Syntheses of single- and double-wall carbon nanotubes by the HTPAD and HFCVD methods

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\textbf{Abstract.} We have developed two novel synthetic methods for carbon nanotubes, namely the high-temperature pulsed arc discharge (HTPAD) method and the hot filament-assisted chemical vapour deposition (HFCVD) method. These methods can provide selective syntheses of single-, double- and multi-wall carbon nanotubes. HTPAD can produce high-quality double-wall carbon nanotubes (DWNTs) with Y/Ni alloy catalysts at 1250 °C. Their catalytic roles on the synthesis of DWNTs are investigated by controlling the compositions of Y and Ni, resulting in the optimum conditions of 2.5 and 4.2 at\%, respectively. No DWNTs, but only SWNTs, can be produced without Y, which shows the importance of Y in the production of DWNTs. HFCVD, on the other hand, using ethanol as a carbon source, can produce high-purity SWNTs with high efficiency. The production rate of SWNT synthesis has been increased by the hot filament-induced pyrolysis of carbon sources, which promises an easy scale-up of the production of SWNTs at low cost.
1. Introduction

Carbon nanotubes (CNTs) have attracted much attention since their discovery, owing to their unique electronic and mechanical properties that originate from their novel quasi-one-dimensional structure [1, 2]. CNT materials also have promising applications in molecular electronic [3] and mechanical devices [4], high-strength mechanical materials [5], hydrogen gas storages [6] and field emission tips [7, 8]. To study these fundamental properties and to develop further applications, selective synthesis of CNTs is crucial, especially in terms of structural control (e.g. the number of layers) and their large-scale production while maintaining their structural uniformity and high graphitization. Several synthetic methods have been developed so far, including laser vaporization [9], steady arc discharge (SAD) [10]–[13] and various types of chemical vapour deposition (CVD) techniques [14]–[20]. The CVD and SAD methods are the most promising techniques for the selective synthesis of CNTs such as multi-(MWNTs), single- (SWNTs) and double-wall (DWNTs) CNTs and for their large-scale, low-cost production. In particular, SWNTs and DWNTs are quite significant since they have more homogeneous structures compared with MWNTs, which enable us to study the detailed properties of CNTs. To selectively produce these SWNTs and DWNTs, we have developed two synthetic methods, the high-temperature pulsed arc discharge (HTPAD) [21]–[24] and the hot filament-assisted CVD (HFCVD) [18].

HTPAD can provide the thinnest DWNTs (1.6–2.0 nm in outer diameter) [23] reported so far in contrast with conventional DWNTs (2–5 nm in outer diameter) [24]. These DWNTs can be regarded as the thinnest and simplest MWNTs having excellent graphitization [25]. They are an ideal system for research on the layer structures with inter-layer interaction [4, 25], since they have exhibited a much higher structural uniformity compared with the usual MWNTs. DWNTs have actually shown novel electronic transport properties as channels for field effect transistors (FETs) [26] and distinct chemical resistance against oxidation due to the layer interaction [24]. For further studies and applications of the thin DWNTs, their selective synthesis based on the growth process is crucial, especially in terms of the metal catalysts employed. Here, we report the importance of the presence of yttrium catalysts in the effective synthesis of DWNTs.

HFCVD, on the other hand, can produce high-purity SWNTs of a similar quality and quantity [18] as those obtained by the conventional CVD method with an electric furnace [17].
In this technique, a hot filament is used to decompose the carbon sources, typically hydrocarbon–hydrogen-mixed gases. The decomposition products usually consist of radicals such as CH\(_2\) and atomic hydrogen as well as unreacted hydrocarbons. A similar method has been applied for the synthesis of various nanocarbon materials [27]–[31], including MWNTs with carbon monoxide [29] and SWNTs with methane and ferrocene [31]. However, the SWNTs produced so far by HFCVD were isolated SWNTs rather than bundles of SWNTs, indicating low SWNT content. Our previous study showed that the efficiency of SWNT production was enhanced even by the simplified HFCVD without a furnace [18]. Here, we report a method to enhance the content of SWNTs with an electric furnace around the reactor by eliminating the lack of uniformity in the temperature. With the improved HFCVD technique, we can synthesize high-purity SWNTs using ethanol vapour as a carbon source at a low pressure, showing that the hot-filament-induced pyrolysis increases the production rate of SWNTs.

2. Experimental

2.1. High-temperature pulsed arc discharge

The experimental set-up has been described elsewhere [21]–[24]. Briefly, the apparatus consists of a furnace (ISUZU KRO-12K), a quartz tube (φ = 25 mm), graphite electrodes, a water-cooled trap and a home-made pulsed HV power supply capable of providing 1.5 kV and 100 A. The electrodes were made from a powder mixture of graphite (99.99%, 23 µm, Toyotanso), nickel (99.9%, 7 µm, Nilaco) and yttrium (99.9%, 10 µm, Nilaco) by pressing it into 2 × 5 × 50 mm and they were located at the centre of the furnace. The pulsed arc discharges (250 µs, 180 A, 70 V and 120 Hz) were generated between the electrodes, which vaporized the cathode in high-temperature Ar buffer gas (1250 °C) [21]–[24]. The vapour from the cathode was annealed in the buffer gas and was converted into soot containing DWNTs.

The catalytic roles of Y and Ni were investigated by varying the atomic ratio of Y from 0 to 7.5 at% while maintaining that of Ni at 4.2 at%. The production efficiency of DWNTs was characterized by SEM (SEM: JEOL JSM-6340F), TEM (TEM: JEOL JEM-2010F) and Raman spectroscopy (Jobin Yvon HR-800). The Raman measurements were performed in a micro Raman mode where an excitation laser (HeNe: 632.8 nm) was employed (φ ~ 1 µm).

2.2. Hot filament-assisted CVD

Figure 1 shows a schematic diagram of the HFCVD apparatus used here. The reactor (φ ≈ 50 mm) and the reservoir for ethanol were made of quartz glass and borosilicate glass, respectively. The quartz substrate was located ~8 cm away from the tungsten filament. The metal catalysts iron acetate (Alrdich) and cobalt acetate (WAKO Chemicals) were dissolved in water and mixed with Y-type zeolite powder (HSZ-390HUA, TOSOH). The relative amounts of these catalysts were 2.5 wt% each against the zeolite support materials. The solution was sonicated for ~30 min and dried at 80 °C for 1 day. The resultant powder (~30 mg) was placed on the quartz substrate. The reactor is directly connected to a vacuum pump.

During the experiments, the quartz glass reactor was pumped by the rotary pump and the reaction pressure was controlled by the valve between the rotary pump and the reactor. Ethanol vapour was supplied from a reservoir to the reactor by vapour pressure (59.0 torr at 25 °C [32]) and was decomposed around the tungsten filament heated to 1800–2200 °C. The temperature of
Figure 1. Schematic diagram of the HFCVD apparatus.

the tungsten filament was monitored by a radiation thermometer (MINOLTA TR630A), where the emissivity of tungsten was set at 0.40 [33]. The temperature of the metal catalyst was controlled by the surrounding electric furnace. The typical reaction time for the synthesis was \( \sim 3 \) min. Black soot containing CNTs was deposited on the quartz substrate even in such a short reaction time. After cooling the reactor to room temperature, the soot containing SWNTs grown on the quartz substrate was examined by SEM, TEM, thermogravimetric analysis (TGA; Shimadzu TGA-50) and Raman spectroscopy.

3. Results and discussion

3.1. High-temperature pulsed arc discharge

Figure 2 shows TEM images of the samples produced by HTPAD with the electrodes having different Y concentrations. The production efficiency of DWNTs is strongly dependent on the Y concentration, where the best condition is achieved at 2.5 at%. At this optimum condition, the concentration of DWNTs among all CNTs is estimated to be \( \sim 30\% \) based on these images. No DWNTs, but only SWNTs, are produced without Y, and excess Y doping above 7.5 at% decreases the production efficiency both of SWNTs and DWNTs and converts almost all the carbonaceous materials into amorphous materials. This Y dependence is confirmed by the radial breathing modes (RBMs) of Raman spectra as shown in figure 3. The diameters of CNTs are evaluated with a well-known relation \( d = \frac{248}{\omega_r} \), where \( d \) (nm) is the diameter and \( \omega_r \) (cm\(^{-1}\)) the frequency of RBM [34]. Figure 3(a) shows that RBM peaks at 165 to 190 cm\(^{-1}\) are observed without Y, which are due to SWNTs with diameters from 1.3 to 1.5 nm. Instead, figures 3(b) and (c) show that peaks at 214 and 136 cm\(^{-1}\) become prominent as the Y concentration increases up to 2.5 at%. Peaks at 214 and 136 cm\(^{-1}\) have been known as fingerprints of the DWNTs corresponding to RBMs of the inner (1.1 nm) and outer (1.8 nm) layers, respectively [23].

The concentration of DWNTs in CNTs can be estimated by the relative intensity ratio between the peaks of DWNTs (214 and 136 cm\(^{-1}\)) and those of SWNTs (150, 165, 180 and 190 cm\(^{-1}\)) [24]. The results show that the production efficiency of DWNTs is enhanced by Y. The peaks due to DWNTs and SWNTs gradually diminish as the Y concentration increases to
Figure 2. TEM images of produced DWNTs and SWNTs by HTPAD with Ni/Y catalysts of (a) 4.2/0, (b) 4.2/2.5 and (c) 4.2/7.5 at%, respectively.
Figure 3. Raman spectra obtained with an excitation of 633 nm from the samples of (a) 4.2/0, (b) 4.2/1.0, (c) 4.2/2.5, (d) 4.2/5.0 and (e) 4.2/7.5 at% of Ni/Y catalysts.

5.0 at% and, finally, they almost disappear at 7.5 at% (figures 3(d) and (e)); the excess presence of Y adversely affects the production of both SWNTs and DWNTs. The average diameters of co-produced SWNTs are also sensitive to the extent of the Y doping, which are detected as the peaks at 150 cm$^{-1}$ (1.65 nm) and 165 cm$^{-1}$ (1.50 nm) (figures 3(b)–(e)). The average diameter
of SWNTs with Y is much higher compared with that obtained without Y; the presence of Y enhances the production efficiency not only of DWNTs but also that of thicker SWNTs. These observations on production efficiency and diameter dependence on Y concentration are consistent with the TEM observations shown in figure 2.

A similar enhancement of average diameter of SWNTs with Y has also been observed in the SAD [35, 36]. Thicker SWNTs are essential for the effective synthesis of DWNTs with SAD and CVD, where higher reaction temperatures and special catalysts such as sulfur are known to play crucial roles in the DWNT synthesis [12, 13, 16]. In fact, temperatures >1200°C are necessary for the synthesis of DWNTs by HTPAD, whereas only SWNTs are produced at temperatures <1200°C [24]. These results strongly suggest that the outer layer of DWNTs may be a template for the inner tube formation. This has been clearly shown by a DWNT synthesis from C₆₀ peapods [37]: fullerenes encapsulated in an SWNT transform into an inner tube of DWNTs, leaving the outer SWNTs unchanged. Since the so-formed DWNTs generally have a layer-to-layer distance similar to that of graphite (0.33 nm), the inner layer becomes stable only when the outer layers are thick enough to minimize the curvature distortion of inner tubes [1].

We suppose that this is the main reason why Y can enhance the production efficiency of DWNTs with the co-produced thicker SWNTs.

In as-produced CNTs with Ni/Y catalyst, Y prevails more homogeneously than Ni; Y exists as metal-carbide clusters whereas Ni tends to form metal particles [38]. Strong ionic interactions between Y and carbonaceous materials have been found in various carbon materials such as carbon–metal clusters [39, 40] and metallofullerenes [41, 42], where the charge transfers from Y to the carbonaceous materials might have taken place. We have noticed a strong similarity in their growth mechanism between endohedral metallofullerenes and SWNTs. For example, the production efficiency of C₆₀ significantly decreases and that of the so-called higher fullerenes increases in the arc-discharge synthesis of metallofullerenes. In the gas phase, bowl-shaped structures of carbon clusters with a metal atom inside have been reported in the metal–carbon clusters [38, 39]. These structures can be regarded as the precursors of metallofullerenes and end-cap structures of CNTs, both of which are important structures for metallofullerenes and CNTs, respectively.

3.2. Hot filament-assisted CVD

Figure 4(a) shows an SEM image of the pristine material produced from ethanol at 40 torr. The temperature of the electric furnace was set at 900°C. The web-like structures of bundles of SWNTs were observed on the zeolite particles with diameters of ~400 nm. The density of the nanotube CVD with a reaction time of ~10 min [17]. Amorphous carbon nanoparticles are seldom seen in TEM images, indicating the high purity of the present CNT sample. The bundles of SWNTs were clearly observed by TEM measurements (figure 4(b)). The number of SWNTs within a bundle was typically of the order of 10. From these observations, it is clear that bulk production of SWNTs was achieved by the present HFCVD.

In a previous study, we reported the bulk synthesis of SWNTs by the simplified HFCVD without an electric furnace [18]. The proportion of the SWNTs in the pristine materials was, however, lower compared with the conventional CVD method with an electric furnace. Substantial amounts of MWNTs existed together with amorphous carbon particles and sheet-like graphitic materials. We supposed that this could be due to the lack of uniformity in the
Figure 4. (a) SEM image of the pristine material from ethanol at 40 torr. The temperature of the furnace was 900°C. Web-like structures of the bundles of SWNTs are observed on the zeolite particles with a diameter of ∼400 nm. (b) TEM image of a cross-section of the SWNTs.

temperature of the quartz substrate. To obtain an appropriate temperature gradient of the substrate, we have used in this study an electric furnace around the reactor. This substantially increased the content of SWNTs. The overall feature obtained by the TEM images of the as-produced soot indicated that >90% of the observed CNTs were SWNTs.

The absolute weight of the produced SWNTs can be quantitatively estimated by TGA [19]. Figure 5 shows a TGA curve of the pristine material. The heating rate was 10 °C min⁻¹ in air. It is generally accepted that the weight loss up to 500 °C can be assigned to the burning of amorphous carbon materials and further loss up to 700 °C is due to the weight loss of carbon nanotubes [20]. The resulting weight above 800 °C can be attributed to the weight of the catalytic
Therefore, the weight per cent of the carbon nanotubes relative to the catalytic powder is estimated to be \( \sim 8.5\% \) based on the TGA curve (figure 5). Considering that the weight of the catalytic powder and the yield of SWNTs were \( \sim 30 \text{ mg} \) and \( >90\% \), respectively, the present HFCVD can produce \( \sim 2 \text{ mg} \) of SWNTs for 3 min, which is similar to that obtained by the conventional CVD method with a reaction time of \( \sim 30 \text{ min} \) [43]. This indicates that the current pyrolysis by the hot filament enhanced the SWNT production rate. It is estimated that the current HFCVD may provide, per unit time, 10 times as much SWNTs as the conventional CVD method.

The resonant Raman scattering technique has been shown to provide a powerful tool for the quantitative characterization of SWNTs, particularly for estimating the quality of SWNTs, together with individual diameters of SWNTs [1]. Figure 6 shows the Raman spectra obtained from the pristine SWNTs. The excitation wavelength is 633 nm from a He–Ne laser. The intense G-band (\( \sim 1590 \text{ cm}^{-1} \)), which is assigned to the tangential mode of the graphene sheet, can be clearly seen in the spectrum. A broad band at \( \sim 1370 \text{ cm}^{-1} \) (D-band) is ascribed to the Raman mode of the amorphous carbon. Therefore, the high intensity of the G-band compared with the D-band suggests the high purity of the sample. The G/D ratio obtained in this study (\( \sim 10 \); figure 6(a)) is very similar to the G/D ratio obtained by the conventional CVD method [17, 44], indicating that the quality of HFCVD-SWNTs is similar to that of CVD-SWNTs.

Figure 6(b) shows an expanded view of the low-frequency region, in which RBM (130–300 cm\(^{-1}\)) of SWNTs is observed. The peak position of the RBM (\( \omega_r, \text{ cm}^{-1} \)) is related to the diameter of SWNTs (\( d, \text{ nm} \)) with \( d = 248/\omega_r \) [34]. The estimated diameter of the SWNTs was widely distributed, ranging from 0.8 to 1.6 nm. These trends are very similar to those observed in the conventional CVD experiment with an electric furnace [17, 43]. Especially, the overall peak distribution of RBMs in figure 6(b) is almost identical with that obtained by ethanol using the CVD method at 900°C [43]. This suggests that the tungsten hot filament did not affect the temperature of the quartz substrate under the present experimental conditions.
Figure 6. (a) Raman spectra of SWNTs from ethanol at 40 torr. The excitation wavelength is 633 nm. (b) An expanded spectrum in the low-frequency region. The estimated diameter with \(d = 248/\omega\) is shown on the upper horizontal axis.

4. Summary

We have developed HTPAD and the HTCVD methods, which can produce selectively high-quality DWNTs and SWNTs in large quantity, respectively. The production efficiency of DWNTs is strongly dependent on the concentration of Y metal catalysts. No DWNTs are produced without Y and the presence of excess Y adversely affects the production of all kinds of CNTs. These results show that Y plays significant roles in the production of DWNTs. On the other hand, the production efficiency of SWNTs is remarkably enhanced, after pyrolysis of ethanol, by using the HFCVD method. The present HFCVD is suited for a large-scale production of SWNTs at low costs.

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