

Isolating Single-Wall Carbon Nanohorns as Small Aggregates through a Dispersion Method

M. Zhang,^{*,†} M. Yudasaka,^{‡,§} J. Miyawaki,[†] J. Fan,[†] and S. Iijima^{†,‡,§}

SORST-JST, NEC, 34 Miyukigaoka, Tsukuba, Ibaraki, 305-8601, Japan and Meijo University, Tenpaku-ku, Nagoya, 468-8502, Japan

Received: August 25, 2005; In Final Form: September 22, 2005

An approach to isolating small aggregates of single-wall carbon nanohorns (SWNHs) is presented. SWNHs are ultrasonically treated in an aqueous solution of surfactant, resulting in dispersion of SWNH aggregates. Subsequent centrifuging enables the separation of small aggregates from larger aggregates or agglomerations and removal of graphitic particles (GG balls), the main impurity. The SWNHs obtained in this way were purified and formed small aggregates, thus exhibiting characteristics superior to those of SWNHs before treatment. We believe that the ability to isolate small SWNH aggregates in an aqueous solution should contribute to their application in the fields of biological sensing and drug delivery systems.

1. Introduction

The single-wall carbon nanohorn (SWNH)¹ is a new type of carbonaceous nanostructured material which was discovered during the investigation of the carbon nanotube² formation mechanism. SWNHs are graphitic tubes that have closed ends with cone-shaped caps (horns) and assemble into spherical aggregates with diameters of about 100 nm. One advantage of SWNHs is that they can be produced with high purity (~90%) and yield (>95%)¹ through laser ablation of a pure graphite rod without any metal catalysts. Another advantage is their large surface areas (1006–1464 m² g⁻¹) and plentiful inner nano-spaces (pore volume 0.47–1.05 mL/g).^{3–5} This suggests SWNHs can be used as carriers in applications requiring, for example, gas adsorption,^{3,6–9} organic material adsorption,^{10–11} and metal catalysts.^{12–14} Their unique physicochemical properties, size of a single aggregate, and freedom from the potential toxicity of contaminating metals also suggest possible applications in the medical field ranging from biological sensing to drug delivery systems (DDS). Fundamental studies on the use of SWNHs as drug carriers have been done.^{15,16}

However, the SWNHs obtained by laser ablation contain 5–15% of micrometer-sized graphitic particles (GG balls),¹⁷ and the SWNH aggregates are often agglomerated because of the van der Waals interaction. These problems limit their applications, especially DDS applications, because large agglomerates and GG balls would prevent smooth transportation in narrow blood vessels. Therefore, purification and obtaining a good dispersion of the SWNHs, preferably to realize a single small spherical aggregate (<100 nm), are critical.

Recently an important advance was made in the dispersion of single-wall carbon nanotubes (SWNTs). It was found that SWNTs could be dispersed in some surfactant solutions, such as sodium dodecyl sulfate (SDS)¹⁸ and sodium dodecylbenzene sulfonate (NaDDBS),¹⁹ with the assistance of ultrasonication and ultracentrifuging. However, the dispersion of SWNHs has not been studied. Here, we report on our successful efforts regarding the dispersion and purification of SWNHs using a

surfactant of NaDDBS. Notably, our results show that the aggregate size of the treated SWNHs was smaller than that before treatment. This represents an important step toward various SWNH applications such as in DDS.

2. Experimental Section

2.1. Dispersion and Purification of SWNHs. We prepared SWNHs by laser vaporization.¹ The purity of the SWNHs was about 85–90%, and about 70% of the SWNHs had a dahlia-shaped structure.²⁰ The method applied to remove large graphitic particles (GG ball) and isolate individual SWNH aggregates was similar to that used in the dispersion of SWNTs.^{18,19} The flowchart in Figure 1 shows the subsequent experimental procedure. Briefly, about 5 mg of as-grown SWNHs was dispersed in 25 mL of D₂O containing 0.5 wt % NaDDBS using a bath-type sonicator for about 30 min. The SWNH dispersion (SWNH (disp)) was then centrifuged at 220 000g for 1–2 h. After being centrifuged the SWNH dispersion separated into three layers (Figure 2). We examined the top (SWNH (upper)) and bottom layers by transmission electron microscopy (TEM). For the TEM observation copper grids with carbon membranes were used.

To remove the NaDDBS surfactant we added ethanol to the upper layers of the SWNH suspension and then filtered the suspension using filter paper with a pore size of 0.05 μm. The SWNHs on the filter paper were re-dispersed in ethanol and filtrated again. The process of filtration and re-dispersion in ethanol was repeated 8–10 times. Thereafter, we referred to the obtained SWNHs as SWNH (rinsed). To check whether there were any graphitic particles in the SWNHs we applied thermogravimetric analysis (TGA) to the obtained SWNHs in a pure O₂ gas flow of 100 cm³/min with a heating rate of 10 °C/min. Before the TGA the SWNHs were dried at room temperature and further treated in H₂ at 1200 °C for 3 h (we refer to these as purified SWNHs) to prevent any residual solvent affecting the SWNH combustion.²¹

Ethanol is a good solvent for dispersing SWNHs, and we also dispersed as-grown SWNHs in ethanol with a bath-type sonicator for about 30 min (SWNH (EtOH)). The particle-size distribution was measured with the light-scattering method and TEM observation for comparison with the distribution of SWNHs dispersed in a NaDDBS aqueous solution.

* Corresponding author. E-mail: minfang@frl.cl.nec.co.jp.

† SORST-JST.

‡ NEC.

§ Meijo University.

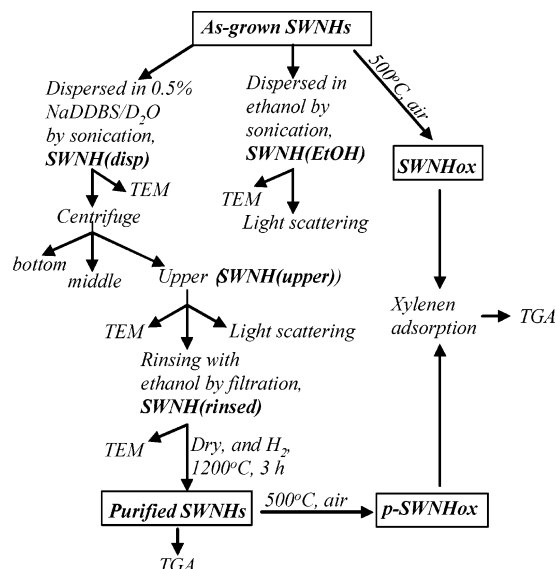


Figure 1. Experimental procedure of SWNH dispersion and purification and for adsorption of xylene in SWNHs.

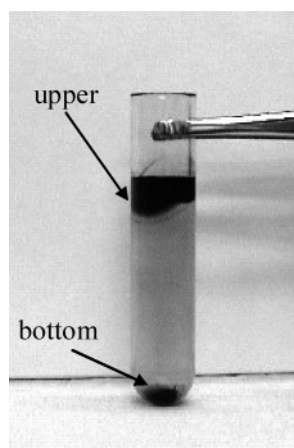


Figure 2. Photograph of SWNHs dispersed in NaDDBS/D₂O after centrifuging.

2.2. Adsorption of Xylene in SWNHs. Because their large material adsorption capacity is an important property of SWNHs for the sort of applications we are considering, we measured the quantity of xylene adsorbed by the purified SWNHs and the as-grown SWNHs. The measurement process we used was reported previously.^{11,22} Holes in the walls of purified SWNHs and as-grown SWNHs were opened through controlled combustion in a furnace with the temperature increasing from room temperature to 500 °C with a heating rate of 1 °C/min.²³ The hole-opened purified SWNHs (p-SWNHox) and as-grown SWNHs (SWNHox) were exposed to air saturated with xylene vapor for 1 h at room temperature. The quantity of xylene adsorbed by p-SWNHox and SWNHox was measured through TGA performed in He.

3. Results

The dispersion of as-grown SWNHs in NaDDBS/D₂O was separated into three layers after centrifuging (Figure 2). The upper layer was a homogeneous dark suspension, the middle one was a limpid solution, and the bottom one was sediment. TEM observation revealed isolated spherical aggregates of SWNHs in the upper suspension (Figure 3a), which were separated from each other by the surfactant. GG balls and large SWNH agglomerates were not observed in the upper layer but

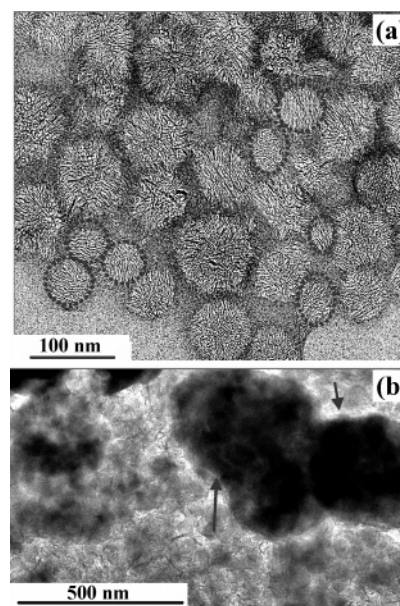


Figure 3. TEM images of dispersed SWNHs in the upper (SWNH(upper)) (a) and bottom (b) layers in the centrifugal tube holding the SWNH–NaDDBS–D₂O suspension after centrifuging as shown in Figure 2. Some smaller SWNH aggregates are indicated by broken circles. Graphitic particles (GG balls) are indicated by arrows.

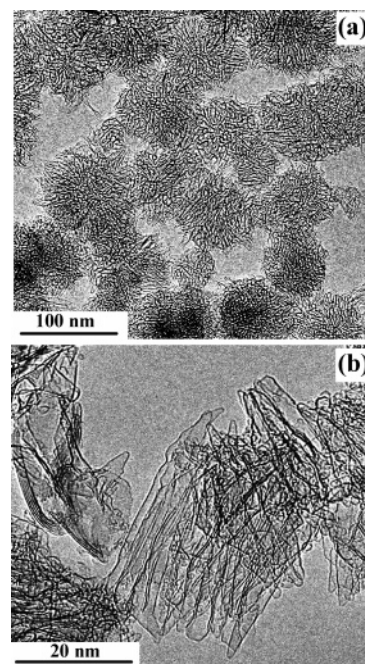


Figure 4. TEM images of (a) SWNHs after treatment with NaDDBS/D₂O and rinsing with ethanol (SWNH(rinsed)) and (b) an SWNH aggregate with smaller diameter.

were observed in the sediment layer (Figure 3b). After we eliminated the surfactant from SWNHs taken from the upper suspension by rinsing them with ethanol, TEM observation (Figure 4a) showed that the SWNHs were very pure and did not contain GG balls or any amorphous carbon materials. Significantly, many small SWNH aggregates and some bundles of horns can be seen in Figure 3a (marked by broken circles) and parts a and b of Figure 4.

Since the NaDDBS surfactant separated the SWNH aggregates from each other, we could measure the aggregate diameters directly from the TEM images (Figure 3a). The main part of the diameter distribution for SWNH aggregates in the

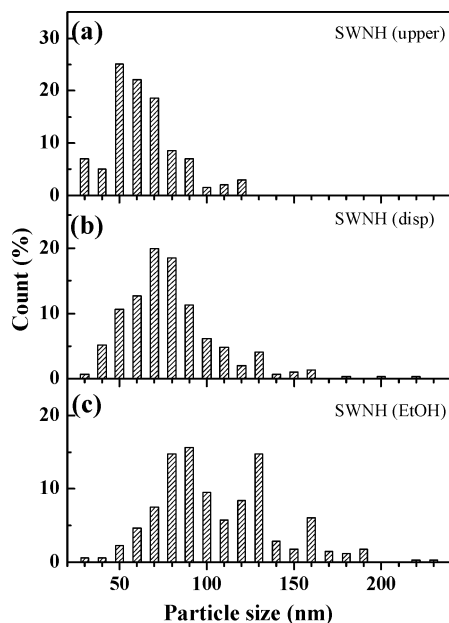


Figure 5. Diameter distribution of SWNH aggregates based on TEM measurements: (a) SWNHs dispersed in NaDDBS/D₂O after centrifuging (SWNH (upper)), (b) SWNHs dispersed in NaDDBS/D₂O before centrifuging (SWNH (disp)), and (c) as-grown SWNHs dispersed in ethanol by sonication for 30 min (SWNH (EtOH)).

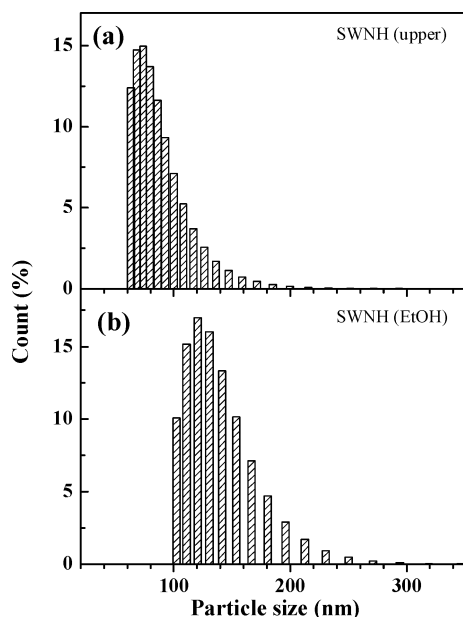


Figure 6. SWNH aggregate diameter distributions based on measurements using the light-scattering method: (a) SWNHs dispersed in NaDDBS/D₂O after centrifuging (SWNH (upper)) and (b) SWNHs dispersed in ethanol (SWNH (EtOH)).

upper suspension (Figure 5a) was in the 50–70 nm range, indicating smaller diameters than those before centrifuging (Figure 5b), which were mainly in the 50–90 nm range. The diameter distribution of as-grown SWNHs after dispersion in ethanol (SWNH (EtOH)) shows that their aggregate sizes were larger and distributed over a wider range (Figure 5c).

We also measured the size distributions of SWNHs by the light-scattering method. The results showed that the main part of the size distribution of as-grown SWNHs after ultrasonication in NaDDBS/D₂O and centrifuging (upper layer) (Figure 6a) covered size values smaller than the corresponding values after ultrasonication in ethanol (Figure 6b). This was consistent

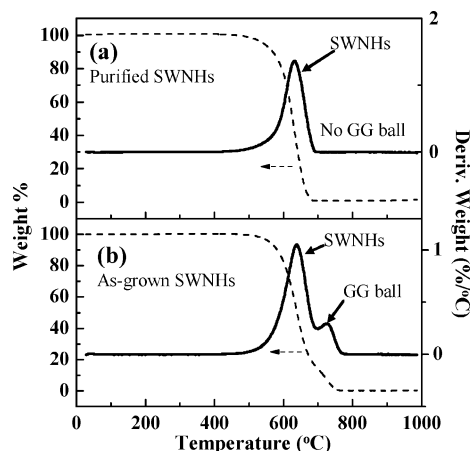


Figure 7. TGA results for (a) SWNHs after treatment with NaDDBS/D₂O and rinsing with ethanol (purified SWNHs) and (b) as-grown SWNHs. Before TGA the two SWNH samples were treated with H₂ at 1200 °C for 3 h. The TGA was performed in O₂ with the temperature increasing from room temperature to 1000 °C at a rate of 10 °C/min.

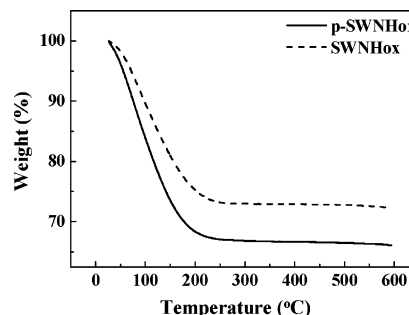


Figure 8. TGA results for p-SWNHox and SWNHox after adsorption of xylene. TGA was performed in He with the temperature increasing from room temperature to 600 °C at a rate of 5 °C/min.

with the TEM measurements. The aggregate sizes measured by this method, though, were larger than those from the TEM observations because of the effect of surfactant adsorbed on the aggregate and the not strictly spherical shapes of SWNH aggregates.

The TGA results for the as-grown SWNHs (Figure 7b) showed that the derivative curve had two peaks corresponding to combustion of SWNHs and GG balls.¹⁷ However, there was only one peak corresponding to the SWNH combustion for the purified SWNHs (Figure 7a). This confirmed that the GG balls were completely removed by the NaDDBS/D₂O treatment assisted by sonication and centrifuging.

Figure 8 shows TGA weight-loss curves for p-SWNHox and SWNHox after adsorption of xylene. The weight loss of p-SWNHox after xylene adsorption was about 34%, while that of SWNHox was about 27%. This indicates that the quantity of adsorbed xylene was 0.51 and 0.37 g, respectively, in each gram of p-SWNHox and SWNHox. This shows that the adsorption capacity of the SWNHs was remarkably improved after dispersion and purification with NaDDBS/D₂O assisted by ultrasonication and centrifuging, followed by removal of NaDDBS using ethanol.

4. Discussion

Our results show that the NaDDBS surfactant isolated each SWNH aggregate and the isolated aggregates floated within the upper layer of the NaDDBS/D₂O solution. This enabled separation of the SWNH aggregates from the agglomerates and GG balls. In addition, the SWNH aggregates in the upper layer

(Figure 2) were smaller in size and had a narrower size distribution than the as-grown SWNH aggregates (Figures 5 and 6).

To investigate why this floating occurred we used a NaDDBS/H₂O solution instead of NaDDBS/D₂O. In this case we found that separation into three layers by centrifuging was impossible. This suggests that the density of SWNH aggregates in the upper layers (Figure 1) was lower than the density of NaDDBS/D₂O (about 1.1 g/cm³) but higher than that of NaDDBS/H₂O (about 1 g/cm³). Naturally, when we used ethanol (0.8 g/cm³) instead of NaDDBS/D₂O all the SWNHs settled at the bottom of the centrifugal tubes. When we dispersed the SWNHox (density 2.05 g/cm³) in NaDDBS/D₂O and applied sonication and centrifuging, all the SWNHox also settled as sediment at the bottom of the centrifugal tubes.

Molecular dynamics simulation has shown¹⁸ that the density of an SWNT in an SDS micelle is about 1.0 g/cm³ and that of a seven-tube bundle of nanotubes in the SDS micelle is about 1.2 g/cm³. This would also be the case for the SWNHs—the small SWNH aggregates would have a lower density than that of the larger aggregates in the NaDDBS micelles. Because of this density difference we could extract the small SWNH aggregates in the upper layer from the mother mixture (Figures 2, 5, and 6).

The smaller SWNH aggregates that we obtained may have resulted from dispersion of agglomerations of several aggregates, which could not be easily found by TEM observation before they were dispersed. The smaller aggregates might also have resulted from the separation of one SWNH aggregate. Although we are not sure how the small aggregates came about, our results demonstrate that it is possible to get smaller SWNH aggregates with high purity, and such SWNHs have a greater material adsorption capacity. This is a significant step toward, for example, DDS applications.

5. Conclusion

We dispersed SWNHs in a D₂O solution of NaDDBS and applied ultrasonication and ultracentrifuging. Our results show that SWNH aggregates can be well dispersed in NaDDBS/D₂O. The main impurity, GG balls, can also be removed completely through this treatment. The obtained SWNH aggregates were smaller and had a narrower size distribution than those before treatment. They also showed characteristics that are preferable for potential applications compared to the characteristics of SWNHs not treated by the dispersion process using NaDDBS/D₂O.

References and Notes

- (1) Iijima, S.; Yudasaka, M.; Yamada, R.; Bandow, S.; Suenaga, K.; Kokai, F.; Takahashi, K. *Chem. Phys. Lett.* **1999**, *309*, 165.
- (2) Iijima, S. *Nature* **1991**, *354*, 56.
- (3) Murata, K.; Kaneko, K.; Kanoh, H.; Kasuya, D.; Takahashi, K.; Kokai, F.; Yudasaka, M.; Iijima, S. *J. Phys. Chem. B* **2002**, *106*, 11132.
- (4) Utsumi, S.; Miyawaki, J.; Tanaka, H.; Hattori, Y.; Itoi, T.; Ichikuni, N.; Kanoh, H.; Yudasaka, M.; Iijima, S.; Kaneko, K. *J. Phys. Chem. B* **2005**, *109*, 14319.
- (5) Yang, C.; Noguchi, H.; Murada, K.; Yudasaka, M.; Hashimoto, A.; Iijima, S.; Kaneko, K. *Adv. Mater.* **2005**, *17*, 866.
- (6) Murata, K.; Kaneko, K.; Kokai, F.; Takahashi, K.; Yudasaka, M.; Iijima, S. *Chem. Phys. Lett.* **2000**, *331*, 14.
- (7) Murata, K.; Kaneko, K.; Steele, W. A.; Kokai, F.; Takahashi, K.; Kasuya, D.; Yudasaka, M.; Iijima, S. *Nano Lett.* **2001**, *1*, 197.
- (8) Bekyarova, E.; Kaneko, K.; Kasuya, D.; Murata, K.; Yudasaka, M.; Iijima, S. *Langmuir* **2002**, *18*, 4138.
- (9) Tanaka, H.; Kanoh, H.; El-Merraioui, M.; Steele, W. A.; Yudasaka, M.; Iijima, S. *J. Phys. Chem. B* **2004**, *108*, 17457.
- (10) Nisha, J. A.; Yudasaka, M.; Bandow, S.; Kokai, F.; Takahashi, K.; Iijima, S. *Chem. Phys. Lett.* **2000**, *328*, 381.
- (11) Fan, J.; Yudasaka, M.; Kasuya, Y.; Kasuya, D.; Iijima, S. *Chem. Phys. Lett.* **2004**, *397*, 5.
- (12) Yoshitake, T.; Shimakawa, Y.; Kuroshima, S.; Kimura, H.; Ichihashi, T.; Kubo, Y.; Kasuya, D.; Takahashi, K.; Kokai, F.; Yudasaka, M.; Iijima, S. *Physica B* **2002**, *323*, 124.
- (13) Yuge, R.; Ichihashi, T.; Shimakawa, Y.; Kubo, Y.; Yudasaka, M.; Iijima, S. *Adv. Mater.* **2004**, *16*, 1420.
- (14) Hashimoto, A.; Yorimitsu, H.; Ajima, K.; Suenaga, K.; Isobe, H.; Miyawaki, J.; Yudasaka, M.; Iijima, S. *PNAS* **2004**, *101*, 8527.
- (15) Murakami, T.; Ajima, K.; Miyawaki, J.; Yudasaka, M.; Iijima, S.; Shiba, K. *Mol. Pharm.* **2004**, *1*, 399.
- (16) Ajima, K.; Yudasaka, M.; Murakami, T.; Shiba, K.; Iijima, S. *Nano Lett.* **2005**, in press.
- (17) Fan, J.; Yudasaka, M.; Kasuya, D.; Azami, T.; Yuge, R.; Imai, H.; Kubo, Y.; Iijima, S. *J. Phys. Chem. B* **2005**, *109*, 10756.
- (18) O'Connell, M. J.; Bachilo, S. M.; Huffman, C. B.; Moore, V. C.; Strano, M. S.; Haroz, E. H.; Rialon, K. L.; Boul, P. J.; Noon, W. H.; Kittrell, C.; Ma, J.; Hauge, R. H.; Weisman, R. B.; Smalley, R. E. *Science* **2002**, *297*, 593.
- (19) Matarredona, O.; Rhoads, H.; Li, Z.; Harwell, J. H.; Balzano, L.; Resasco, D. E. *J. Phys. Chem. B* **2003**, *107*, 13357.
- (20) Kasuya, D.; Yudasaka, M.; Takahashi, K.; Kokai, F.; Iijima, S. *J. Phys. Chem. B* **2002**, *106*, 4947.
- (21) Miyawaki, J.; Yudasaka, M.; Iijima, S. *J. Phys. Chem. B* **2004**, *108*, 10732.
- (22) Yudasaka, M.; Fan, J.; Miyawaki, J.; Iijima, S. *J. Phys. Chem. B* **2005**, *109*, 8909.
- (23) Fan, J.; Yudasaka, M.; Miyawaki, J.; Iijima, S. Submitted for publication.