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Interlayer spacing anomaly of single-wall carbon nanohorn aggregate

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Abstract

Newly found single-wall carbon nanohorns (SWNH) are synthesized by a CO_2 laser vaporization of a pure carbon target in an Ar gas. Purification method using centrifugal separation and structural features of aggregated form of SWNHs (SWNH aggregate) are studied in this Letter. Although the X-ray diffraction profile taken for highly purified SWNH aggregates does not show any sharp 002 diffraction corresponding to that of the ordinary graphite, a huge broad diffraction comes to be observed. This huge broad diffraction is well explained by the double layer diffraction model associated with two graphene sheets apart from 0.40 nm. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The single-wall carbon nanotubes (SWNT) can be synthesized via the arc burning or the pulsed laser vaporization of carbon materials with suitable metal catalyst, such as Fe, Ni and Co (and their bi-metallic combination), etc., in an inert gas [1–5]. For the generation of SWNTs with high yield, it is necessary to use bi-metallic catalyst such as Co–Ni, Fe–Ni for the pulsed laser vaporization [5] and Ni–Y for the arc burning [6]. However, recently synthesized new fullerene group material, so called, single-wall car-

bon nanohorns (SWNH) can be prepared with high vield (>95% from transmission electron micrographs [7]; one graphitic nano-particle or amorphous carbon nano-particle can be found in every ~ 20 SWNH aggregates) by a CO_2 laser vaporization of a pure graphite target in an atmospheric pressure of Ar gas. Details of the preparation method and high-resolution transmission electron microscopy (HRTEM) study for SWNHs have been reported previously [7]. Individual SWNHs have unique structural feature represented by a typical diameter of ~ 2 nm with a length of 30-50 nm. The end of this tube is closed by a conical cap with a cone angle of 20°. These individual SWNHs have a tendency to aggregate together and make dahlia flower-like structured particle (SWNH aggregate).

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In this Letter, we describe the purification procedure of SWNHs and discuss about the structural feature of aggregated SWNHs studied by X-ray diffraction (XRD).

2. Purification of SWNH aggregates

Although the purity of as-prepared SWNHs is already in excess of 95% [7], further purification of dahlia flower-like SWNH aggregates can be achieved by centrifugal separation using a colloidal suspension of SWNHs as describes below. The as-prepared SWNHs are dispersed in ethanol with a concentration of ca. 1 mg of SWNHs per 30 ml of ethanol by sonication using a conventional ultrasonic bath. The suspension liquid prepared in this way is spun at 9000 rpm (\sim 7600 G) for 30 min. and then the suspension liquid above sediment is decanted and stocked. The SWNH aggregates are in this suspension liquid. The ethanol is evaporated by the rotary evaporator at the temperature of 40°C. Then the solid remained are gathered for the present study. Here we show a flow chart of above purification procedure in



Fig. 1. Purification procedure of SWNH aggregates by centrifugal separation.

Fig. 1. Separation yield for pure SWNHs from asprepared SWNHs was ~40% by weight. Purity of the final product is not estimated quantitatively, but it should be greater than ~95%.

3. X-ray diffraction

XRD profiles taken for as-prepared SWNHs and purified SWNHs are in Fig. 2 together with the XRD profile for Si substrate. Inset transmission electron micrograph of Fig. 2 indicates typical SWNH aggregates (a cross-sectional schematic of SWNH aggregate is also indicated). The as-prepared SWNHs showed sharp 002 diffraction, which is normally observed for graphite. This sharp diffraction stems from the slightly included micrometer sized graphite flakes in the sample and they were accidentally formed during the preparation of SWNHs. The centrifugally separated SWNHs have no such sharp 002 diffraction as shown in the center XRD profile of Fig. 2. Instead of the sharp 002 diffraction peak, a huge broad peak is observed at $2\theta \sim 21^\circ$ for the purified SWNHs. Although this peak seems to become stronger, we do not consider that the sonication or centrifugalization process used in purification procedure creates this feature: the diffraction peaks associated with (100) and (101) spacings of micrometer-sized graphite (normally ~ 5-10% in strength as compared with 002 diffraction) overlap with broad and weak 10 diffraction of SWNH and makes a peak at $2\theta \sim 42.9^{\circ}$ apparently stronger. Therefore, a broad peak at $2\theta \sim 21^{\circ}$ for as-prepared SWNHs becomes relatively weaker as compared with the diffraction strength of the peak at $2\theta \sim 42.9^{\circ}$. In other words, if no graphite flakes include in the sample like purified SWNHs, a broad peak at $2\theta \sim 21^{\circ}$ looks relatively strong as compared with the peak at $2\theta \sim 42.9^{\circ}$.

XRD profile taken for 'sediment' (not shown) indicated almost the same with that taken for as prepared SWNHs. That is, the micrometer-sized graphite flakes are not only material to be precipitated by the centrifugal separation, but also the SWNHs are included in sediment. To increase the separation yield from $\sim 40\%$, it is thus necessary to repeat purification procedure several times by using



Fig. 2. X-ray diffraction (XRD) profiles of as-prepared (top) and purified (center) SWNH aggregates. The samples were put onto the Si substrate and the base line profile of XRD was corrected. Absolute diffraction strength between the samples cannot be compared, since the mounted sample quantities per area are different. Two sharp peaks indicated by arrows are unknown. Small peak indicated by * is from Si substrate (see bottom XRD profile). Cu K_{α} was used as an X-ray source. Inset micrograph indicates typical SWNH aggregates and schematic represents a cross-sectional view of SWNH aggregate.

sediment as a starting material: e.g., $60 \sim 70\%$ of separation yield was achieved by 3 times repetition.

An asymmetric diffraction peak observed at $2\theta \sim 42.9^{\circ}$ is assigned to 10 reflection, which is typically



Fig. 3. Electron micrographs of individual SWNHs. The SWNHs aggregate together by van der Waals interaction and make the double-layered plane region, which can be clearly recognized at the region indicated by arrow.

observed for multiwall carbon nanotubes [8] due to turbostratic stacking of graphene sheets. ¹ Spacing of (10) is estimated at 0.211 ± 0.002 nm, which is almost the same as that of ordinary graphite (0.213 nm) within the experimental error.

Here we show transmission electron micrographs (see Fig. 3), indicating aggregated structure of SWNHs. Top panel is a micrograph which shows mostly the side view of SWNHs, and bottom one

shows mostly the top view. One may can find that the SWNHs aggregate together by van der Waals interaction and make double-layered region, which can be clearly recognized at the region indicated by arrow in Fig. 3. To determine the distance between the double-layered planes from lattice image of HRTEM, it is necessary to take through-focus images to correct wave aberration of the electron lens. Hence, the direct measurement of distance between the planes from lattice image sometimes dose not give correct information about the plane distance. Regarding to 002 diffraction profile from the ordinary graphite which has infinite number of graphene lavers, a sharp diffraction profile will be obtained. On the other hand, for the finite number of graphene layers, the X-ray scattering theory tells that the linewidth of the diffraction profile depends on the number of layers. The XRD profile I from the layers with the number of stacks N is represented by the multiplication of the structure factor F_s and the diffraction function F_d , and is written by the following equation with variables *n* and *m*:

$$I \propto a^2 \frac{\sin^2 \pi n}{\left(\pi n\right)^2} \cdot \frac{\sin^2 N \pi m}{\sin^2 \pi m} \equiv a^2 F_s \cdot F_d.$$
(1)

Here, *n* is equal to $(a/d_{002}) \cdot m$, when the thickness of the cross-section for the X-ray scattering is represented by *a* and the spacing between the layers is represented by d_{002} . In order to simulate the experimental data, we use the wavenumber *Q* as the horizontal axis of XRD profile. In the simulation, *Q* is represented by $(2\pi/d_{002}) \cdot m$ and *a* was set at 0.182 nm.²

The simulated XRD profiles for N = 2, 3, 4 and 10 using Eq. (1) are represented by the solid lines in Fig. 4 together with the experimental XRD profile. Although the simulations were carried out by a single component for d_{002} , the experimental result is well fit by N = 2 (double layer diffraction) with $d_{002} = 0.40$ nm as shown in Fig. 4 (thick solid-line). A mis-fitted region observed in higher Q tail of the XRD profile can be explained by introducing much narrower components for d_{002} .

¹ Turbostratic stacking (or structure) is visualized by orienting the neighboring graphitic sheets in parallel, but whose translational and rotational correlations between the sheets are random.

 $^{^{2}}$ Thickness for the x-ray scattering from the carbon layer was selected as the same with the diameter of C⁺⁰ atom.



Fig. 4. Simulation of XRD profile by the finite-layered model. XRD profile is simulated by the multiplication of the structure factor F_s and the diffraction function F_d (see Eq. (1)). Illustration is a model of the X-ray scattering from the finite number of layers (S_0 and S are, respectively, the incident X-ray and the scattered one). Here, a is a thickness of the cross-section for the X-ray scattering d_{002} is a spacing between the layers. The simulated profiles are indicated by the solid-lines with the number of layers N = 2, 3, 4 and 10. Here, unknown sharp peaks indicated by arrows in Fig. 2 were eliminated from the data.

To simulate a mis-fitted region in higher Q tail of 002 diffraction, we used a polygonal approximation applied to the cylindrical part of SWNH and the atomic scattering factor of C. When the shape of the cylindrical part of each SWNH is simplified by dodecagonal shape and the apexes of dodecagon between the triangularly packed SWNHs are faced together, an asymmetric 002 diffraction lineshape can be reproduced and 004 diffraction comes to be overlapped with 10 peak. This simplified model implies the non-parallelism of bilayer planes. However, the average spacing between the non-parallel layers was the same value (0.40 nm) obtained from the simplest simulation presented above.

Regarding the simulation of XRD profile applied to highly disordered layer-like carbon specimens, Liu et al. [9] analyzed the experimental XRD profile associated with (002) spacing using a mixture of randomly oriented graphene sheets made of singlelaver, bilaver and trilayer. Here, the single-layer component normally gives featureless scattering at low 2θ region like background. Such single-layer contribution, which may be from the cone region of SWNH. is subtracted in our data indicated in Figs. 2 and 4. More detailed analysis of the entire XRD profile, including background and *hkl* or *hk* reflections, taken from layer disordered carbon specimen was carried out by Zhou [10]. They introduced nonparallelism of bilaver planes and bending of single graphene sheet in order to fit XRD peaks with higher reflection indices (especially the peaks appear at $O > \sim 50 \text{ nm}^{-1}$ or $2\theta > \sim 75^{\circ}$ for Cu K α). In our experiment, only a weak diffraction was observed at $2\theta \sim 79^{\circ}$ in high 2θ region for purified SWNHs (see Fig. 2). A peak position of this weak signal is rather difficult to determine with enough accuracy. Hence we did not analyze entire XRD profile.

According to the XRD analysis, wider van der Waals spacing for the aggregated SWNHs (0.40 nm) than that for the ordinary graphite (0.336 nm) was obtained. This should originate in an averaged spacing of the horn-wall to horn-wall distance, since the SWNHs cannot form a crystalline structure due to the distribution of diameters of the cylindrical part of SWNHs (frequent diameter is ~ 2 nm) and the conical shape of tip region represented by the cone angle of $\sim 20^{\circ}$. Latter of which certainly makes the spacing wider and induces the turbostratic nature. Actually, the turbostratic feature for the aggregated SWNHs can be confirmed by the fact for lack of clear hkl reflection: an asymmetric diffraction line assigned to 10 reflection from a two-dimensional lattice was detected as shown in Figs. 2 and 4. The tail toward higher Q (or 2θ) region probably corresponds to (101) spacing ³ of double layer diffraction.

³ Here, (101) spacing can be estimated at 0.204 nm using $d_{002} = 0.40$ nm and $d_{10} = 0.211$ nm obtained for SWNHs. Hence, 101 diffraction will be appeared at Q = 30.8 nm⁻¹ (or $2\theta = 44.4$ degrees for Cu K_{α}).

Regarding to the interlayer spacing for graphite, one of the authors (S.I.) reported the increase of the interlayer spacing as the number of layers decreased. and for double layers 15% wider spacing was observed as compared with that for the ordinary graphite [11]. This value is comparable to the present value (0.40 nm) obtained for the SWNH aggregate. By the second-order perturbation treatment of the interlayer interactions in two-dimensional graphitic structure, it was concluded that the interlayer interactions are governed by orbital interaction as well as by van der Waals interaction [12]. In other words, reduction of the orbital interaction causes the interlayer spacing wider. In the turbostratic graphite, there is less matching of the carbon atoms between the lavers. which reduces the orbital interactions and results the wider interlayer spacing. In addition, the graphene lavers of SWNH aggregate are somewhat wound (see Fig. 3), which also causes the reduction of the orbital interaction and makes the interlayer spacing much wider.

In this study, it was found that the centrifugal separation worked well for the purification of SWNHs. The XRD analysis indicated the wider spacing (~ 0.40 nm) for the van der Waals distance of the aggregated SWNHs as compared with that of the ordinary graphite. This wider distance may be used for the doping space of the donor and acceptor materials such as alkaline metals and halogens. Study on the doping properties of SWNH aggregates with Li, K and Br will be reported shortly [13].

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References

- [1] S. Iijima, T. Ichihashi, Nature 363 (1993) 603.
- [2] D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez, R. Beyers, Nature 363 (1993) 605.
- [3] Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, A. Kasuya, Y. Nishina, J. Phys. Chem. Solids 54 (1993) 1849.
- [4] S. Seraphine, D. Zhou, Appl. Phys. Lett. 64 (1994) 2087.
- [5] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. 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.
- [6] C. Journet, K.W. Maser, P. Bernier, A. Loiseau, M.L. Chapelle, S. Lefrant, P. Deniard, R. Lee, J.E. Fischer, Nature 388 (1997) 756.
- [7] S. Iijima, M. Yudasaka, R. Yamada, S. Bandow, K. Suenaga, F. Kokai, K. Takahashi, Chem. Phys. Lett. 309 (1999) 165.
- [8] Y. Saito, T. Yoshikawa, S. Bandow, M. Tomita, T. Hayashi, Phys. Rev. B 48 (1993) 1907.
- [9] Y. Liu, J.S. Xue, T. Zheng, J.R. Dahn, Carbon 34 (1996) 193.
- [10] P. Zhou, R. Lee, A. Claye, J.E. Fischer, Carbon 36 (1998) 1777.
- [11] S. Iijima, Chemica Scripta 14 (1978) 117.
- [12] K. Yoshizawa, T. Kato, T. Yamabe, J. Chem. Phys. 105 (1996) 2099.
- [13] S. Bandow, A.M. Rao, G. Sumanasekera, P.C. Eklund, F. Kokai, K. Takahashi, M. Yudasaka, S. Iijima, in preparation.