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Single-walled carbon nanotube formation with double laser vaporization technique

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Abstract. Single-walled carbon nanotubes (SWNTs) were prepared with double laser vaporization of a graphite target and a metal/alloy target inside an electric furnace at 1200 °C ambient temperature with 500 torr Ar gas atmosphere. Each target was vaporized simultaneously with a different Nd:YAG laser. Several kinds of metal/alloy target (Ni, Co, Fe, and permalloy) were tested in order to see the difference in the resulting SWNT yield and the diameter distribution of them. The Raman spectra of SWNT-containing soot prepared by use of this technique with permalloy/carbon system indicated that permalloy gives almost the same yield as compared with Ni/Co carbon composite rod with single laser vaporization technique, though the diameter distribution of them is slightly different. Also, time-resolved images of the plume by carbon and permalloy nanoparticles after laser vaporization were collected using a high-speed video camera. These images suggest that the hot plumes due to carbon and permalloy nanoparticles do not mix together so extensively, at least in a few hundred microseconds after laser vaporization. The effect of time delay between two laser pulses on the yield and the diameter distribution of SWNTs was also presented and discussed.

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1 Introduction

Since the single-walled carbon nanotubes (SWNTs) were discovered in 1993 [1], the new frontier of material science and technology by making use of them had attracted many researcher's interests. However, the preparation of purified SWNTs in large amounts are still not achieved, partly because the formation process of them has not been fully understood as yet. Recently, the catalytic chemical vapor deposition (CCVD) technique, one of the most promising method for the large scale production of SWNTs, has been developed by several researchers [2–6]. Among them, the CCVD technique by using alcohol as the carbon source, showed that one can prepare high-purity SWNTs as raw material at relatively lower temperature (700−800 °C), in comparison with the laser-oven technique and the electric arc-discharge technique [2].

As the common feature among these preparation methods for SWNTs, it is well known that metal nanoparticles should coexist with carbon source. In this proceeding, the metal/alloy nanoparticles and carbon material are vaporized independently by use of double laser vaporization technique, and then mixed them together in the inert gas atmosphere at relatively high temperature, in order to investigate the role of the metal/alloy nanoparticles in the formation process of SWNTs.

2 Experimental

SWNTs were prepared by double laser vaporization technique with several kinds of metal/alloy (Ni, Co, Fe, and permalloy (Permalloy 78, the Nilaco Corp.)) target and a graphite target using a laser furnace apparatus [7–10]. Briefly, metal target (6 mm in diameter) was inserted in the center of graphite target (20 mm in diameter), both of them are fixed to the molybdenum rod which was rotating inside the quartz tube (see the inserted figure in Fig. 4). Throughout the whole experiment, argon gas was used as buffer gas and the pressure of argon gas inside the quartz tube was maintained at 500 torr. The target and the growth zone were heated by an electric furnace and maintained at 1200 °C. We used two sets of pulsed Nd:YAG laser system, each of which vaporized the metal/alloy target and the carbon target, respectively. The condition for the laser vaporization of graphite target is 300 mJ/pulse throughout the whole experiment, and the laser power and

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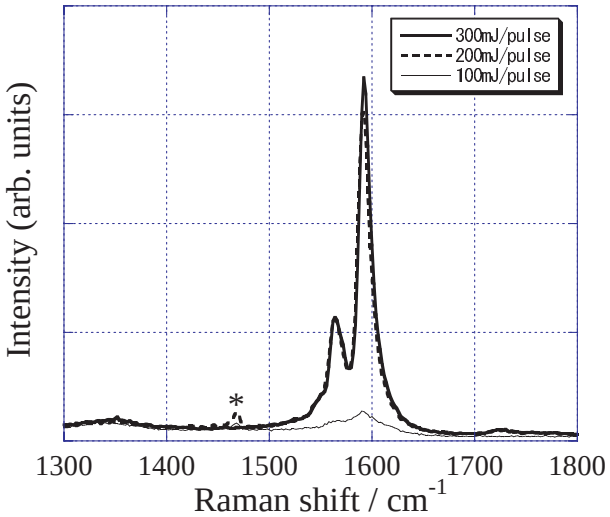

Fig. 1. Raman spectra of SWNTs obtained by dual laser ablation of permalloy and carbon targets with 100 mJ/pulse, 200 mJ/pulse, and 300 mJ/pulse laser power for the vaporization of permalloy target.

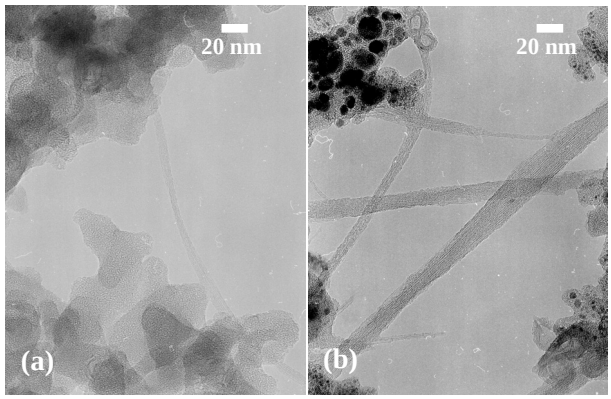

Fig. 2. TEM images of SWNTs obtained by dual laser ablation of permalloy and carbon targets with (a) 100 mJ/pulse and (b) 300 mJ/pulse laser power for the vaporization of permalloy target.

the time delay for the vaporization of metal/alloy target from the vaporization of carbon target were varied in the experimental condition described in the following.

In the first experiment, the condition for laser vaporization of metal/alloy target was changed to 100, 200, and 300 mJ/pulse, respectively. In the second experiment, the condition for laser vaporization of metal/alloy target was maintained to 300 mJ/pulse, while the time delay between two lasers was changed to 10, 30, 50, 70, and 90 ms. After laser vaporization for 30 min, the soot was collected and used for Raman spectroscopy with Ar ion laser (488nm), and transmission electron microscopy (TEM). Also, a high-speed video camera (KODAK EKTAPRO H4540 with 25 μs time window) was used in order to obtain the in situ behavior of emission by carbon and metal/alloy nanoparticles generated immediately after laser vaporization [11,12].

3 Results and discussion

Figure 1 shows high-frequency Raman spectra (1300–1800 cm^{-1}) of SWNTs obtained by double laser vaporization technique with 100 mJ/pulse, 200 mJ/pulse, and 300 mJ/pulse laser power for the vaporization of permalloy target. Figure 1 clearly indicates that SWNTs were prepared with 200 mJ/pulse and 300 mJ/pulse laser power, since these spectra have a characteristic peak due to SWNTs at $1592\pm2\,cm^{-1}$. The spectral features of them are almost the same to those of SWNTs obtained by ordinary single laser vaporization of Ni/Co (0.6 atom% + 0.6 atom%) carbon composite rod [13,14]. However, with 100 mJ/pulse laser power, the Raman spectral feature becomes obscure. Additionally, with 100 mJ/pulse and 200 mJ/pulse laser power, Figure 1 suggests an indication of tangential A_g mode ("pentagonal pinch mode") of C_{60}, which was designated by an asterisk (∗) at $1468\pm1\,cm^{-1}$ in the spectra.

Typical transmission electron microscopy (TEM) images obtained with these samples are shown in Figure 2. Figure 2a represents the TEM image of the soot with SWNTs obtained by dual laser ablation technique with 100 mJ/pulse laser power for the vaporization of permalloy target. It shows that there are few metal nanoparticles seen in the TEM image, suggesting that the amount of permalloy nanoparticles is not enough for the preparation of SWNTs. In fact, there are very few SWNTs seen in the TEM image of Figure 2a, and those SWNTs have a thin bundle structure (6−7 nm in diameter). On the other hand, the TEM image of the soot with SWNTs obtained by the same procedure with 300 mJ/pulse laser power for the vaporization of permalloy target, shown in Figure 2b, indicates that there exists lots of metal nanoparticles and SWNTs. Most of them have a thicker bundle structure (≥10 nm) than those seen in Figure 2a. These experimental findings strongly suggest that a proper combination of metal/alloy target and carbon target can make SWNTs, even though they do not coexist (*e.g.*, as a composite rod) before laser vaporization.

Figure 3 summarizes low-frequency Raman spectra (100−300 cm^{-1}) of SWNTs, each of which was obtained using several different metal/alloy (Ni, Co, Fe, and permalloy) targets. As a reference, SWNTs obtained by single laser vaporization of Ni/Co (0.6 atom% + 0.6 atom%) carbon composite rod is also included in the figure (drawn by using thin dotted line). Figure 3 shows, among several kinds of metal/alloy system, Ni and permalloy targets are shown to make SWNTs, though in the present experimental condition, the SWNT yield in the soot obtained with Ni target is found to be lower than that obtained with permalloy target. It is interesting to note that permalloy gives almost the same Raman intensity as that obtained with Ni/Co (0.6 atom%+0.6 atom%) carbon composite rod by single laser vaporization, while the spectral features are slightly different, suggesting that the diameter distribution of SWNTs becomes larger.

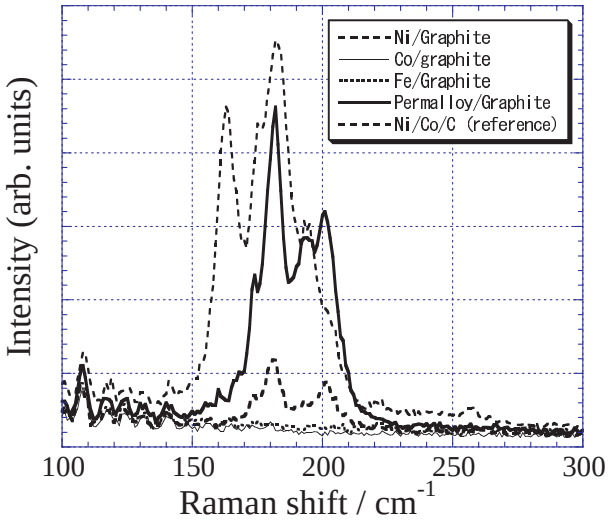

Fig. 3. Raman spectra of SWNTs obtained by dual laser ablation of (a) Ni, (b) Co, (c) Fe, and (d) permalloy targets with carbon targets. Typical Raman spectrum obtained for SWNTs by single laser ablation of Ni/Co (0.6 atom%+0.6 atom%) carbon composite rod is also included in the figure.

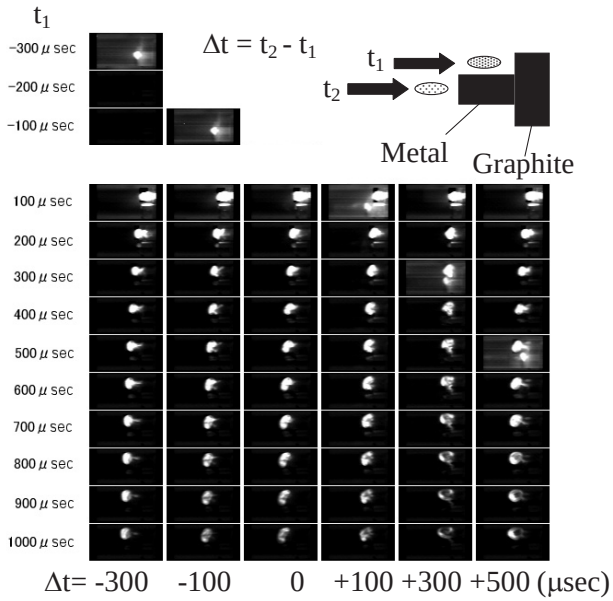

Fig. 4. Time and spatial evolution of emission by the plume of carbon and metal nanoparticles immediately after laser irradiation of a graphite rod (each image covers an area of 50 mm × 24 mm). The vertical axis gives the time t_1 defined by the vaporization of graphite target as an origin. Δt is defined by $t_2 - t_1$, where t_2 is the time defined by the laser vaporization of metal target as an origin. The data for $t_1 = 0$ μs are omitted because they are heavily overlapped with the intense emission.

According to the element analysis, the main components of permalloy nanoparticles shown in Figure 2b are found to be Ni(82−87%) and Fe(13−15%). Since the diameter distribution of SWNTs is influenced by the ambient temperature and/or the kinds and ratio of the metal targets, which was reported in the earlier investigation [11,12], it is likely to be considered that the inclusion of Fe in the Ni slightly change the diameter distribution of SWNTs in comparison with that prepared with Ni/Co (0.6 atom% + 0.6 atom%) carbon composite rod.

Figure 4 shows high-speed video camera images of the time and spatial evolution of the emission by the plume of carbon and permalloy nanoparticles after laser vaporization, each of which was obtained with different time delay (Δt = −300, −100, 0, +100, +300, and +500 μs, respectively) between two laser systems for double laser vaporization. Figure 4 clearly shows that, though the images of carbon nanoparticles last as long as 1000 μs, those of permalloy nanoparticles disappear within 100 μs. In the case of carbon nanoparticles, it was confirmed that the increase of blackbody emission due to the formation of fullerene-like species was the cause of long life of the emission to 1000 μs [11,12]. Therefore, the internal temperature of permalloy nanoparticles is considered to be decreased to the ambient temperature of the electric furnace, *i.e.*, 1200 °C in the present experimental condition, within 100 μs. Also, it is likely to consider that fullerenes can be prepared in the soot, if there is little supply of metal/alloy nanoparticles in the present experimental condition. Actually, in the low laser power condition (100 mJ/pulse and 200 mJ/pulse), one can distinguish the Raman peak at 1592 ± 2 cm^{-1} due to the tangential A_g mode of C_{60} in Figure 1. Additionally, Figure 4 indicates that the area occupied by the carbon nanoparticles does not mix so extensively with the area occupied by permalloy nanoparticles within 1000 μs. From that finding, one can expect that it is unnecessary for metal/alloy nanoparticles to coexist with carbon source before laser vaporization. It is interesting to point out that, in the CCVD method for the preparation of SWNTs, the metal/alloy nanoparticles were prepared first in the pores of zeolite, then carbon source was supplied as hydrocarbon or alcohol [2–4].

Figure 5 shows low-frequency Raman spectra (100–300 cm^{-1}) obtained for SWNTs by double laser vaporization of permalloy and carbon targets with different time delay (Δt). The notation for Δt is the same as shown in the inserted figure of Figure 4. Figure 5 indicates that the Raman spectral intensities, especially those around 200 cm^{-1} decreased with Δt = 50 ms and 90 ms, indicating that the formation of SWNTs was slightly influenced when the carbon source was supplied to the permalloy nanoparticles after the long time interval. An H_g mode of C_{60} was also observed (designated by an asterisk (∗) in Fig. 5) at 275 ± 1 cm^{-1} in the Raman spectra obtained with Δt = 50 ms time delay. Since the formation of metal/alloy nanoparticles was assumed to be finished within a few ms, it is likely that the nucleation process and the elongation process for the formation of SWNTs occurs after finishing the formation of metal/alloy nanoparticles. It may resemble to the CCVD process, where the preparation of metal nanoparticles occurs before introducing carbon source as hydrocarbon or alcohol [2–4].

In several techniques such as physical carbon vapor deposition in ultrahigh vacuum or CVD technique applied for the growth of nanotubes [17,18], the formation

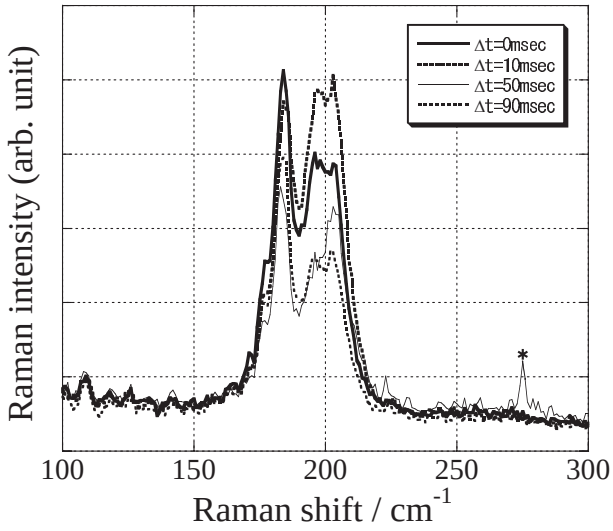

Fig. 5. Raman spectra obtained for the SWNTs by dual laser vaporization of permalloy and carbon targets with different time delay. The notation for Δt is the same as shown in the inserted figure of Figure 4.

of small metal particles is considered to be important for the catalytic effect in the supply of carbon feedstock in the growth process of them. In these techniques, metal particles are preformed, then carbon is supplied by several different ways. The experimental finding obtained here clearly demonstrates that the formation of metal particles and carbon feedstock can be separated before the nanotube formation even in the case of laser vaporization of metal/carbon system.

It is also interesting to note that the nanotube formation is influenced by the time interval Δt larger than 10 ms. Figure 5 shows that the highest nanotube yield is obtained at $\Delta t = 10$ ms. According to the previous investigation of the movement of carbon particles by using laser scattering technique [16], it is confirmed that the carbon particles proceed to the opposite way to the ambient gas flow within 10 ms after laser vaporization, (*i.e.*, from right to left, see Fig. 4 as a reference), then turn the direction and follow the ambient gas after that. Therefore, at $\Delta t = 10$ ms, it is considered that carbon particles encounters metal particles generated immediately after laser vaporization of metal target, where carbon species are considered to be dissolved into the metal particles, which may have higher internal temperature than the ambient gas atmosphere.

In summary, the double laser vaporization technique with the proper combination of metal/alloy targets and carbon targets confirmed the preparation of single-walled carbon nanotubes (SWNTs), where the experimental condition for the preparation of metal/alloy nanoparticles and that of carbon source seems to resemble to that of recently developed CCVD technique.

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