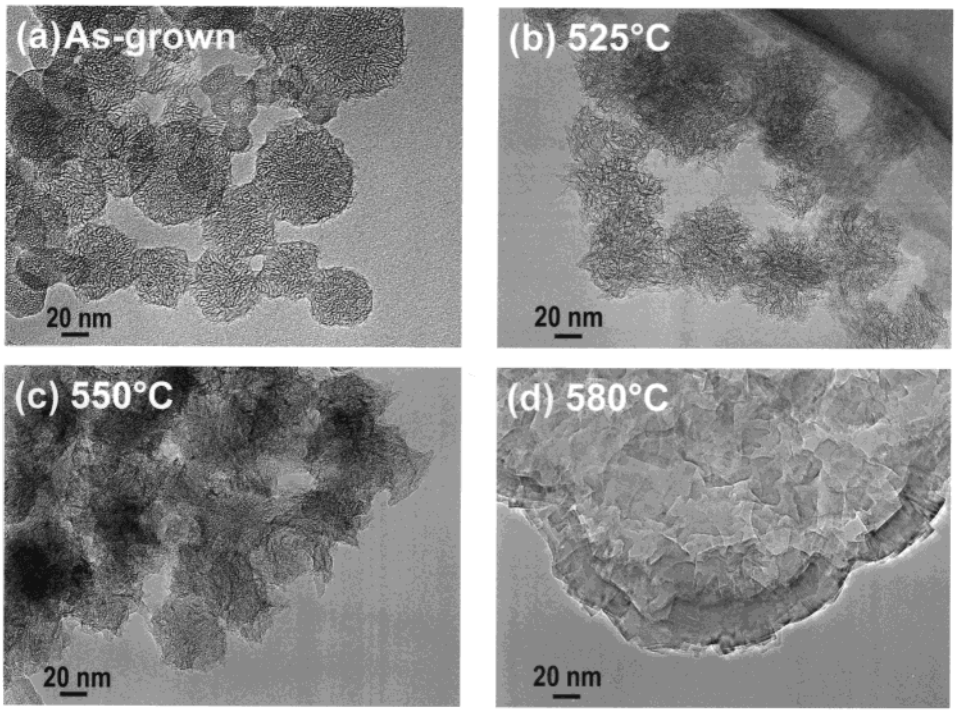

Figure 7. TEM images of (a) as-grown and (b−d) heat-treated "bud-like" SWNH aggregates, produced in N_2 at 760 Torr.

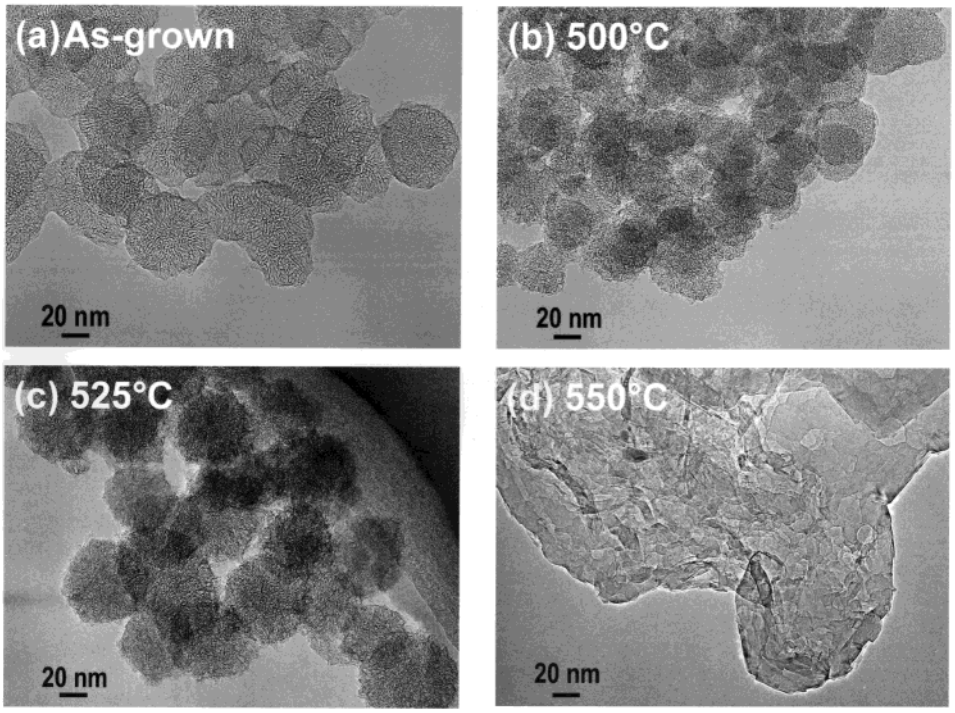

Figure 8. TEM images of (a) as-grown and (b−d) heat-treated "bud-like" SWNH aggregates, produced in He at 760 Torr.

°C, aggregates with structures similar to those of dahlia-like aggregates remained (Figure 7b). However, the tubule-like structures coalesced at 550 °C (Figure 7c). Only a small quantity of graphite-like particles, similar to those in Figure 5d, remained after the aggregates were burned at 580 °C (Figure 7d). The Raman spectra for the "bud-like(N_2)" SWNH aggregates (not shown here) indicated that burning at temperatures below 400 °C had little effect on the structure, but defects increased and graphene-sheet size decreased at temperatures between 500 and 575 °C. The Raman spectra also indicated that graphite remained after burning at 580 °C.

The "bud-like(He)" SWNH aggregates (Figure 8a) also decreased in diameter and 70% of the aggregates disappeared during partial burning at 500 °C (Figure 8b). Almost all of the "bud-like(He)" SWNH aggregates disappeared at 525 °C, and only a small quantity of a-C particles remained (Figure 8c). At 550 °C (Figure 8d), only graphite-like particles, similar to those in Figures 5d and 7d, remained. The Raman spectra for "bud-like(He)" SWNH aggregates (not shown here) exhibited no remarkable changes when the burning temperature was below 300 °C, but indicated an increase in defects and a decrease in graphene-sheet size after burning at temperatures between 500 and 525 °C. The Raman spectra also indicated that graphite remained after burning at 550 °C.

4. Discussion on Growth Mechanism

Carbon was vaporized from a carbon target using CO_2 laser irradiation, which continued for 500 ms (a pulse width) in our experiments. The energy needed by these vaporized carbon species to construct graphene sheets is carried by the vaporized carbon species themselves.[8] A large mass of ambient gas at high pressure was required for the formation of the "dahlia-like" SWNH aggregates, and as the gas mass and pressure decreased, the "bud-like" SWNH aggregates were formed, and a-C became the main product remaining. The partial burning of "dahlia-like" or "bud-like" SWNH aggregates in an O_2 atmosphere indicated that the graphene sheets of the "dahlia-like" SWNH aggregates were well constructed while those of the "bud-like" aggregates were less so, and those of a-C were much less so.

These results suggest that the evolution of vaporized carbon species to SWNHs requires not only high energy but also a low diffusion rate for the carbon species. The details of the formation mechanism of SWNHs and their aggregates are still unclear. However, graphene sheets would be formed without much difficulty given high energy and a low diffusion rate for the carbon species. Once the graphene sheets were formed, SWNHs would be formed automatically from the graphene sheets according to the results of a computer simulation.[8] The partial burning of the "dahlia-like" SWNH aggregates showed that they were composed of SWNHs and thin graphene sheets. These two components were extremely robust and coalesced inside the aggregates. Furthermore, the diameters of the dahlia-like SWNH aggregates were almost uniform. Hence, the mechanism for the growth of SWNH aggregates from vaporized carbon species may involve a highly condensed liquid state.

5. Conclusion

In our experiments, we succeeded in selectively producing SWNH aggregates. "Dahlia-like" SWNH aggregates were produced with a yield of 95% when Ar at 760 Torr was used as the buffer gas. "Bud-like" SWNH aggregates were formed with a yield of 70 or 80% when He or N_2 at 760 Torr were used. The yields and diameters of the "bud-like" SWNH aggregates decreased in the following order, Ar > N_2 > He, and also decreased with a decrease in the pressure of the buffer gas. We found that a single aggregate of the "dahlia-like" SWNHs is composed of tubules and graphene sheets, while the "bud-like" aggregate has a uniform structure made of tubules.

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References and Notes

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