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Formation of single-wall carbon nanotubes in Ar and nitrogen gas atmosphere by using laser furnace technique

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Abstract. The formation of single-wall carbon nanotubes (SWNTs) by using laser vaporization technique in different ambient gas atmosphere was investigated. SWNTs were prepared with Rh/Pd (1.2/1.2 atom%)-carbon composite rod in Ar and nitrogen gas atmosphere, respectively. Raman spectra of raw carbon materials including SWNTs and photoluminescence mapping of dispersed SWNTs in a surfactant solution demonstrate that the diameter distribution of SWNTs prepared in Ar atmosphere is narrower than those obtained by using CVD technique (e.g. HiPco nanotube), even when the ambient temperature is as high as 1150 °C. It was also found that nitrogen atmosphere gives wider diameter distribution of SWNTs than that obtained with Ar atmosphere. Furthermore, the relative yield of fullerenes (obtained as byproducts) is investigated by using HPLC (high-performance liquid chromatography) technique. It was found that the relative yield of higher fullerenes becomes lower, when nitrogen is used as an ambient gas atmosphere. Based on these experimental findings, a plausible formation mechanism of SWNTs is discussed.

PACS. 36.40.-c Atomic and molecular clusters – 61.46.Df Nanotubes – 81.05.Tp Fullerenes and related materials

1 Introduction

Since single-wall carbon nanotubes (SWNTs) have been discovered in 1993 [1,2], several different kinds of experimental technique (arc-burning [2], laser-furnace [3], CVD (Hipco [4], CoMoCAT [5], ACCVD (alcohol catalytic CVD) [6], DIPS [7], a water-assisted "super-growth" technique [8], etc.)) have been developed and extensively applied for the preparation of them, in order to make SWNTs of high yield and highly-selective (not only in the sense of diameter distribution but also chirality distribution). Furthermore, the formation mechanism of SWNTs in each technique was also extensively discussed. For example, the "VLS (Vapor-Liquid-Solid)" model [9] is proposed for the formation of SWNTs by using CVD technique, where the diameter distribution of SWNTs is considered to be determined by that of alloy nanoparticles supplied as catalyst. However, since every technique has its own unique experimental condition for the preparation, and it seems to be a little difficult to find out the common features among them.

A laser furnace technique, first developed by Smalley and others for the preparation of metal-containing endohedral fullerenes [10], was also found to be applicable for the preparation of SWNTs [11]. This technique was applied for the study of formation process of C_{60} and other higher fullerenes [12], since it has the advantage that one can control the experimental parameter (e.g. the kind of ambient gas, the gas pressure, the ambient temperature) independently. In combination with a high-speed video camera, it was suggested that the initial exothermic process for the formation of precursors within a few ms, is important for the formation of C_{60} and other higher fullerenes having a round carbon-cage structure [13].

In this proceeding, the formation of SWNTs by using Rh/Pd-carbon composite rod in Ar and nitrogen gas atmosphere was investigated. In the previous study, Rh/Pd catalyst was found to give SWNTs having smaller diameters (less than 1 nm) in Ar gas atmosphere below 1250 °C ambient temperature [14]. This diameter distribution is comparable to those of C_{60} and other higher fullerenes. It is also convenient that one can analyze the chirality distribution of these thin SWNTs further by UV-VIS-NIR absorption and photoluminescence mapping technique, which was recently developed by Weisman and others, [15] and extensively applied for SWNTs prepared by using CVD technique [16]. Nitrogen gas is chosen because

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the yield of SWNTs was found to become higher, when Ni/Co-carbon composite rod was used as target, both by using laser furnace technique [17] and arc-burning technique [18]. It is interesting to investigate whether any difference can be seen in the diameter distribution of SWNTs, when Rh/Pd-carbon composite rod is used for laser furnace technique in Ar and nitrogen atmosphere.

2 Experimental

SWNTs were prepared by laser vaporization of Rh/Pd (1.2/1.2 atom%)-carbon composite rod by using a laser-furnace apparatus at 1150 °C. Both Ar and nitrogen were used as an ambient gas atmosphere, respectively. The gas pressure was kept 750 torr, since the yield of SWNTs were found to become higher when the ambient gas pressure is above 500 torr [17]. A second harmonic (532 nm) of Nd:YAG laser (Spectra Physics, GCR-290, 300 mJ/pulse, 10Hz) was used for laser vaporization.

The obtained raw carbon material containing SWNTs were analyzed with micro-Raman system (HORIBA Jovin Yvon, LabRAM HR-800) with Ar ion laser (488 nm). After dispersed in sodium dodecyl benzenesulfate (SDBS) solution according to Weisman and others [15], a chiral distribution of mono-dispersed SWNTs was investigated by UV-VIS-NIR absorption spectroscopy (SHIMADZU, UV-3100PC) and by photoluminescence mapping (Lambda Vision, PLE-250S). In order to investigate the correlation with the formation of higher fullerenes, the similar experimental condition, except for the lower ambient gas pressure (100 torr), was applied, and the obtained raw carbon material was dissolved into toluene, and the extracted fullerenes were analyzed by the standard HPLC system with toluene as eluent and with buckyprep column (Nacalai tesque, COSMOSIL Buckyprep column, 4.6 mm $\phi \times 250$ mm).

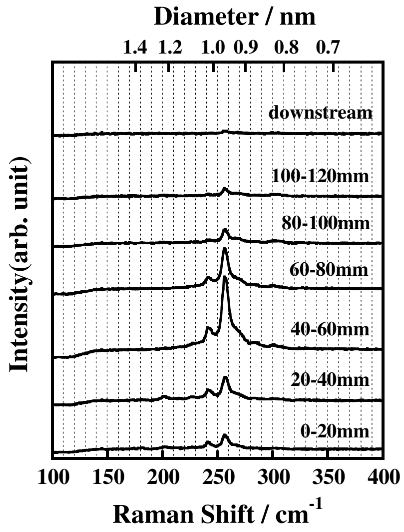

Fig. 1. Raman spectra of SWNTs obtained by laser vaporization of Rh/Pd (1.2/1.2 atom%)-carbon composite rod in 750 torr Ar atmosphere.

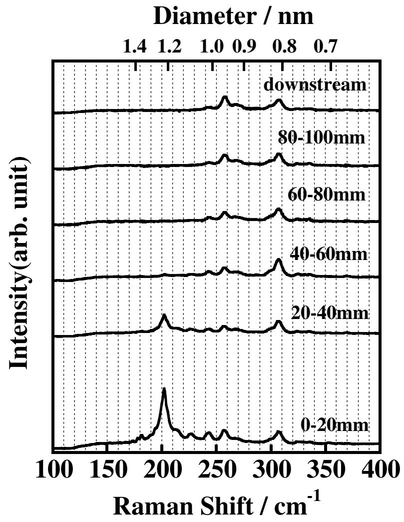

Fig. 2. Raman spectra of SWNTs obtained by laser vaporization of Rh/Pd (1.2/1.2 atom%)-carbon composite rod in 750 torr nitrogen atmosphere.

3 Results and discussion

3.1 Raman spectra

Figures 1 and 2 show Raman spectra of raw carbon material including SWNTs, prepared by using laser furnace technique with Rh/Pd-carbon rod in 750 torr Ar and nitrogen atmosphere, respectively. From the peak position of each Raman spectrum, one can estimate the diameter distribution of them by using the formula $D(\text{nm}) = 248/\omega_R(\text{cm}^{-1})$, where D indicates the diameter of SWNT and ω_R denotes the Raman frequency of the radial breathing mode of SWNT. The numbers attached to each spectrum indicate the distance from the center of the furnace to the downstream way of the ambient gas. The raw carbon material including SWNTs was collected from each position, and was used, as it is, for Raman analysis.

Figure 1 indicates typical Raman spectra of SWNTs obtained by laser vaporization of Rh/Pd-containing carbon target at low ambient temperature (below 1250 °C), as has been already shown in the previous study [14]. It also indicates that the diameter distribution does not change so much from place to place. On the other hand, Figure 2 demonstrates that, in nitrogen atmosphere, the diameter distribution is wider than that obtained in Ar atmosphere. Also, it is interesting to point out that Figure 2 shows the Raman peak around 310 cm^{-1}, corresponding to SWNTs having smaller diameters (ca. 0.8 nm), is clearly seen. This peak can hardly be seen in the case of Ar gas atmosphere. This Raman peak can often be recognized when SWNTs having small diameters are prepared by using CVD technique [6]. In addition, in Figure 2, it was found that the relative intensity of the peak around 200 cm^{-1}, corresponding to SWNTs having larger diameters (larger than 1 nm) diminishes as the distance becomes far away from the center of the furnace. These experimental findings suggest that the ambient gas influences not only on the formation of SWNTs, but also the on the diameter distribution of them.

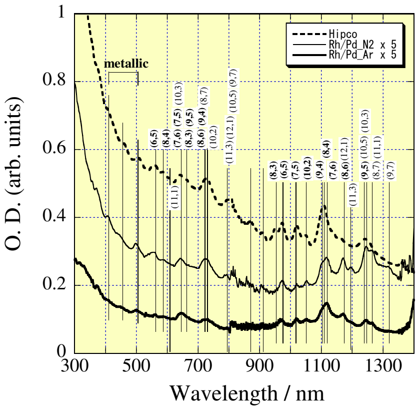

Fig. 3. UV-VIS-NIR spectra of dispersed SWNTs in sodium dodecyl benzenesulfate (SDBS) solution.

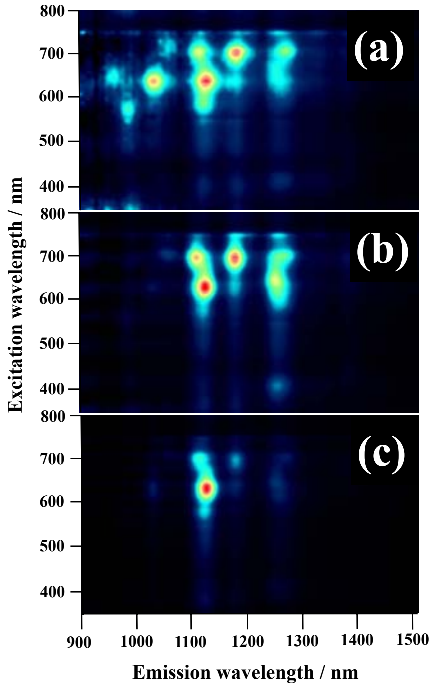

Fig. 4. (Color online) Photoluminescence mapping of dispersed SWNTs in sodium dodecyl benzenesulfate (SDBS) solution. (a) HiPco nanotubes. (b) SWNTs prepared in nitrogen atmosphere. (c) SWNTs prepared in Ar atmosphere.

3.2 UV-VIS-NIR spectra and photoluminescence mapping

Figure 3 shows UV-VIS-NIR absorption spectra of monodispersed SWNTs prepared by using laser furnace technique with Rh/Pd-carbon composite rod in Ar and nitrogen atmospheres, shown together with that of standard Hipco nanotubes. Each of them was prepared according to Weisman's procedure, i.e., by dispersion of the raw carbon material including SWNTs into SDBS solution [15]. In comparison with data of the Hipco nanotubes, the lines indicating the position of absorption peak of the semiconductive SWNTs having possible chiralities were drawn in the spectra. It is found that most of the absorption peaks are recognized as those by semiconductive SWNTs in these spectra. It is also interesting to point out that, while the position of each absorption peak is the same among three spectra, the intensity distribution corresponding to the chirality distribution of SWNTs, is different. Though the chilarity distribution of SWNTs prepared in nitrogen seems to be as wide as that of Hipco nanotubes, it is found to be narrower in Ar atmosphere.

Photoluminescence mapping data shown in Figure 4 also agree well with the tendency described above. In comparison with the case of Hipco nanotubes (Fig. 4a), it is demonstrated that the chiral distribution of SWNTs prepared in nitrogen atmosphere seems to become narrow (Fig. 4b). Furthermore, in the case of Ar atmosphere (Fig. 4c), SWNTs indicated by the chiral index (7,6) appears as the main semiconductive nanotubes. This experimental finding is consistent with the absorption spectra shown in Figure 3, where the absorption peak corresponding to the chiral index (7,6) is clearly seen as the main feature in the spectra for SWNTs prepared in Ar atmosphere.

3.3 Comparison with the formation of higher fullerenes

In the previous study, it was mentioned that, when Rh/Pd-carbon composite rod is used for laser furnace apparatus with 500 torr Ar atmosphere and at 1150° ambient temperature, the relative yield of higher fullerenes becomes higher [19]. On the other hand, as was seen in the previous section, the chiral distributions of SWNTs having smaller diameters comparable to those of higher fullerenes, are different between in Ar atmosphere and in nitrogen atmosphere. Therefore, it is interesting to investigate the relative yield of higher fullerenes prepared as byproducts in the material prepared with Rh/Pd-carbon composite rod by using laser furnace technique in nitrogen atmosphere.

Figure 5 shows HPLC chromatograms for fullerenes extracted from the raw soot prepared by laser vaporization of Rh/Pd-carbon composite rod in Ar and nitrogen gas atmosphere (100 torr), respectively. HPLC data obtained for those by the laser vaporization of pure graphite target in Ar and nitrogen atmosphere is also included as references in the figure. It is clearly seen, that the relative yield of higher fullerenes decreases drastically when Rh/Pd-carbon composite rod was vaporized in nitrogen gas atmosphere.

The reason why the relative yield of higher fullerenes prepared in Ar and nitrogen atmosphere is so different, is considered in the following way. Based on the experimental findings for blackbody emission taken with a combination of laser furnace apparatus and a high-speed video camera, the cooling rate of carbon nanoparticles can be estimated [13]. By applying this technique, it is found that the cooling rate becomes faster in nitrogen atmosphere than in Ar atmosphere [20]. In the formation process of C_{60} and other higher fullerenes, the initial a few ms is important because the precursors having cage-like structures are prepared at that time, where high internal temperature has to be kept during the formation. If the cooling

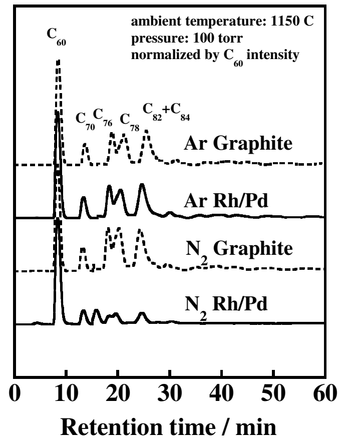

Fig. 5. HPLC spectra of higher fullerenes prepared by using laser furnace technique using Rh/Pd-carbon composite rod in Ar and nitrogen atmosphere. Those using pure carbon rod are also shown as references (indicated by dashed line).

process is so fast as that the carbon cage structure can not be completely closed in nitrogen atmosphere, the yield of higher fullerenes is considered to decrease, as is the case shown in Figure 5.

The formation process of SWNTs, as is different from that of fullerenes, requires the existence of metal/alloy particles. From the experimental findings that SWNTs having smaller diameter distribution (less than 1 nm) are prepared in nitrogen atmosphere (Fig. 2), while the relative yield of higher fullerenes drastically decreases (Fig. 5), it is likely to be considered that the imperfect precursors for higher fullerenes are used for the formation of thin SWNTs on Rh/Pd particles in nitrogen atmosphere. On the other hand, Figure 2 also suggests that the precursors for SWNTs having larger diameters (above 1 nm) exist in the raw material prepared in nitrogen atmosphere. Actually, after laser vaporization process terminates, successive post-annealing procedure for raw carbon materials gives new Raman signals corresponding to SWNTs, particularly for those prepared in Ar atmosphere [21]. This phenomenon has been already pointed out in the study using Ni/Co-carbon target [22].

4 Summary

SWNTs were prepared by laser vaporization of Rh/Pd (1.2/1.2 atom%)-carbon composite rod by using a laser-furnace technique, in nitrogen and Ar ambient gas atmosphere, respectively. It was found that the diameter distribution was different between in both cases. In consideration with the formation process of fullerene species, especially that in the initial a few milli-seconds, the formation process of SWNTs was discussed.

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