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Synthesis of single wall carbon nanotubes by using arc discharge technique in nitrogen atmosphere

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Abstract. Single wall carbon nanotubes (SWNTs) were prepared with arc discharge technique using Ni/Co carbon composite rod in He, Ar, and N_2 atmosphere, respectively. The yield and the diameter distribution of them were compared with each other. The results show that N_2 atmosphere at low pressure gives the highest yield for the formation of SWNTs, almost comparable to that obtained with laser furnace technique. It also declares that He atmosphere seems to make SWNTs having smaller diameter distribution than those obtained in N_2 and Ar atmosphere. These findings were summarized and used for the discussion related to the formation mechanism of SWNTs.

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

1 Introduction

The formation mechanism and the development of mass production of single wall carbon nanotubes (SWNTs) in purified form have been the important issues since the discovery of SWNTs in 1993 [1], because any application of them requires further purification procedure in order to get rid of the impurities such as metal particles and/or amorphous carbon materials generated at the same time.

In the early 1990's, the arc discharge technique has been extensively used for the synthesis of SWNTs, e.g., using Ni/Y [2] or Rh/Pt [3] carbon composite rods in He atmosphere. However, the ratio of metal atom in the composite rod usually exceeds more than 1 atom%, and therefore, it was found that those SWNTs include lots of metal particles and can not be considered as starting materials aimed for further purification procedure at present. On the other hand, recent development of chemical vapor deposition technique, e.g., Hipco [4] and alcohol CCVD [5] technique, show that SWNTs can be prepared in better quality, though the elimination of metal particles or supported materials is still left unresolved.

A laser furnace technique, which is well known as a best tool for investigating the formation mechanism of SWNTs, can provide SWNTs of highest purity in comparison with other technique, though this technique gives only a very small amount of soot containing SWNTs (less than ca. 50 mg/hour). Thus, a more simple technique which can provide a big amount of soot containing SWNTs of almost the same quality as those supplied by laser furnace technique, is expected for further application. In this presentation, based on the recent experimental finding that SWNTs were prepared in the highest purity in N_2 atmosphere by using laser furnace technique [6], the formation of SWNTs was investigated with arc discharge technique in He, Ar, and N_2 atmosphere, respectively. Using Ni/Co (0.6/0.6 atom%) carbon composite rod, which is normally used for the formation of SWNTs with a laser furnace technique, the yield and the diameter distribution of SWNTs were compared with each other by Raman spectroscopy and transmission electron microscopy (TEM). The experimental findings are summarized and used for further discussion.

2 Experimental

SWNTs were prepared by using a DC arc discharge apparatus with Ni/Co (0.6/0.6 atom%) carbon composite rods. Briefly, a target rod (6 mm in diameter) was set as a cathode, and a carbon target (15 mm in diameter) was set as an anode. A typical DC arc current was set to 50–60 A. And the pressure of the ambient gas (He, Ar, N_2, respectively) before arc discharge was varied from 50 to 1000 torr (in the maximum) in each.

The obtained soot containing SWNTs was collected from the ceiling of the apparatus, and used for Raman

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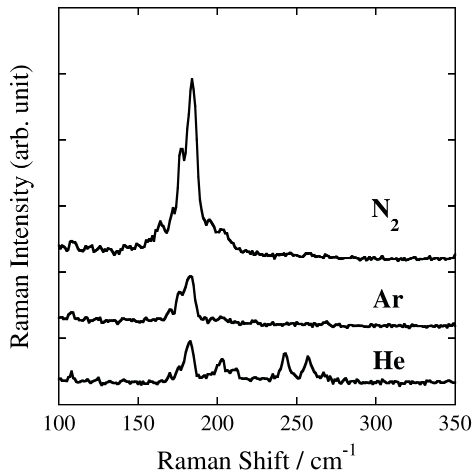

Fig. 1. Raman spectra of SWNTs obtained by arc discharge of Ni/Co (0.6/0.6 atom%) carbon composite rod in He, Ar, and N_2 atmosphere. The pressure before arc discharge is 50 torr.

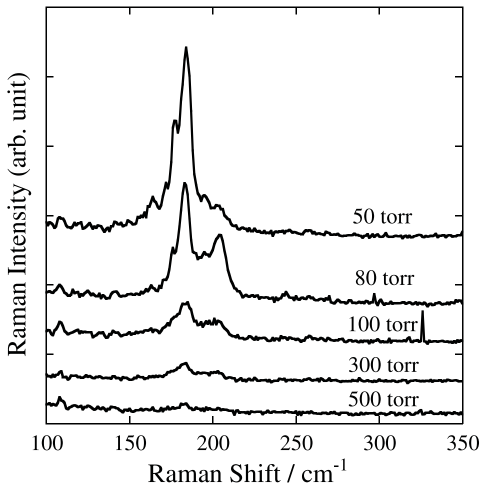

Fig. 2. Raman spectra of SWNTs obtained by DC arc discharge of Ni/Co (0.6/0.6 atom%) carbon composite rod in N_2 atmosphere. The pressure before arc discharge was 50, 80, 100, 300, and 500 torr, respectively.

spectroscopy with Ar ion laser (488 nm), and transmission electron microscopy (TEM), in order to check the purity of SWNTs in the raw soot and the diameter distribution of them.

3 Results and discussion

Figure 1 shows typical Raman spectra of SWNTs in the raw soot obtained with DC arc discharge technique in the low frequency region (100–350 cm^{-1}). Each soot was prepared in He, Ar, and N_2 atmosphere of 50 torr, respectively. From the peak position of each Raman spectrum, one can estimate the diameter distribution of SWNTs 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 Raman spectra of SWNTs grown in N_2 and Ar atmosphere at 50 torr are dominated by a peak around 183 cm^{-1}, indicating a narrow diameter distribution around 1.35 nm. In contrast, the Raman spectrum in He atmosphere at 50 torr exhibits several peaks in a range from 183 to 257 cm^{-1} corresponding to the diameter distribution from 0.96 to 1.35 nm. It looks like similar to that obtained by Saito et al. [3]. Also, Figure 1 demonstrates that the peak intensity of the Raman signal obtained in N_2 atmosphere is highest.

Figure 2 summarize Raman spectra of SWNTs obtained in N_2 atmosphere with different ambient gas pressure, in the low frequency region (100–350 cm^{-1}). It is interesting to point out that Raman peak intensity decreases monotonously as the N_2 pressure increases above 50 torr. At less than 50 torr, the Raman intensity drops off rapidly and can not be seen (not shown). Figure 2 also indicates that the diameter distribution of SWNTs becomes broader and shifts to the smaller diameter distribution as the N_2 pressure increases from 50 torr to 500 torr, which seems to be in contrast with the finding reported by Saito et al. for the formation of SWNTs using Rh/Pt catalyst in He atmosphere with DC arc discharge technique, where the diameter distribution of SWNTs shifts toward the larger when He pressure increases from 50 torr to 600 torr [3]. As a reference, when He was used as an ambient gas atmosphere with Ni/Co catalyst, the pressure effect on the diameter distribution of SWNTs was found to be the almost the same as was obtained by Saito et al.

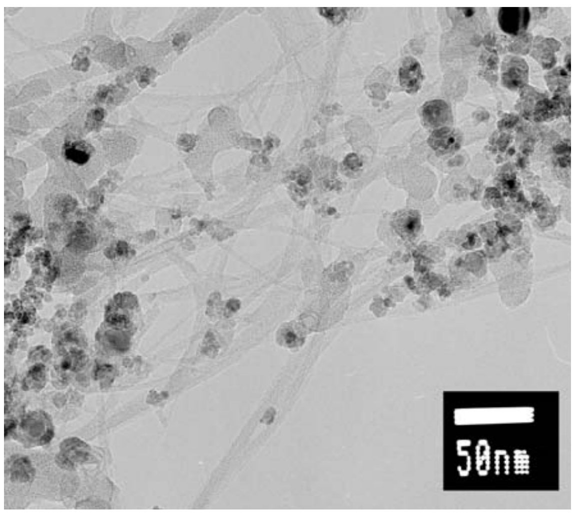

Fig. 3. TEM image of the soot containing SWNTs by DC arc discharge of Ni/Co (0.6/0.6 atom%) carbon composite rod in 50 torr N_2 atmosphere.

The change in Raman intensity well corresponds to the change in the morphology of the soot obtained as raw material. For example, between 50 and 500 torr N_2 atmosphere, the soot obtained from the ceiling of the apparatus looks like a film, while at less than 50 torr or at larger than 500 torr N_2 atmosphere, the obtained soot looks like powder. Figure 3 shows a typical TEM image of the raw soot containing SWNTs prepared by DC arc discharge at 50 torr N_2 atmosphere. Though the bundle structure is

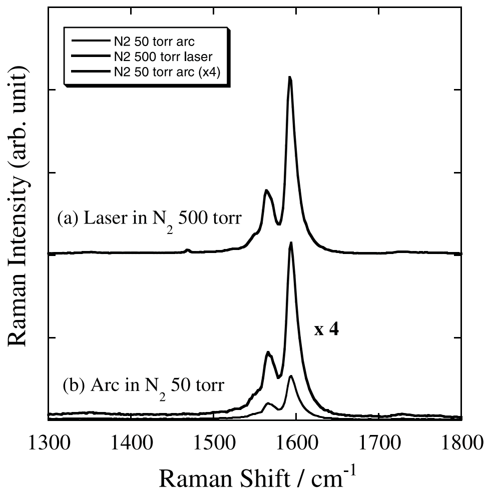

Fig. 4. Comparison of Raman spectrum of the raw soot prepared with laser furnace technique (above) and that prepared with DCarc discharge technique (below).

seen in Figure 3, the number of SWNTs in each bundle is typically less than 10, which is different from that of SWNTs prepared by the laser furnace technique.

In Figure 4, Raman spectra in the high frequency region (1300–1800 cm^{-1}) including G-band and D-band structure, due to the SWNTs produced with DC arc discharge and laser furnace technique using the same Ni/Co carbon composite rod, are shown for comparison. It is interesting to note that, even in the case of DC arc discharge technique, the intensity of D-band in the spectrum, which is considered to be an index of carbonaceous impurities, seems to be as low as is obtained by laser furnace technique.

Considering that the ambient gas has two kinds of effect, i.e., cooling effect and caging effect during fullerenes and SWNTs are generated [7,8], the discrepancy between He and N_2 described above is explained well in the following. According to the in situ observation of the emission of carbon nanoparticles generated by laser furnace technique [7], He gas has strong cooling effect and weak caging effect. Therefore, the number density of He required for caging carbon materials for the growth of SWNTs in a certain space during the arc burning, should be high, in order to keep the local temperature and maintain the growth of SWNTs. The reason why the diameter distribution of SWNTs at low He pressure is large, can be explained that the area for the formation and growth of SWNTs in arc burning apparatus spreads over the apparatus at low He pressure, and thus the local temperature is different from space to space, resulting in the wide diameter distribution of SWNTs.

Since higher fullerenes can be generated effectively in He atmosphere at higher pressure with arc discharge technique, which coincides with the observation with laser furnace technique at higher ambient gas temperature [8], it is likely to consider that the diameter distribution of SWNTs also becomes larger when He pressure increases, because the diameter distribution of SWNTs shifts toward the larger when the ambient gas temperature increases up to 1300 °C by laser furnace technique [10].

On the other hand, N_2 has weaker cooling effect and enough caging effect. Therefore, the growth of SWNTs is maintained even when the N_2 pressure is as low as 50 torr. However, when N_2 pressure increases further, the local temperature increases higher than that considered to be enough temperature for the growth of SWNTs, and thus the growth of SWNTs is suppressed above 50 torr. It is interesting to point out that the formation of SWNTs were also suppressed as the ambient gas temperature increases above 1300 °C by using laser furnace technique with Ni/Co carbon composites rod [10].

In summary, conditions for making SWNTs with arc discharge technique were systematically investigated in He, Ar, and N_2 atmosphere, respectively. It was found that N_2 gives the highest yield of SWNTs at 50 torr. The Raman spectra and TEM images were summarized and compared with each other and with those by laser furnace technique, and used for further discussion on the formation process of SWNTs.

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