Research Report

Control of Diameter Distribution of Single-walled Carbon Nanotubes Using the Zeolite-CCVD Method

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Abstract

Single-walled carbon nanotubes (SWCNTs) have been synthesized on zeolite powder with Fe/Co catalysts by catalytic chemical alcohol-vapor deposition (CCAVD). We first used a cold wall reactor at atmospheric pressure. The reactor system was then modified: radio-frequency heating was used for zeolite-CCAVD. The G/D ratio (~25) obtained is equivalent to that obtained by conventional CCAVD under reduced pressure. This indicates the high purity of the present specimen. The diameter distribution of the synthesized SWCNTs, estimated by analysis of resonant Raman spectroscopy using excitation wavelengths at 488, 514.5 and 633 nm, shifts towards larger diameters with increasing synthesis temperature and decreasing carbon supply rate (ethanol temperature). We present a diameter-selective growth model that is based on the relationship between the carbon supply rate, synthesis temperature and catalyst size.

Keywords Carbon nanotubes, Chemical vapor deposition, TEM, Raman spectroscopy

1. Introduction

Since the discovery of carbon nanotubes (CNTs),(1) various types of synthetic technique have been developed, such as laser ablation,(2) arc discharge,(3) plasma-enhanced chemical vapor deposition(4) and thermal chemical vapor deposition (CVD).(5-7) A variety of catalytic CVD (CCVD) techniques have attracted a great deal of attention from materials and device researchers because of their applicability to the large-scale and low-cost production of high-purity CNTs.

We have recently performed selective synthesis of single-walled (SWCNTs),(8, 9) double-walled (DWCNTs)(10) and multi-walled carbon nanotubes (MWCNTs)(11, 12) using the zeolite-CCVD method. SWCNTs were developed for field-effect transistors,(13) quantum wires(14), and electrical wiring(15) by exploiting their chirality-dependent semiconducting or metallic properties. Fabrication of electronic devices requires high-quality SWCNTs with controllable length and chirality. Such devices can be fabricated more easily by low-temperature in situ processes directly on substrates, such as large diameter silicon wafers. Maruyama et al.(16) were the first to achieve synthesis of high-purity SWCNTs from alcohol by a modified version of the conventional CCVD method,(8, 9, 11, 12) hereafter referred to as catalytic chemical alcohol-vapor deposition (CCAVD). Murakami et al. have also demonstrated the synthesis of high purity SWCNTs on silicon and quartz substrates(17) and mesoporous silica thin films(18) using the CCAVD method. Hiraoka et al.(10) recently reported high-yield synthesis of DWNTs via the zeolite-CCVD method, incorporating acetylene as the reaction gas.

There are several reports that demonstrate control of CNT diameter using size-controlled catalysts such as ferritins and nanoparticles.(19-21) However, despite intense efforts, uniform SWCNTs have still not been synthesized. Recently, synthesis of SWCNTs with a narrow diameter distribution (0.8-1.1 nm) was reported(22) using sublimed fullerenes as carbon source. However, the quantity of SWCNTs obtained was much lower than in ethanol CCVD,(16) and a small number of MWCNTs were also observed. Another study(23) employed oxidation processes as an ex-situ method of diameter control. This method helps narrow down the diameter distribution by preferentially burning off small SWCNTs, however, it results in a reduced yield.

All conventional CCAVD methods to date have been performed in a resistance heated hot wall reactor under reduced pressure. Reported here for the first time is the use of a cold wall reactor at atmospheric pressure. The reactor system has been modified by the use of radio-frequency (RF) heating for CCAVD specifications. The main feature of this system is to enable rapid heating profile of the susceptor. Thus, catalysts can be effectively activated for a short duration without aggregation of the catalyst particles. In addition, pressure reducing control valves are not necessary in the atmospheric-pressure system. This paper reports the synthesis and characterization of SWCNTs obtained using this modified CCAVD method. A model to account for the diameter selective growth of SWCNTs is also presented on the basis of the results of this study and other published data.(16)

2. Experimental

An Fe/Co bimetallic catalyst was prepared by impregnating a commercially available Y-type zeolite support with an aqueous solution of iron acetate and cobalt acetate.(8-12) The concentrations of Fe and Co were both 2.5 mass% of the catalytic powder. The catalyst was first dried in an oven at 80 ^{o}C, and calcined in flowing air (1 l/min) at 900 ^{o}C for 60 min.

After calcination, the catalyst was sprayed onto a silicon carbide-coated carbon susceptor and then loaded into a water-cooled double-wall quartz tube. The cold-wall reactor was, for the first time, used to synthesize SWCNTs (**Fig. 1**). The cold-wall reactor was evacuated to a base pressure of less than 5 Pa with a rotary pump. Ar gas flow in the quartz tube was held at 2 l/min for 10 min at room temperature using a mass flow controller. The susceptor was heated in Ar at a flow rate of 200 ml/min up to the growth temperature for only 5 min.

The carbon supply was varied by controlling the temperature of ethanol in the stainless steel vessel. The vessel temperature was maintained constant at 0, 25, or 40 ^{o}C with a temperature-controlled bath.

CVD growth was then performed on the catalyst for 10 min at atmospheric pressure in a gas mixture created by bubbling Ar through the ethanol at a flow rate of 200 ml/min. Typical synthesis temperatures were 900 and 1000 °C, as measured by an optical pyrometer. After the reaction, the furnace was cooled down to room temperature in 60 min, using flowing Ar (2 l/min). The pristine soot was then collected as a charcoal-like powder on the susceptor.

The pristine soot was characterized by transmission electron microscopy (TEM) and micro-Raman spectroscopy. TEM (JEOL JEM2000EX, 200 kV) was used to image the SWCNT structures. The diameter distribution of SWCNTs was determined by resonance Raman spectroscopy (LabRAM HR800, Jobin Yvon) in a darkroom at room temperature. The 488 nm (2.54 eV) and 514.5 nm (2.41 eV) lines from an Ar ion laser and the 633 nm (1.96 eV) line from a He-Ne laser were used for excitation.

3. Results and discussion

3. 1 Synthesis of SWCNTs by zeolite-CCAVD

Figure 2 shows TEM images of SWCNTs in the pristine soot synthesized at (a) 900 °C and (b) 1000 °C. SWCNTs predominated in all pristine soot specimens. The SWCNT yield increased with ethanol temperature. The vapor pressure of ethanol at 0, 25 and 40 °C is 1.7, 7.9 and 18 kPa, respectively.[24] Hence, higher carbon supply rates seemed to lead to higher SWCNT yields. However, high carbon supply rates were found to generate additional carbon deposition, such as MWCNTs and amorphous carbon. MWCNTs were also found, to a certain extent, at synthesis temperatures lower than 900 °C. SWCNT formation presumably requires a low carbon supply rate and high temperature. Such conditions favored the synthesis of SWCNTs, rather than MWCNTs, with the formation of pentagonal carbon rings caused by a C-C bond fluctuation.[25, 26]

Figure 3 shows Raman spectra of the pristine soot grown at various temperatures of the susceptor and the ethanol liquid container. The 633 nm line from a He-Ne laser was used as the excitation wavelength. All the spectra exhibited radial breathing modes (RBMs) ranging from 100 to 300 cm^{-1} and the G-band, together with the BWF (Breit-Wigner-Fano) peaks around 1590 cm^{-1}. The D-band (at around 1350 cm^{-1}), a rather weak signal in all cases, was ascribed to the Raman mode of the amorphous carbon and/or the disordered graphene sheet. Thus, the higher intensity of the G-band as compared to the D-band suggested that the specimen was highly pure. The G/D ratio obtained here (~25, Fig. 3) was higher than that (~4) achieved by the conventional CCVD method[8, 9] and equivalent to that obtained by the conventional CCAVD method.[16] This was also indicative of the high purity of the present specimen.

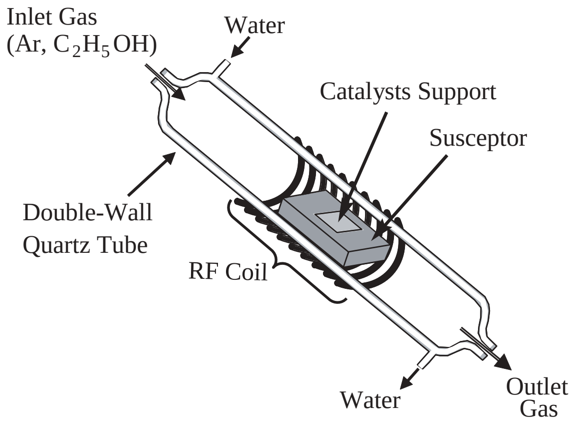


Fig. 1 Schematic of a cold wall reactor, showing the water-cooled double-wall quartz tube and the radio frequency coil.

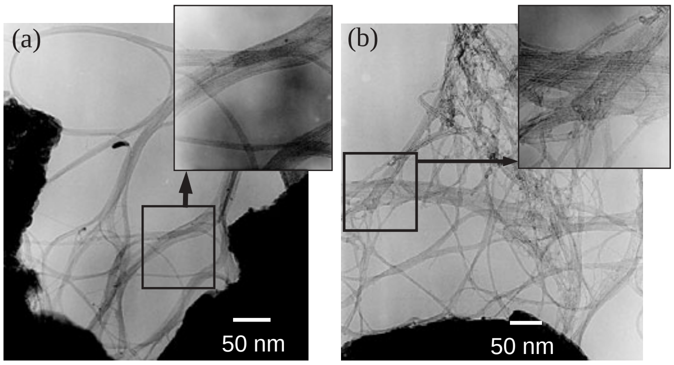


Fig. 2 TEM images of the pristine soot containing SWCNTs, synthesized at (a) 900 °C and (b) 1000 °C. Dark areas in both images are zeolite surfaces. Web-like bundles of SWCNTs grown on the zeolite are observed in both images. In both cases, the stainless steel vessel of ethanol was kept at 0 °C.

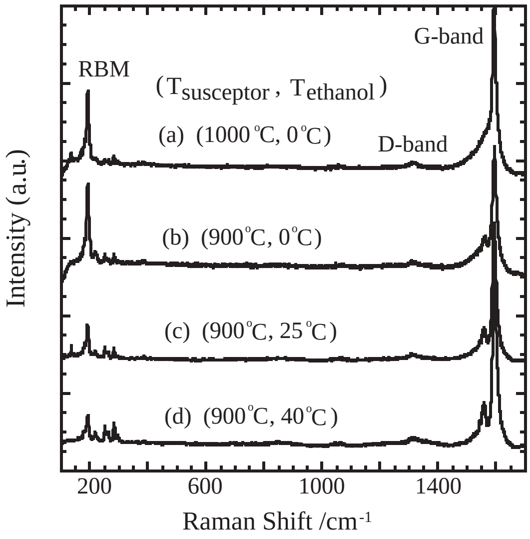
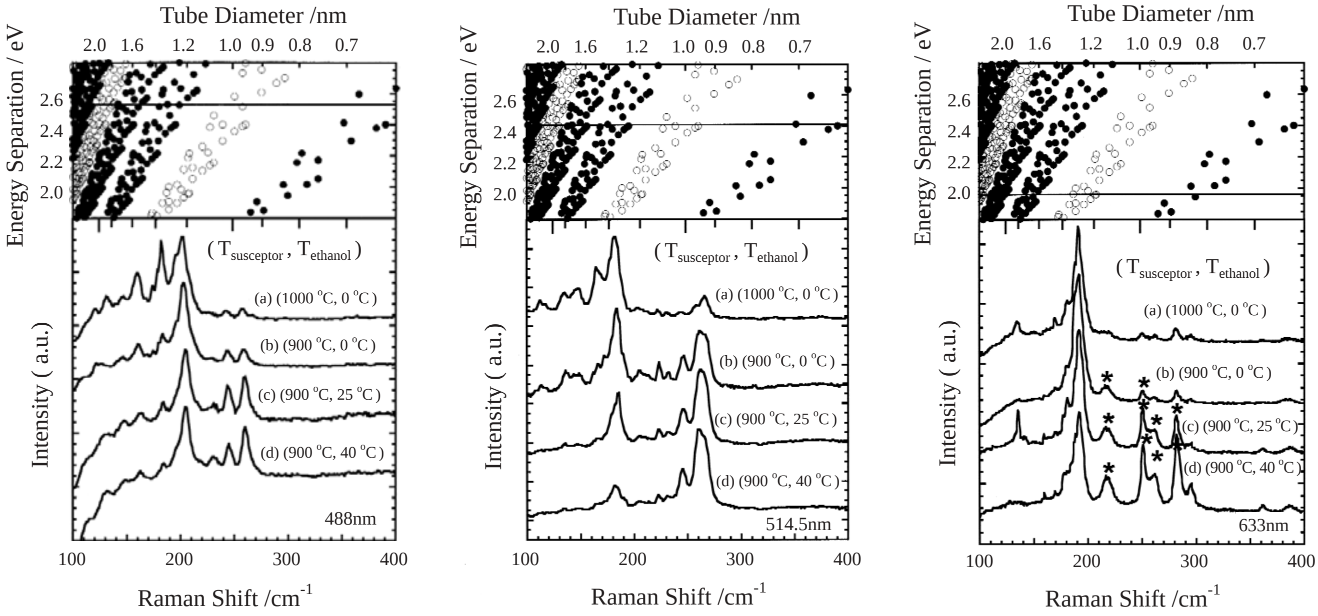


Fig. 3 Raman spectra of the pristine SWCNTs synthesized by the current CCAVD technique at various synthesis and ethanol temperatures. Excitation wavelength is 633 nm (1.96 eV).

3. 2 Resonant Raman measurements of SWCNTs

Influences of the synthesis temperature and carbon supply rate on the diameter distribution of SWCNTs were investigated using resonant Raman spectroscopy. The RBM signals of the specimens measured with excitations at 488, 514.5 and 633 nm are shown in **Figs. 4**(A), (B) and (C), respectively. The Kataura plot (a_{cc} = 0.144 nm, γ_0 = 2.9 eV),27) with the horizontal line corresponding to the laser excitation energy, is presented at the top of each figure, where solid and open circles denote semiconducting and metallic SWCNTs, respectively. Here, the measurement point (laser spot) was fixed during the RBM measurement by using modulated excitation wavelengths to estimate precisely the diameter distribution at any given point on a specimen grown under a particular condition. The diameter d (nm) of SWCNTs in Fig. 4 was estimated from the widely used relationship $d = 248/\omega$, where ω (cm^{-1}) is the RBM Raman shift.28, 29)

The RBM peak positions measured at each



(A) (B) (C)

Fig. 4 Radial breathing modes of the pristine SWCNTs synthesized by the modified CCAVD method at various synthesis and ethanol temperatures (excitations at (A) 488, (B) 514.5, and (C) 633 nm). (a), (b): synthesis temperature dependence, (b)-(d): ethanol temperature (vapor pressure) dependence of diameter distribution. The Kataura plot for the corresponding range is also presented with data at each laser excitation energy, for semiconducting (●) and metallic (○) SWCNTs.

excitation condition are consistent with those predicted by the Kataura plot, except at 633 nm. The RBM peaks denoted by asterisks in Fig. 4(C) cannot be explained on the basis of the Kataura plot and may be related to bundle structures.[22] A comparison of the results of three laser wavelengths clearly revealed that the distribution of SWCNTs shifted towards larger diameters as the synthesis temperature was increased. A similar temperature dependence of the diameter distribution was reported by Bandow et al. in connection with their laser furnace experiment[30] and by Okamoto et al. in the conventional CCVD technique.[8] By contrast, as the carbon supply rate was increased, the distribution shifted towards smaller diameters.

3. 3 A model for diameter-selective growth

Let us now examine the relationship between SWCNT growth and synthesis temperature, carbon supply rate, and catalyst size. First, we consider the effect of catalyst size. Our catalyst preparation technique involving the impregnation presumably produced catalysts with a wide size distribution on the zeolite support. This is suggested by the finding that a variety of CNTs, such as SWCNTs, DWCNTs and MWCNTs, could be synthesized on the same catalyst support by varying the growth conditions, although sufficient evidence could not be gleaned from TEM observation of the prepared catalysts. Thus, we believe that, in our study, the aggregated and/or fractured metal catalysts, with diameters ranging from sub-nanometer to 10 nm on the zeolite support, selectively acted as 'seeds' for the formation of SWCNTs.

It is reported that average SWCNT diameter is proportional to the average size of the catalyst nanoparticles used in CVD processes.[19-21] Generally, catalytic activity is inversely proportional to the size of catalyst particles[31] and promoted by temperature increase. Thus, smaller diameter SWCNTs are likely to be formed on smaller catalysts, which are active even at low temperatures and low carbon supply rates.

At higher synthesis temperatures, larger diameter SWCNTs are likely to be generated on larger catalysts as a result of the improvement in catalytic activity. The number of smaller SWCNTs, on the other hand, is reduced because of their structural instability[23] and the etching process using OH radicals,[16] and/or hydrogen molecules[32] potentially emitted as a by-product of the catalytic reduction during the formation of SWCNTs. In contrast to the temperature dependence of the diameter distribution, the formation of smaller SWCNTs are likely to be facilitated with increasing carbon supply rate at a low temperature. The increase in smaller SWCNTs is thought to be due to the sufficient supply of carbon atoms.

Maruyama et al. reported that production of slightly larger diameter SWCNTs is enhanced by using methanol rather than ethanol.[16] Their results can be explained by the number of OH radicals in each molecule. Vapor pressure of methanol is about twice that of ethanol at a given temperature.[24] Thus, a higher carbon supply rate with methanol can generate not only smaller diameter SWCNTs, but also larger diameter SWCNTs, even on a large size catalyst having a slightly lower activity. However, the high concentration of OH radicals in methanol prevents smaller diameter SWCNTs from nucleating on the small size catalyst as a result of the etching process.

On the basis of the above considerations, we propose that the diameter selective growth results from a competition between the deposition and the etching of carbon atoms. According to this competition growth model, the combination of a narrow catalyst size distribution and the optimal growth conditions will eventually enable the diameter selective growth.

4. Conclusion

High-purity SWCNTs (G/D ratio: ~25) containing only trace amounts of impurities, such as amorphous carbon, have, for the first time, been synthesized at atmospheric pressure using catalytic chemical alcohol-vapor deposition. Larger SWCNTs are synthesized at the synthesis temperature of 1000 °C and ethanol temperature of 0 °C. This is in good agreement with previous studies on the temperature dependence of diameter distribution. Smaller SWCNTs, on the other hand, are obtained at a synthesis temperature of 900 °C and ethanol temperature of 40 °C. The diameter distribution of SWCNTs can be controlled by adjusting the synthesis temperature and carbon supply rate through optimization of catalytic activity and deposition/etching rate of carbon atoms, respectively.

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