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Synthesis of Single- and Double-Wall Carbon Nanotubes by Gas Flow-Modified Catalyst-Supported Chemical Vapor Deposition

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SUMMARY The synthesis of single- and double-wall carbon nanotubes by gas flow-modified, catalyst-supported chemical vapor deposition (CCVD) is reported. We have investigated the gas flow condition dependence on the synthesis of carbon nanotubes (CNTs) by placing blocks in the CCVD reactor. Carbon nanotubes having large diameters are preferentially grown under turbulent flow conditions. This indicates that the diameter distribution of CNTs can be controlled by modification of the gas flow condition in the CCVD.

key words: *carbon nanotubes, chemical vapor deposition, raman spectroscopy, transmission electron microscopy*

1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], the science and applications of CNTs have evolved into various research fields. In particular, single-wall carbon nanotubes (SWCNTs) [2]–[5] and double-wall carbon nanotubes (DWCNTs) [6]–[13] have attracted significant attention due to their potential for novel applications [2], [8]. SWCNTs have been demonstrated as channels in field effect transistors, which show high transconductance [2], while DWCNTs have exhibited high resolution and high aspect ratio imaging together with longer lifetimes when used as tips of atomic force microscopy [8]. To realize such applications, it is crucial to develop synthesis methods that can control the diameter and the number of walls of the CNTs.

Catalyst-supported chemical vapor deposition (CCVD) is one of the most promising techniques to achieve high-yield synthesis of SWCNTs [3]–[5] and DWCNTs [9]–[13]. To control the diameter and number of walls of the CNTs, the reaction temperature [9], [10], support materials [9], [10] and catalyst metals [11], [12] have been parameterized in CCVD. The high-yield synthesis of DWCNTs by CCVD has been achieved at a higher temperature than that of SWCNTs, and the average diameters of both SWCNTs and DWCNTs increase as the growth temperature increases [9], [10].

Recently Hart et al. reported that the uniformity of vertically aligned multi-wall carbon nanotubes (MWCNTs) grown on silicon substrates were improved by controlling the gas flow condition, which is a new parameter in CCVD [14]. The gas flow, smoothed by placing a Si_3N_4-coated silicon substrate above the sample, enhances uniformity of the morphology of the MWCNTs. However, details of gas flow dependence on the synthesis of CNTs have not yet been clarified.

Here, we report the synthesis of SWCNTs and DWCNTs by a gas flow-modified CCVD method. Gas flow dependence of the synthesis of CNTs was investigated by placing blocks in the reactor of the CCVD apparatus to alter the gas flow. We found that the diameter distribution of CNTs could be controlled by modification of the gas flow condition in CCVD.

2. Experimental

Details of CCVD syntheses of MWCNTs [15], [16], SWCNTs [4] and DWCNTs [9] on zeolite supports have been reported previously. Briefly, the metal catalyst used was prepared by dissolving iron acetate and cobalt acetate in ethanol and then mixing with commercially available Y-type zeolite. 2.5 wt% each of Fe and Co were used. The synthesis of CNTs was carried out in a horizontal quartz tubular reactor, with ethanol [3] used as the carbon source. The catalyst was activated for 30 min at 300°C with a 100 ccm Ar flow, and the temperature was raised up to 800°C for the synthesis. Ethanol vapor was introduced into the quartz tube along with 100 ccm of Ar flow for 30 min. After the reaction, the furnace was cooled to room temperature with using flowing Ar.

To control the gas flow in the quartz tube of the CCVD apparatus, blocks were placed near the catalyst, as shown in Figs. 1(a)–(c). In "Normal" CCVD, the catalyst on the quartz plate is placed in the center of the quartz tube. The gas in normal CCVD flows straight through the quartz tube. As shown in Fig. 1(b), in "Walled" CCVD, a wall to modify the gas flow was placed downstream to the catalyst. The gas flow hits the wall and becomes turbulent near the catalyst in this setup. Figure 1(c) shows the setup for "Covered" CCVD, wherein the catalyst is covered except for the inlet of the cover. The gas flow goes into the cover and becomes turbulent in the cover. The wall and cover were made from a copper plate, since the catalytic activity of the copper to synthesize CNTs is very low [17]. After the CCVD, the copper wall and cover still had metallic luster, indicating that they did not work as catalysts.

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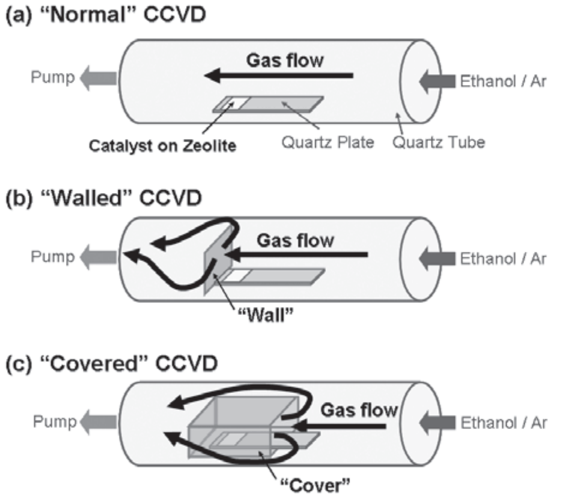

Fig. 1 Schematic images of the reactors of (a) "Normal," (b) "Walled," and (c) "Covered" CCVD.

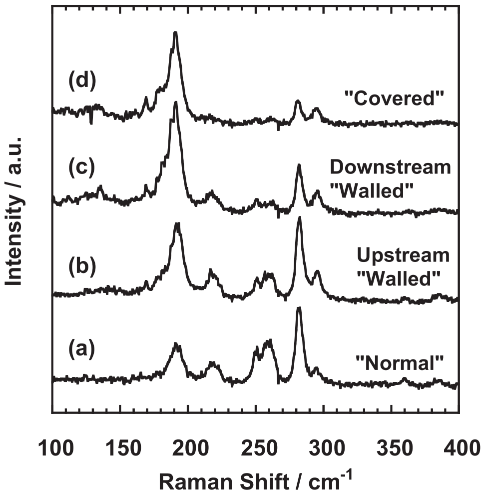

Fig. 2 Gas flow dependence on Raman spectra of the radial breathing mode (RBM) region. (a) "Normal" CCVD, (b) upstream and (c) downstream in "Walled" CCVD, and (d) "Covered" CCVD.

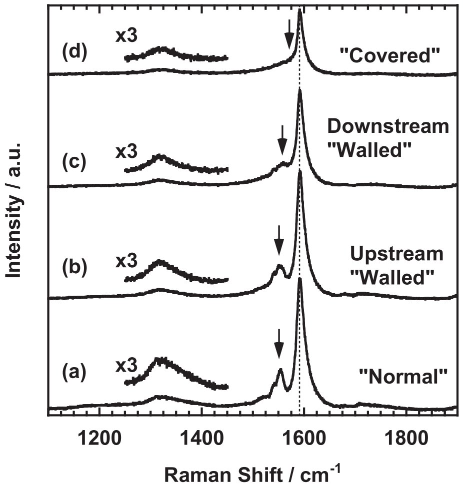

Fig. 3 Gas flow dependence on Raman spectra for the G-band region. (a) "Normal" CCVD, (b) upstream and (c) downstream in "Walled" CCVD, and (d) "Covered" CCVD. The vertical arrows and line indicate the peak positions of G^- and G^+, respectively.

The as-produced samples were characterized by high-resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100F) and Raman spectroscopy (Horiba Jobin Yvon, HR-800). The HRTEM was operated at 120 kV. Raman measurements were carried out at room temperature, using 632.8 nm laser lines for excitation.

3. Results and Discussion

The color of the powder synthesized by the normal CCVD is black, whereas a dark-gray powder was uniformly obtained by the covered CCVD. The carbon content in the sample grown by normal CCVD is higher than that by the covered one, because the color of the sample synthesized by CCVD on zeolite indicates the carbon amount. In the walled CCVD, two different colored powders were obtained. The powder in the upstream region was black, whereas a dark-gray powder was obtained in the downstream area (i.e., near the wall) since the gas flow downstream is turbulent due to the presence of the wall, as shown in Fig. 1(b). In the walled CCVD, the CNTs grown at the upper and lower sides were collected separately.

Figure 2 shows the gas flow condition dependence on the Raman spectra in the low frequency region. Raman peaks between 100 and 400 cm^{-1}, called radial breathing modes (RBM), correspond to the atomic vibration of carbon atoms in the radial direction. These features are very useful for characterizing diameters using "$d = 248/\omega$" [18], where d is the diameter of the CNTs and ω is the observed Raman shift. The spectrum from upstream of the walled CCVD is similar to that of the normal CCVD. There is no significant effect on CNTs grown upstream in the walled CCVD since the catalyst is far from the wall. On the other hand, peak distributions of the samples synthesized by the covered CCVD and downstream in the walled CCVD shift to a lower wavenumber, indicating that CNTs grown by these methods have larger diameters compared to the normal ones. This is also confirmed by the peak positions of G^-, which are shoulder peaks of the G-band as shown in Fig. 3. G^- corresponds to the mode with atomic displacements along the circumferential direction [19]. The peak positions of G^- include information on the diameters of the CNTs. G^- peaks of the covered CCVD and downstream to the walled one were observed at a higher frequency compared to that for the normal case as shown in Fig. 3. This also indicates that CNTs with large diameters are preferentially grown under turbulent flow conditions.

One of the reasons for the preferential growth of large diameter CNTs is a low carbon supply to the catalysts under the turbulent flow condition compared to the normal one. In the covered CCVD, the rate of gas flow into the cover, which includes a fresh carbon source, is reduced because the outlet is closed as shown in Fig. 1(c). This results in a low carbon supply to the catalyst metals, which are placed in the cover. Wang et al. reported that the diameter distribution of SWCNTs shifts toward larger diameters as the carbon supply rate decreases in CCVD on silica supports [20]. The diameters of SWCNTs depend on the sizes of carbon caps formed on the catalyst metals. When carbon supply rate is lower, larger carbon caps are formed since catalyst metals grow larger before the carbon caps could be stabilized on their surfaces because of their continuous aggregation during CVD [20]. The diameter distribution of CNTs therefore shifts toward larger diameters in the turbulent flow conditions. The present results indicate that controlling the diameter distribution of CNTs by the carbon supply rate could be realized not only by changing the flow rate but also by modification of the gas flow conditions in the CCVD. The low carbon supply under the turbulent flow conditions is also confirmed from the intensities of D-band in the Raman spectra. The intensity of D-band in the sample synthesized by the normal CCVD is higher than those by the covered CCVD and in the downstream region of the walled CCVD because of the excess carbon supply.

The diameters and number of walls of the CNTs were characterized by HRTEM observations as shown in Figs. 4(a)–(c). Figure 4(a) shows a typical TEM image of CNTs synthesized by normal CCVD. Results of HRTEM of samples synthesized by normal CCVD indicate that the majority of the CNTs are SWCNTs. HRTEM observations of the sample synthesized by covered CCVD indicate that it is mainly composed of SWCNTs having larger diameters than those grown by normal CCVD. As shown in Fig. 4(b) SWCNTs of more than 3 nm diameter can be observed. DWCNTs having outer diameters more than 4 nm are also observed, as seen in Fig. 4(c). In normal CCVD on zeolite [9] and mesoporous silica [10], high-yield synthesis of DWCNTs can be achieved when large diameter SWCNTs and DWCNTs are obtained by high temperature growth. Although large diameter SWCNTs and DWCNTs are synthesized by the covered CCVD, the relative yield of DWCNTs is low unlike high temperature growth by normal CCVD. This indicates that the growth conditions for large diameter SWCNTs and DWCNTs are not sufficient for high-yield synthesis of DWCNTs. Conditions such as high catalytic activity, which is realized under high temperature growth, are also needed to achieve selective synthesis of DWCNTs.

4. Conclusions

The gas flow condition dependence of the synthesis of CNTs has been investigated by placing blocks in the reactor of the CCVD apparatus. CNTs with large diameters were preferentially grown under turbulent flow conditions. The origin for this is the decreasing carbon supply rate due to the modified gas flow. The results suggest that diameter distribution of CNTs can be controlled by modification of the gas flow conditions in CCVD.

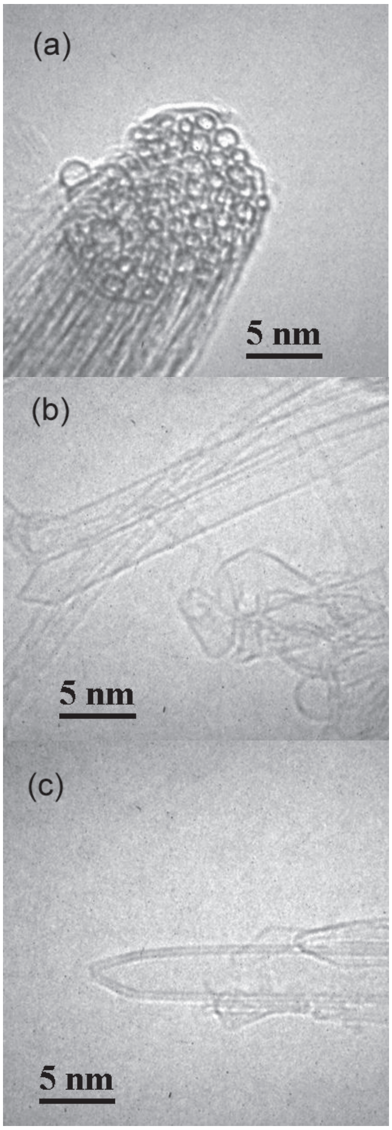

Fig. 4 Typical TEM images of (a) SWCNT bundles grown by “Normal” CCVD, (b) SWCNTs and (c) an edge of DWCNT synthesized by “Covered” CCVD.

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