Synthesis of single-walled carbon nanotubes using laser-vaporized metal nanoparticle catalyst [†]

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Abstract

SWNTs were synthesized by laser-vaporized CCVD (catalytic chemical vapor deposition). The diameter distributions and the abundance of SWNTs synthesized at different temperatures and using different catalysts were investigated by Raman spectroscopy. Further, this technique was compared with other synthesis techniques (laser-oven and conventional-alcohol CCVD), and C_{60} was synthesized simultaneously as a byproduct only using the laser-oven technique. With increasing synthesis temperature, the diameter distribution shifted towards larger diameters, and the G/D ratio became larger as the synthesis temperature increased to 1000°C. Ni, Co, and Fe played a catalytic role, though Fe was less effective under our experimental conditions. The diameter distribution of SWNTs synthesized with the Fe catalyst was shifted to smaller values compared to those synthesized with Ni or Co catalysts.

Keywords: SWNTs; Laser vaporization; CVD; Raman spectroscopy

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1. Introduction

Since the discovery of single-wall nanotubes (SWNTs) [1], many synthesis techniques, such as the laser-oven technique [2], the arc-discharge technique [3], and various catalytic chemical vapor deposition (CCVD) techniques [4] have been developed. We have proposed a CCVD technique using alcohol as the carbon source (ACCVD), which has been shown to produce high-quality SWNTs [5] and can be performed at a significantly lower temperature compared to other CCVD techniques. Although, recently, the ACCVD technique has become increasingly popular, the mechanism for the growth of SWNTs from ethanol vapor and the effect of the metal catalyst during the formation process are not yet well understood. Nishide et al. developed laser-vaporized CCVD [6], which combines laser vaporization and ACCVD. In this technique, nanoscale catalyst particles are generated by the pulsed-laser vaporization of a metal rod, with ethanol vapor employed as the carbon source to synthesize SWNTs. Although this technique is not suitable for the mass production of

SWNTs, it is appropriate for research into their growth mechanism because various parameters, such as the type of the metal catalyst, pressure, mass flow of alcohol (i.e., the carbon source), and the temperature of the electric furnace, can be controlled individually. Nishide et al. synthesized SWNTs with Fe, Ni, Co, and Ni/Co catalysts at 850°C, and examined the influence of the synthesis temperature on the yield and diameter distribution for the Co catalyst.

The present study examines this technique in further detail by comparing the SWNTs with those synthesized by a conventional laser-oven ACCVD technique. It also examines the influence of the synthesis temperature on the yield and diameter distribution with Ni and Fe catalysts.

2. Experiment

Fig. 1 shows a schematic drawing of the laser-vaporized CCVD apparatus. It consists of a nanosecond pulsed Nd:YAG laser (wavelengths 1064 nm and 532 nm), two vacuum chambers, an electric furnace with a quartz tube (20 mm in diameter, 100 cm long) inside it, a molybdenum rod and a target rod (6 mm in diameter). Vacuum chambers terminate both ends of the quartz tube into which the molybdenum rod, which carries the target rod on its tip, is inserted. During the experiment, ethanol vapor (the carbon source) flows into the quartz tube at
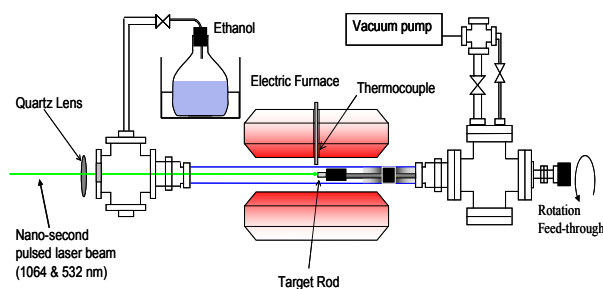

Fig. 1. Schematic drawing of the laser-vaporized CCVD technique.

Fig. 2. TEM image of SWNTs synthesized by laser-vaporized CCVD (900 °C, Ni catalyst).
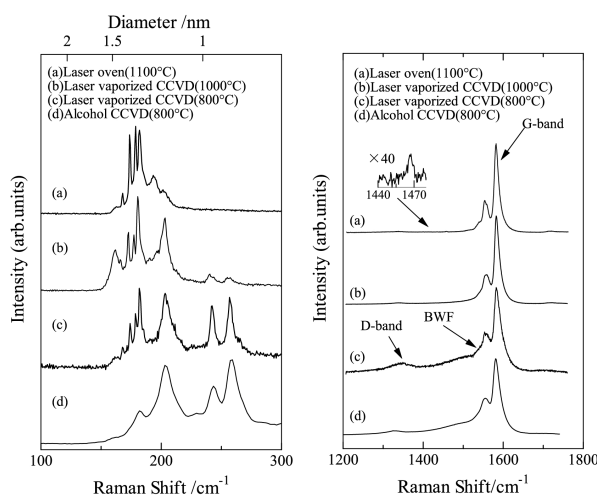

Fig. 3. (Left panel) The low-frequency and (right panel) high-frequency regions of the Raman spectra of the collected as-grown soot prepared by several synthesis techniques. (a) Laser oven (1100 °C, catalyst: Ni/Co); (b) the laser-vaporized CCVD (1000 °C, catalyst: Ni),;(c) laser -vaporized CCVD (800 °C, catalyst: Ni); (d) ACCVD (800 °C, catalyst: Fe/Co fine particles supported on Zeolite) [5].

3. Results and discussions

3.1 Comparison of the laser-oven and conventional alcohol CCVD techniques

Fig. 2 shows a typical TEM image of the as-grown soot synthesized by laser-vaporized CCVD at 900 °C (Ni catalyst). As shown in the figure, many of the synthesized SWNTs form bundles. Compared to soot prepared by the conventional laser-oven technique [7, 8], more metal particles exist in the raw soot prepared by the present laser-vaporized CCVD. Nishide et al. reported [6] that these metal particles are coated with graphitic layers, as these do not dissolve readily in hydrochloric acid.

Fig. 3(left panel) shows the low-frequency and (right panel) the high-frequency regions of the Raman spectra for the collected as-grown soot prepared by several synthesis techniques: (a) the laser-oven (1100°C, catalyst: Ni/Co), (b) the laser-vaporized CCVD (1000°C, catalyst: Ni), (c) the laser-vaporized CCVD (800 °C, catalyst: Ni), and (d) ACCVD (800 °C, catalyst: Fe/Co fine particles supported on zeolite) [5]. Ethanol vapor was used as the carbon source for both the laser-vaporized CCVD and ACCVD. SWNTs were not synthesized at 1100 °C by laser-vaporized CCVD because the ethanol decomposes. In Fig. 3 (left panel), the peaks in the range from around 160 to 210 cm^{-1} correspond to radial breathing modes (RBM). They provide indications on the SWNT diameter distribution, based on the correlation between the diameter d and the RBM Raman shift ϖ, used to define the scale of the diameter axis: $d/nm = 248/ (\varpi/cm^{-1})$ [9]. The RBM spectra for the laser-oven and the laser-vaporized CCVD at 1000 °C cover a range of around 160-210 cm^{-1}, corresponding to the diameter distribution of 1.2 - 1.5 nm. However, the RBM peak around 250 cm^{-1}, corresponding to the diameter

a constant pressure of 40 Torr. The quartz tube is heated to a temperature between 700 °C and 1100 °C. A mixture of the fundamental and of the second harmonic of the Nd:YAG laser (with a typical beam intensity of 200 mJ/pulse and a frequency of 10 Hz) was irradiated onto the surface of the metal target rod to ablate catalyst particles. The target is attached to the tip of the rotating molybdenum rod to expose a fresh surface of the target continuously to the beam. After 30 min of laser ablation, the resulting soot, which includes SWNTs, is deposited onto the molybdenum rod and onto the inner wall of the quartz tube (around the outlet of the electric furnace). It is then collected for characterization.

The laser-oven technique involves a similar procedure, but N$_2$ is used as the buffer gas instead of ethanol vapor and a Ni/Co (0.6/0.6 at wt%) carbon composite rod is attached to the tip of the molybdenum rod instead of the metal rod. The temperature of the electric furnace is between 800 °C and 1100 °C and the N$_2$ gas is maintained at atmospheric pressure and a flow rate of 0.15 L/min. The laser-beam intensity to ablate the surface of the rod was typically 80 mJ/pulse. The ablated carbon and metal particles serve as the carbon source and catalyst, respectively, for synthesizing SWNTs. After 30 minutes of laser ablation, the soot is collected in a similar manner to the laser-vaporized CCVD technique. The diameter distribution and the yield of SWNTs are again evaluated by Raman spectroscopy (using 488, 532 and 785 nm excitations).

Fig. 4. Raman spectra of SWNTs synthesized by laser-vaporized CCVD at different temperatures (800 °C and 1000 °C) and with different catalysts (Ni and Fe). (Left panel: the low-frequency region, right panel: the high-frequency region).
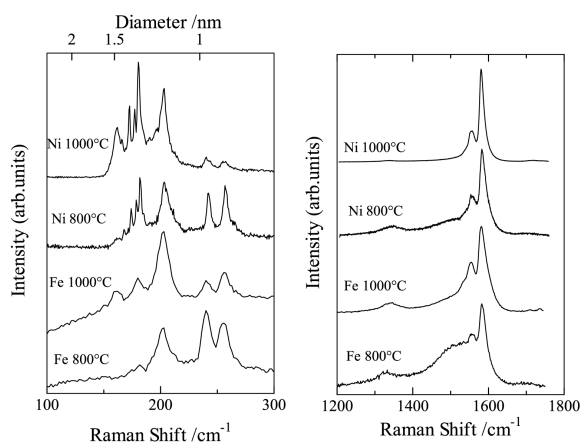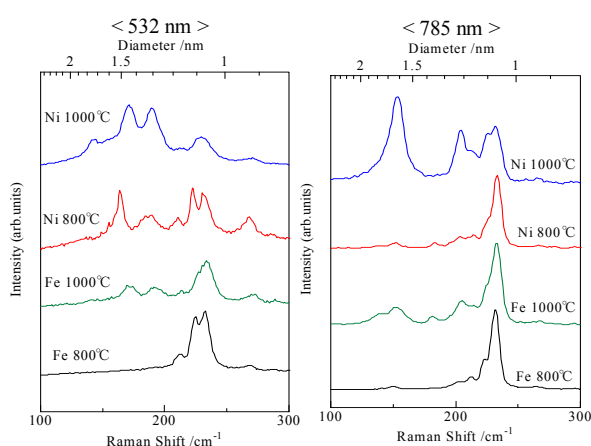

Fig. 5. Raman spectra of SWNTs synthesized by laser-vaporized CCVD at different temperatures (800 °C and 1000 °C) and with different catalysts (Ni or Fe), under 532 nm and 785 nm excitation.

distribution around 1.0 nm, was observed only with laser-vaporized CCVD. The RBM spectra of the laser-vaporized CCVD (at 800 °C) and ACCVD cover a wide range, 160-265 cm^{-1}, corresponding to the diameter distribution of 0.9-1.6 nm. This result suggests that the synthesis temperature is the dominant factor in defining the diameter distribution and a condition (in gas phase or supported on substrate) of metal catalysts.

In Fig. 3 (right panel), high-frequency Raman peaks are observed in all cases. The G-band (a superposition of 1593 cm^{-1} and 1568 cm^{-1}), which originates in the cylindrical graphite structure of SWNTs, is characteristic of semiconductor SWNTs [10, 11]. The broad peak observed around 1550 cm^{-1} is the Breit-Wigner-Fano (BWF) line, and this indicates that the SWNTs are metallic [12, 13]. The D-band, located around 1350 cm^{-1} and because of amorphous carbon or defects in the carbon network, was hardly observed for synthesis at 1000 °C but appeared weakly at 800 °C. Peaks that originate in C$_{60}$ were observed around 1468 cm^{-1} [14]only in the soot synthesized using the laser-oven technique. Thus, fullerenes seem to be synthesized simultaneously as a byproduct. Earlier studies have suggested different SWNT growth mechanisms for the laser-oven and the CCVD techniques [6]. In the context of the laser-oven technique, the "fullerene cap model" [15] proposes that carbon in fullerene cap structures is a precursor to SWNTs. It is well known that fullerenes are always synthesized as a byproduct in the laser-oven technique and that the diameter distribution of SWNTs is influenced by the size distribution of the higher fullerenes [7, 15]. It is therefore conceivable that a few fullerene cap structures grow to form C$_{60}$ under our experimental conditions of the laser-oven technique, and that the growth mechanism relevant for each technique results in different diameter distributions.

3.2 Influence of metal catalyst in SWNT synthesis

Fig. 4 shows Raman spectra of as-grown soot prepared by

the laser-vaporized CCVD technique at different temperatures (800 °C and 1000 °C) and with different catalysts (Ni and Fe). The left panel shows the low frequencies and the right panel the high frequencies. The result for Ni is almost the same as that of a previous study where Co was used as the catalyst [6].

With increasing synthesis temperature, the center of gravity of the peaks is shifted towards lower frequencies and the distribution becomes narrower. The RBM spectrum (Ni, 1000 °C) mainly covers the range 160-210 cm^{-1}, corresponding to the diameter distribution of 1.2-1.5 nm. Specifically, thin nanotubes with a diameter of around 0.96 or 1.02 nm are barely observed at 1000 °C while their presence is abundant at 800 °C. In the case of Fe catalyst, the RBM peaks around 240-255 cm^{-1} are largest at 800 °C. However, at 1000 °C, the peaks around 200 cm^{-1}, corresponding to the diameter of around 1.2 nm, become dominant. Comparing the spectra corresponding to 800 °C and 1000 °C, the tendency observed for both catalysts is that the higher synthesis temperature gives a higher yield of large SWNTs. More large SWNTs are synthesized at 1000 °C with Ni catalyst than with Fe. It is possible that the size distributions of Ni and Fe metal particles, produced by laser ablation of the metal rod, are different, resulting in different SWNT diameter distributions. Further study, e.g., by TEM, is necessary to understand this difference.

In the right panel in Fig. 4, the BWF lines are observed clearly at 800°C and their intensity decreases as the synthesis temperature increases to 1000°C for both catalysts, consistent with the result of the RBM region. The G/D ratio (the ratio between intensity of the G-band and D-band), which measures the yield of SWNTs, increases as the reaction temperature rises for both catalysts. If the BWF line dominates the G-band structure, it is difficult to use the G/D ratio as a measure of the yield. Comparing the spectra of SWNTs synthesized with Ni or Fe at 1000 °C, the BWF line is barely observed in the case of Fe. It is therefore difficult to discuss the difference in yield for Fe and Ni quantitatively. However, a qualitative assessment is possible for the following reasons: (1) The D band is
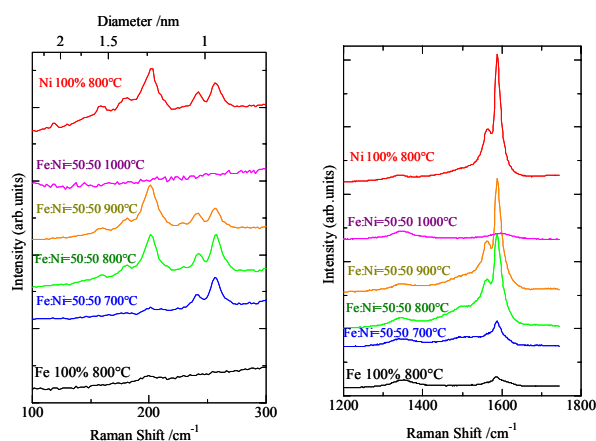
Fig. 6. Raman spectra for SWNTs synthesized by conventional ACCVD at different synthesis temperatures under 488 nm excitation with Fe, Fe/Ni, or Ni catalyst supported on zeolite (Left panel: the low-frequency region, right panel: the high-frequency region).

hardly observed in the Ni spectra but is strong with Fe; (2) the BWF line is indeed observed in the Fe case but it is not dominant. Referring to the RMB region, the semiconductor SWNTs are predominant with Fe at 1000 °C. Thus, SWNTs are more abundant in a given amount of soot when Ni catalyst is used, while Fe is an ineffective catalyst.

Because Raman spectra depend on the excitation wavelength, we also used other excitation lasers with wavelengths 532 nm and 785 nm. Fig. 5 shows Raman spectra of SWNTs synthesized by the laser-vaporized CCVD technique at different temperatures (800 °C and 1000 °C) and with the two catalysts (Ni and Fe). As shown in the figure, the diameter distribution is shifted towards larger values for Ni than for Fe. Though these Raman spectra do not provide the complete diameter distribution of SWNTs cannot be observed from these Raman spectra, it is clear that more large SWNTs were synthesized with Ni.

Fig. 6 shows Raman spectra for SWNTs synthesized by conventional ACCVD at different temperatures with Fe, Fe/Ni or Ni catalysts supported on zeolite for 488 nm excitation (left panel: low frequencies; right panel: high frequencies). Two distinct features are apparent, compared with laser-vaporized CCVD. Firstly, SWNTs are synthesized with laser-vaporized Fe catalyst, but not with Fe catalyst supported on zeolite. Secondly, SWNTs are synthesized by the laser-vaporized CCVD technique at 1000 °C (Ni catalyst), but not with Ni catalyst supported on zeolite.

It is not clear at present why SWNTs are not synthesized with Fe catalyst supported on zeolite. However, it is possible that the size of Fe catalyst supported on zeolite is not small enough to allow SWNT synthesis. It is well known that small metal particles (1~2 nm) are suitable for SWNT synthesis. Thus, because laser ablation of the Fe rod produces a broad range of nanoparticle sizes, SWNTs can be synthesized by laser-vaporized CCVD. Further detailed study (for example by controlling the size of Fe catalyst particles) will be needed to confirm this hypothesis.

The difference in the maximum temperature at which SWNTs are synthesized is likely to result from the different position of the catalyst in the electric furnace. A metal rod that generates catalyst particles by laser irradiation is placed at the center of the quartz tube. On the other hand, the quartz boat containing zeolite is situated on the inner wall of the tube. In our apparatus, the thermocouple measures the temperature at the outer surface of the quartz tube rather than at its center. Therefore, the actual temperature for SWNT synthesis by laser-vaporized CCVD may be lower than that measured by the thermocouple.

4. Conclusion

SWNTs were synthesized by laser-vaporized CCVD. We compared this technique with other synthesis techniques and investigated its dependence on the type of metal catalyst used. Compared with the laser-oven technique and conventional ACCVD, the synthesis temperature seems to be a dominant factor for determining the diameter distribution of the SWNTs but the situation (in gas phase or supported on substrate) of metal catalysts. However, a few differences in the diameter distribution were observed between the laser-oven technique, laser-vaporized CCVD, and ACCVD. In addition, C_{60} was produced as a byproduct only with the laser oven, which suggests a different precursor to the SWNTs. A tendency, observed with both Ni and Fe catalysts, is that a higher synthesis temperature yields more large SWNTs. However, at 1000 °C, more large SWNTs are synthesized with Ni than with Fe. In addition, Fe appears to be an ineffective catalyst compared to Ni.

Acknowledgements

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