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Carbon nanotubes forming cores of fibrous aggregates of carbon nanohorns

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A B S T R A C T

Cores of fibrous aggregates composed of radially assembled graphene-based single-walled carbon nanohorns, named as carbon nanobrushes (CNBs), were observed using electron microscopes. As a result, a carbon nanotube (CNT), probably single-layer structure, exposed from the CNBs was observed. From cross section images of CNBs, three round structures of about 2.5 nm diameters were also observed clearly at center part of single-walled carbon nanohorn (SWCNH) aggregate, which indicates the cross section of bundled single-walled CNTs. Therefore, we found that CNTs were localized at the core of CNBs. From these results, as for the formation mechanism of CNBs, it is supposed that the CNT functions as a template and SWCNHs radially gather on the CNT.

1. Introduction

Nanocarbon materials, represented by carbon nanotubes (CNTs) and graphenes, are extremely fascinating because of their unique structural, electrical, and mechanical properties [1–7]. Discovered by Iijima et al in 1998, “single-walled carbon-nanohorn aggregates (spherical SWCNHs) are another type of nanocarbon materials [8,9]. Each SWCNH is a graphene-based pseudo tubule having diameters of 2–5 nm and lengths of 40–50 nm [8-10], and about two-thousands of them assemble radially to form a spherical aggregate with diameters of about 100 nm (spherical SWCNHs) [8]. Spherical SWCNHs are attractive materials due to their high dispersibility in solutions [11] and large specific surface area [12]. However, when used for applications such as compound materials [13], electrochemical capacitors [14,15], sensing applications [16], catalytic supports [17] and batteries [18], high electrical conductivity has been also required. Recently, a new type of nanocarbons having high dispersibility, high electrical conductivity, and large specific surface area has been discovered [19]. It is fibrous aggregates of single-walled carbon nanohorns, which is named as carbon nanobrushes (CNBs), whose structure resembles a chenille stem and/or a pipe cleaner. CNBs are prepared by CO_2 laser ablation of an iron-containing carbon target at room temperature and ambient pressure under nitrogen atmospheres [19]. Since the preparation method is similar to that of spherical SWCNHs, which achieved a production rate above 1 kg/day [20], the large-scale production of CNBs would be realized easily.

So far, the core part in CNBs having a complicated structure has not been clear. Accordingly, in this study, the structure, especially the core structure, of CNBs was clarified by electron-microscopy observation. The CNB formation mechanism was also briefly discussed.

2. Experimental

CNBs were prepared by CO_2 laser ablation of an iron-containing carbon target at room temperature and ambient pressure under nitrogen atmosphere. The iron-containing carbon target, with a cylindrical form (diameter of 3 cm and height of 5 cm), was purchased from TOYO TANSO Co., Ltd. The target was prepared by the compression and sintering of iron-containing cokes. The iron content in the target was 1 at. %. The CO_2 laser power and target rotation speed were 3.2 kW and 1 rpm, respectively. The laser ablation was performed for 30 s. The gas pressure in the growth chamber was sustained at 700–800 Torr by controlling the evacuation rate while the buffer gas of nitrogen was kept at a flow rate of 10 L/min.

The morphology of the CNBs was observed by a scanning

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electron microscope (SEM) (Hitachi S-4800) and a scanning transmission electron microscope (STEM) (Hitachi HD-2300). The SEM and STEM were operated at 1.0 kV and 120 kV, respectively. A cross-section image of the CNBs was observed by a transmission electron microscope (TEM) (Hitachi H-9000UHR). The TEM was operated at 300 kV. The observed sections were prepared by embedding the CNBs in resin and thinning by argon-ion milling (Gatan Dural Mill 600).

3. Results and discussion

Fig. 1 shows SEM and STEM images of the obtained samples. A lot of string-like and spherical structures were observed as shown in Fig. 1a. The former is CNBs and the latter is spherical-aggregates of SWCNHs. Length and diameter of the CNBs were several micrometers and about 100 nm, respectively. In the high magnification STEM images of the CNBs (Fig. 1b), the SWCNHs radially gathered and were one-dimensionally connected as previously reported [19]. Each SWCNH is graphene-based pseudo tubules having diameters of 2–5 nm and lengths of 40–50 nm [8-10]. The structure of the CNB is schematically represented in Fig. 1a. Graphene sheets with layer numbers of 2–20 and thickness of 0.34–7 nm [21] were also contained in the CNB and spherical-aggregates of SWCNHs (Fig. 1b, black arrows). Black particles in the CNB and spherical-aggregates of SWCNHs were the iron catalysts with sizes of several nanometers to several tens nanometers (Fig. 1 b, blue arrows). We found two types of the tip structures. One was the assembly of several spherical-aggregates of SWCNHs (Fig. 1c). The other type showed smaller string-diameters, where the SWCNHs take various directions from radially to parallel (Fig. 1d). The newly discovered CNB has the structure quite different from that of the spherical-aggregates of SWCNHs or the CNTs. The CNB formation mechanism is interesting and necessary to optimize the preparation parameters for the large-scale production. Here, in this report, we show that CNTs exist at the core of CNBs, which inspired various discussions for the formation mechanism of CNBs.

A thin tube-like structure was sometimes found connecting the edges of two CNBs as shown in Fig. 2a. This thin tube-like structure extends from the core parts of the CNBs. Fig. 2b shows STEM image of low magnification of the CNB. At first glance, the CNB was cut in the middle. However, from the high magnification image, we found that a carbon nanotube (CNT), probably single-layer structure, is exposed from the CNBs (Fig. 2c). The CNTs exposing from CNBs during STEM observation were stable, which implies that defects of CNT are considerably small. The schematic representation is also shown in Fig. 2d. The diameter of the CNT was about 4 nm (Fig. 2c), which is larger than the typical diameters of single-walled carbon nanotube, 1–2 nm. From STEM observations, the diameter distribution of carbon nanotubes was about 2 to 4 nm.

To confirm that SWCNTs is located at the core of CNBs, the cross section of the resin-embedded CNBs was observed with TEM (Fig. 3). The CNBs and spherical-SWCNHs have been observed and uniformly dispersed in resin (Fig. 3a). Here, the region marked by a green-dotted-line-square is magnified as shown in Fig. 3b and c. As indicated by the orange dotted circle, three round structures of about 2.5 nm diameter were apparently observed at the core part of the aggregate structure, which indicates the cross section of bundled single-walled CNTs [22]. The round structures can also be interpreted in such a way that the several single-walled carbon nanohorns lie parallel to the incoming electron beam [8]. However, at the present time, we tentatively think that CNTs exist at the core part of CNBs as shown schematically in Fig. 3b. It is also concluded from TEM observation that there are CNTs at the core of CNBs, and they exist as single CNTs or bundles of CNTs.

On the basis of the above-described results, the formation mechanism of CNBs is considered as follows. When an iron-

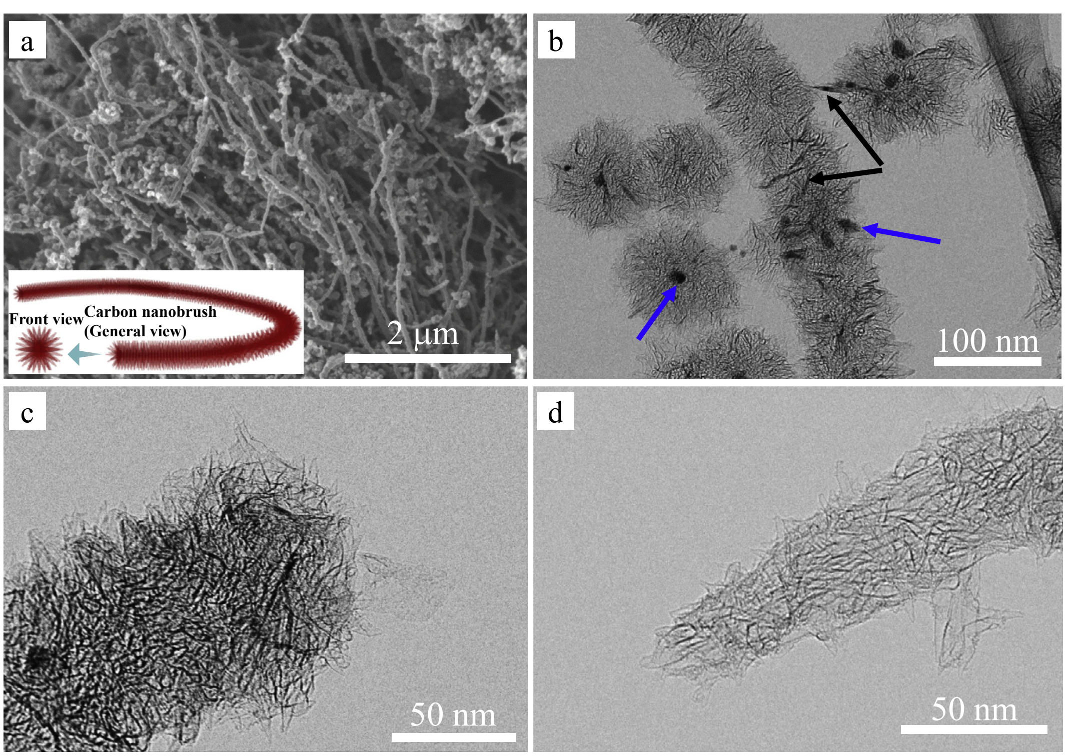

Fig. 1. SEM and STEM images of the obtained samples. (a) SEM images of overall structure of CNBs and spherical-SWCNHs. (b) STEM image of CNBs and spherical-SWCNHs. The black arrows indicate the few graphene sheets observed from the side directions. Blue arrows indicate the iron-catalyst particles. (c) and (d) STEM images of the CNB tips. (A colour version of this figure can be viewed online.)