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Production of Single-Walled Carbon Nanotubes by Modified Arc Discharge Method

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Abstract

Single-walled carbon nanotubes (SWNTs) are synthesized by the arc discharge method in He gas, where three directions of discharge current relative to gravity are selected and their production rates are compared. The soot production rate for the upward discharge current is larger than those for the horizontal and downward discharge currents. Also, the qualities of the produced SWNTs for the three cases are almost the same. The effect of a steady magnetic field (3.0 mT) perpendicular to the discharge current direction ($\mathbf{J} \times \mathbf{B}$ arc discharge) is also examined. This magnetic field increases the soot production rate for all three discharge current directions. The estimated ratio of the number of SWNT bundles to the number of carbon particles is higher for the upward discharge current in the case of $B = 0$. This ratio increases significantly for the horizontal and downward discharge currents when a magnetic field is applied.

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1. Introduction

Since the first ever production of carbon nanotubes (CNTs) by the arc discharge method in 1991¹⁾, tremendous interest has been stimulated by their extraordinary mechanical, thermal, and electrical properties.^{2,3)} Because of these unique properties, CNTs have become promising candidates for many potential applications, such as in electronic devices,^{4,5)} electroconductive films,⁶⁾ probe tips for microscopy,⁷⁾ supercapacitors,⁸⁾ composite materials,⁹⁾ and chemical gas sensors.¹⁰⁾ The large-scale and low-cost production of CNTs is necessary for their widespread use. Iijima and Ichihashi¹¹⁾ and the IBM group¹²⁾ produced single-walled carbon nanotubes (SWNTs) by the arc discharge method. However, the mass production of high-quality and diameter-controlled SWNTs has not been realized.¹³⁾ SWNTs produced by the arc discharge method have fewer structural defects than those produced by lower-temperature methods.¹⁴⁾ SWNTs are produced in the hot He gas region near the arc plasma, where heat convection blows hot carbon species upward, and the reaction time is limited. Therefore, if the discharge direction relative to gravity is changed, the production conditions of SWNTs in the hot gas region will be changed. In an attempt to improve the production of SWNTs, a magnetic field was applied in the arc plasma ($\mathbf{J} \times \mathbf{B}$ arc discharge), and the production rate of CNTs was increased.¹⁵⁻¹⁷⁾ When a magnetic field is applied perpendicular to the discharge current, the arc plasma jets out in the $\mathbf{J} \times \mathbf{B}$ direction. Modification by the $\mathbf{J} \times \mathbf{B}$ arc discharge could lead to the efficient production of SWNTs in the arc discharge method.

In this work, we have experimentally studied the effect of the discharge current direction relative to gravity and the effect of a steady-state magnetic field on SWNT production. Raman spectroscopy and transmission electron microscopy (TEM) are used to determine the quality and production efficiency of SWNTs in the produced soot.

2. Experimental Setup and Method

A schematic of the experimental setup is shown in Fig. 1(a). A stainless-steel reactor of 18 cm diameter and 20 cm height is used, in which a carbon cathode (15 mm diameter and 35 mm length) and a rectangular-type C-Ni-Y composite anode ($6 \times 6 \times 40 \text{ mm}^3$, Toyo Carbon Cluster Mate, including 4.2 wt% Ni and 0.9 wt% Y) are set. The anode is grounded and can be moved by a motor drive to adjust the gap distance between the electrodes, d_G . First, the reactor is evacuated using a rotary pump to less than 1 Pa, and helium gas is introduced so that the pressure, $p(\text{He})$, becomes 60 kPa and then the reactor is closed. A constant discharge current, $I_d = 50 \text{ A}$, is applied by a regulated DC power supply (Daihen ARGO-300P), and discharge is started by contact ignition. d_G and the voltage between the electrodes, V_{rod} , are adjusted to approximately 5 mm and 25 V, respectively. As the anode is consumed, d_G is adjusted and the rod voltage is kept constant. In this experiment, the He pressure and discharge current are chosen from the fact that they were found to be suitable for producing SWNTs by the arc discharge method in our previous study.¹⁵⁾ After the discharge time, $t_d = 30 \text{ min}$, has elapsed the reactor is opened and the produced soot is separately collected from the upper, sidewall, and bottom parts of the chamber. The hard carbon deposit on the cathode is also collected separately, which contains mainly multiwalled carbon nanotubes¹⁸⁾ and is not considered when estimating the SWNT production rate. The soot production rate, W_{soot} , is calculated from the total weight of soot on the upper, sidewall, and bottom parts of the chamber. The soot production efficiency, $W_{soot}/\Delta W_{anode}$, is calculated from the ratio of the soot production rate to the consumed weight of the anode per unit time, ΔW_{anode} .

To study the effect of the discharge current direction on SWNT production, the reactor is rotated to realize three different discharge current directions (horizontal, upward, and downward directions) as shown in Fig. 1(b), keeping the other discharge conditions the same. To study the effect of a magnetic field, a steady magnetic field of 3.0 mT is applied in the three current directions by placing a pair of ferrite-type rectangular magnets ($60 \times 80 \times 100 \text{ mm}^3$) outside of

the chamber in such a way that the $\mathbf{J} \times \mathbf{B}$ force is perpendicular to the discharge current. From our previous study, $B = 3.0$ mT was found to be suitable for ensuring the stable acceleration of the arc plasma.¹⁵⁾

To analyze the samples, a Raman spectrometer (JASCO NR-1800, $\lambda = 532$ nm) is used. A transmission electron microscope (Hitachi H-7500, acceleration voltage of 80 kV) is used to observe the morphology and content of SWNTs and the impurities in the soot.

3. Results and Discussion

The effects of the discharge current direction relative to gravity and the effect of a magnetic field perpendicular to the current direction on the production of soot are examined, and the results are shown in Fig. 2. The variations of W_{soot} and $W_{soot}/\Delta W_{anode}$ without and with a magnetic field ($B = 3.0$ mT) for the three different current directions are presented. Several factors such as the change in the anode shape during its sublimation may have affected the production of soot. Therefore, the soot is produced at least three times in each configuration and the standard errors are presented in the graphs using error bars.

It is found that in the case of $B = 0$, the soot production rate for the upward discharge current is 20% larger than that for the horizontal discharge current, but for the downward discharge current the rate is 36% lower. The soot production efficiencies, $W_{soot}/\Delta W_{anode}$, are similar for the upward and horizontal discharge currents. However, for the downward discharge current, it is about 20% less than that for the horizontal current. The lower soot production rate for the downward current can be interpreted as being due to redeposition of the carbon species on the anode. The anode rod itself interrupts the flow of carbon vapor and causes the redeposition,¹⁶⁾ resulting in the lower soot production efficiency. In this case, the hot gas reaction is also disturbed by the anode. For the upward discharge current, the flow of ablated species is in the

same direction as the heat convection. Thus, the reactive species remain in the hot gas environment for a longer time and the production rate of SWNTs is expected to be higher.

When the magnetic field is applied, it is found that both W_{soot} and $W_{soot}/\Delta W_{anode}$ increase for all three cases of the discharge current. These increases in W_{soot} are 134%, 60%, and 198% for the horizontal, upward, and downward discharge currents, respectively. In this case, the Lorentz force acting on the electrons is much larger than the buoyancy of He gas and the collision frequency between electrons and He atoms is very high ($\sim 4 \times 10^{11}$ Hz). Therefore, the electron energy is effectively transferred to the motion of He atoms.¹⁹⁾ The magnetic field can artificially induce stronger heat convection, and it blows the sublimated carbons, resulting in an increase in the sublimation rate of the anode. As a result, W_{soot} increases. The magnetic field is expected to increase the discharge voltage, which increases the input power and the sublimation rate of the anode.¹⁵⁾ However, in this experiment, the increase in discharge voltage is 0.5 to 1.0 V, which can be regarded as having a negligible effect on the soot production rate. In the case of the downward discharge current, this $\mathbf{J} \times \mathbf{B}$ force helps the carbons to avoid being redeposited on the anode and increases the production rate.²⁰⁾ Finally, in the presence of the magnetic field, the soot production rate for the horizontal current is higher than those for the other two currents.

The produced SWNTs, which are included in the soot, are analyzed by a Raman spectrometer. Raman spectra, which include the radial breathing mode (RBM) and the G mode and D mode, are presented in Figs. 3 and 4, respectively. The dominant RBM peaks in all the cases are at approximately 167 cm^{-1} , for which the SWNT diameter is calculated to be 1.48 nm.²¹⁾ The SWNTs produced in the $\mathbf{J} \times \mathbf{B}$ case have similar diameter distributions to those in the $B = 0$ case. The other broad peak at approximately 183 cm^{-1} indicates an SWNT diameter of approximately 1.34 nm. This peak is slightly enhanced by the magnetic field only for the horizontal discharge current. For the downward and upward discharge currents, the diameter distributions remain similar after applying the magnetic field.

In Fig. 4, the peak intensity of the G band, I_G , is always much larger than that of the D band, I_D , for all the samples. When $B = 0$, I_D for the downward current is larger than those for the other current directions, as shown in Fig. 4(c). In this case, more disordered carbons or SWNTs having defects such as vacancies, 7-5 pairs, and dopants in the walls may exist in the soot.^{21,22)} From Fig. 4, the intensity ratio of the D band to the G band, I_D/I_G , is calculated and the result is shown in Fig. 5. I_D/I_G is the highest (0.117) for the downward discharge current, as shown in Fig. 4(c), and thus there are fewer SWNTs or more defects in the SWNTs than for the other two current directions. The value of I_D/I_G is found to be lowest (0.024) for the upward current direction. Hence, in the case of $B = 0$, it is expected that the content and quality of SWNTs will be highest under the upward discharge current condition²²⁾. It is conjectured that under this condition the current flows parallel to the upward direction of heat convection, and the production conditions near the arc flame become more uniform and the cooling of the carbon species is more stable, resulting in better conditions for the production of SWNTs.

When the magnetic field is applied, I_D/I_G decreases in the case of the horizontal and downward discharge currents, as shown in Fig. 5. On the other hand, for the upward discharge current, I_D/I_G increases from 0.024 to 0.061, which indicates that the quality of SWNTs in the soot is deteriorated by the magnetic field. In this case, the $\mathbf{J} \times \mathbf{B}$ direction is perpendicular to the direction of heat convection, and it is conjectured that the acceleration of the evaporated carbon species perpendicular to the direction of heat convection cools them more quickly, thus reducing the reaction time and affecting the synthesis of SWNTs. In the case of the horizontal discharge current, the $\mathbf{J} \times \mathbf{B}$ direction is parallel to the direction of heat convection, and it is conjectured that sublimated carbon species diffuse into the hot gas region where the nanotube synthesis takes place. Therefore, the amount and quality of the SWNTs are enhanced, which is indicated by the decrease in I_D/I_G from 0.039 to 0.027. In the case of the downward discharge current, the magnetic field accelerates the evaporated carbon species perpendicular to the upward direction of

heat convection, and therefore they can effectively form SWNTs with higher quality instead of being redeposited on the anode.

Typical TEM images of the soot for the three discharge current directions with $B = 0$ are shown in Figs. 6(a)–6(c). From these images it is confirmed that the soot contains fewest SWNTs for the downward current. This result is in good agreement with the results of Raman analysis as shown in Fig. 4. It is conjectured that in this case the sublimated reactive species from the anode are quickly redeposited on the anode owing to the upward heat convection. TEM images of the soot for the three current directions with the magnetic field ($B = 3.0$ mT) are shown in Figs. 6(d)–6(f). Owing to the $\mathbf{J} \times \mathbf{B}$ force, the number of SWNTs increases considerably in the cases of the horizontal and downward currents but decreases in the case of the upward current. The number of SWNT bundles, N_{ntb} , is counted in TEM images of the same magnification ($\times 50000$), which cover an area of 4×10^6 nm². The results for the three current directions are shown in Fig. 7(a). The number of carbon particles, N_{cp} , is also counted in the same TEM images, where both metal catalyst particles and simple amorphous-like carbon particles are considered. The usual shape of the particles is spheroid. When the shape is far from spheroid, two or more particles are counted, assuming that spherical particles were connected to make this shape. In these images, the densely stacked regions of carbon particles and SWNTs are excluded because of the difficulty of counting. The ratio N_{ntb}/N_{cp} is calculated for the three discharge currents at $B = 0$ and 3.0 mT and is presented in Fig. 7(b). As this ratio is the number ratio of SWNT bundles to carbon particles in the same region, the results are used to confirm the relative numbers of bundles of SWNTs in the samples. The ratio shows a correlation with the number of SWNTs for each current direction. When $B = 0$, the ratio is 48% higher for the upward discharge current than for the horizontal current, whereas it is 42% lower for the downward discharge current. By applying the magnetic field, the ratio increases by 33% for the horizontal discharge current and 88% for the downward discharge current, while it is slightly decreases for the upward discharge current. Therefore, it is

expected that by applying the magnetic field, the number of SWNT bundles is increased for the horizontal and downward discharge currents. These findings also support the results of the Raman measurement, and as N_{ntb}/N_{cp} is always less than 1.0, it can be assumed that the carbon particles in the soot are similarly distributed to those of the SWNTs for all the discharge currents. The diameter of the nanotubes obtained from the TEM measurement is found to vary from 1.10 to 1.75 nm, with the largest number of SWNTs having a diameter of approximately 1.50 nm, which confirms the results of the RBM measurement in Fig. 3. Under each discharge current condition there are 1 to 8 nanotubes per SWNT bundle, and in most cases a bundle consists of 3 to 4 nanotubes. The lengths of the SWNTs, as measured from the TEM images, are 0.5 μm to more than 1 μm , but SWNTs longer than 1 μm cannot be measured from the typical TEM images as they are not completely contained in the images. To check the reproducibility of measurements, 3-7 TEM images of the soot produced under each discharge condition are taken and error bars are obtained by calculating the standard deviation of the results in Figs. 7(a) and 7(b).

From these results it is conjectured that in the horizontal current case, the $\mathbf{J} \times \mathbf{B}$ force is in the direction of heat convection and carbon atoms remain for longer in the hot gas atmosphere, thus forming more SWNTs. On the other hand, in the case of the upward discharge current, the carbon species are quickly removed from the hot gas region by the horizontal $\mathbf{J} \times \mathbf{B}$ force and do not have sufficient time to form the SWNT structure. However, in the case of the downward current, the number of SWNTs increases, because the flow of the carbon species induced by the $\mathbf{J} \times \mathbf{B}$ force helps to avoid redeposition on the anode.

4. Conclusions

The production efficiencies of soot and SWNTs are compared for three directions of the discharge current relative to gravity. In the case of $B = 0$, it is found that the soot production rate

is 20% larger for the upward discharge current than for the horizontal discharge current, whereas it is 36% lower for the downward discharge current. Under the $\mathbf{J} \times \mathbf{B}$ condition ($B = 3.0$ mT), the soot production rate is increased 2.35-fold for the horizontal discharge current, 1.60-fold for the upward discharge current, and 3.00-fold for the downward discharge current compared with those for $B = 0$.

In all the discharge cases, the diameter distribution of SWNTs is centered around 1.48 nm, which is found from both Raman and TEM measurements. When $B = 0$, among the three discharge conditions, the quality of the SWNTs produced in the case of the upward current is highest. By applying the magnetic field, the quality of the SWNTs is enhanced for the horizontal and downward discharge currents but deteriorates for the upward discharge current compared with those when $B = 0$.

Compared with the horizontal discharge current, the ratio of the number of SWNT bundles to the number of carbon particles is 48% higher for the upward discharge current, whereas it is 42% lower for the downward discharge current when $B = 0$, as estimated from the measurement of the TEM images. Under the $\mathbf{J} \times \mathbf{B}$ condition, the ratio increases by about 33% for the horizontal current and by about 88% for the downward current, but decreases slightly for the upward current compared with those when $B = 0$.

From these results, it can be confirmed that the discharge current direction and the application of a magnetic field can considerably affect the production rate of SWNTs. However, fluid simulation of the effect of the magnetic field is not yet complete and should be investigated in the near future.

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Figure Captions:

- Fig. 1. (Color online) (a) Schematic of the experimental setup. (b) Three discharge current directions and magnetic field directions.
- Fig. 2. (Color online) (a) Production rates of the soot, W_{soot} , for the three current directions. The differences for the two magnetic fields ($B = 0$ and 3.0 mT) are also shown. (b) Soot production efficiency, $W_{soot}/\Delta W_{anode}$, for the three current directions and two magnetic fields. $p(\text{He}) = 60$ kPa, $I_d = 50$ A, $t_d = 30$ min, and $d_G = 5$ mm.
- Fig. 3. (Color online) RBM of the Raman spectra showing the variation of the diameter distribution for the (a) and (d) horizontal, (b) and (e) upward, and (c) and (f) downward current directions. In (a) – (c), $B = 0$, and in (d) – (f), $B = 3.0$ mT.
- Fig. 4. (Color online) D and G bands of Raman spectra of the soot produced for the three discharge current directions. (a) and (d): horizontal current, (b) and (e): upward current, and (c) and (f): downward current. In (a) – (c), $B = 0$, and in (d) – (f), $B = 3.0$ mT.
- Fig. 5. (Color online) Variation of I_D/I_G in the Raman spectra for the three current directions, evaluated from Fig. 4. Here the standard error bars are obtained by calculating I_D/I_G from several Raman spectra of samples produced under the same conditions.
- Fig. 6. (Color online) TEM images of the soot for the $B = 0$ (a) – (c) and $\mathbf{J} \times \mathbf{B}$ (d) – (f) conditions, produced with the three discharge current directions: (a) and (d) horizontal, (b) and (e) upward, and (c) and (f) downward. The magnification of the TEM images is $\times 50000$.
- Fig. 7. (Color online) (a) Number of SWNT bundles (N_{ntb}) counted from typical TEM images for the three current directions. (b) Ratio of the number of SWNT bundles to the number of carbon particles, N_{ntb}/N_{cp} , counted from the TEM images for the three current directions. The measurement area is 4×10^6 nm² and the magnification of the TEM images is $\times 50000$.

Figures:

Fig. 1 (Double column, width 145 mm, height 120 mm)

Fig. 2 (Single column, width 85 mm, height 125 mm)

Fig. 3 (Double column, width 145 mm, height 150 mm)

Fig. 4 (Double column, width 145 mm, height 150 mm)

Fig. 5 (Single column, width 75 mm, height 60 mm)

Fig. 6 (Double column, width 145 mm, height 183 mm)

Fig. 7 (Single column, width 85 mm, height 125 mm)