The structural evolution of thin multi-walled carbon nanotubes during isothermal annealing

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Abstract

Systematic isothermal annealing has been carried out on catalytic chemical vapor deposition-derived highly disordered multi-walled carbon nanotubes in order to understand the structural evolution of carbon nanotubes kinetically. After specified isothermal time the crystallographic parameters strongly depend on annealing temperature, and can be divided into three stages. Rapid structural enhancement in the range from 1800 to 2200°C originates from the abrupt evolution of the residual catalytic compounds and is seen as partially aligned small fringes along the tube length. The lack of further structural ordering at temperatures above 2400°C and the low activation energy (ca. 90kJ/mol) are thought to be the result of the limited space available for further structural development considering the nano-sized multi-walled carbon nanotubes.

Keywords: Carbon nanotubes, Graphitization, Heat treatment, X-ray diffraction, Raman spectroscopy

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1. Introduction

Since carbon nanotubes have excellent mechanical properties, electronic and thermal conductivity [1-3], they could be very promising in the fabrication of nanocomposite, field emission display and nano-electronic device [4]. Although there are still many challenges in characterization of nanotubes [1, 2, 5], it is no doubt that the microstructure of carbon nanotube has important influence on their mechanical and physical properties [4-8]. Especially for the chemical vapor deposition (CVD)-derived multi-walled carbon nanotubes (MWNTs) containing the residual metal catalyst and structural defects, post treatment is critically needed to improve the carbon purity and structural perfection. In this sense, thermal annealing has been suggested as the effective and practical method to improve the structural order and purity of carbon nanotubes. Lambert et al. [9] confirmed that the catalytic metal particles could be removed by annealing the synthesized carbon nanotubes above the evaporation temperature of the

metal catalyst. Andrews et al. [10] also reported some results about the effect of the thermal annealing on the structural perfection of the CVD-derived MWNTs through the thermal treatment at 1600, 2250 and 3000°C for 45minutes. Although there is no data about the effect of isothermal annealing time, it is supposed that the (002) interlayer spacing would continue to contract if given infinite time at temperature. Recently, Kim et al. [11] discussed the variations of microstructure and morphologies by thermally treating CVD-derived tubes at 2800°C. Both the physical and structural parameters have been highly improved upon thermal annealing, however the concentrated stress generated by the abrupt change of density during the annealing process also results in some defects. Unfortunately, there is no systematic study on the structural changes in MWNTs by isothermal annealing.

The purpose of this study is to understand the structural changes of the CVD-derived highly disordered MWNTs kinetically. Thus, thermal annealing is carried out in various temperatures ranging from 900 to 2800°C for different duration time from 2 to 60minutes. The effects of annealing temperature and duration time on the structure and purity are investigated by x-ray diffraction (XRD), Raman and transmission electron microscopy (TEM), X-ray fluorescence (XRF), ^{57}Fe transmission Mössbauer spectroscopy (TMS) and field emission scanning electron microscope (FE-SEM).

2. Experimental

The carbon nanotubes used in this study were synthesized in a vertical tubular reactor by CVD-based floating reactant system using ferrocene and thiophene (catalyst precursor), toluene (carbon feedstock) and hydrogen (carrier gas). The detailed reaction condition has been described in our previous study [12]. Annealing was carried out in a graphite-resistance furnace operating in a high-purity argon gas atmosphere in a semi-continuous system. We applied same thermal history for all samples as follows: (1) reach to the specified temperature with a heating rate of 20°C/min, (2) hold at the specified temperature for the determined time, (3) then, cool down to ambient argon gas atmosphere.

The purity (residual iron and sulfur content) was measured by X-ray fluorescence analysis (Rigaku ZSX mini) with Pd K_α X-ray source, the measurable limit is 30ppm for iron and 100ppm for sulfur. Meanwhile, ^{57}Fe transmission Mössbauer spectroscopy (TMS) was also applied, which is a useful method to analyze the containing of different Fe phase [13].

A JEOL X-ray diffractometer system (JDX-3532) was used to characterize the structural property with a Cu K_α X-ray source. The (002) peak position and its full width

at half maximum (FWHM) were measured using a standard X-ray powder diffraction procedures, 20% pure silicon powder was added as an internal standard to ensure accurate determination of diffraction peak position. The spacing between carbon layer planes d_{002} and the apparent crystallite dimension in the c-direction (L_c) were determined from these X-ray diffraction data. In order to compare the absolute diffraction intensity of different samples, 40mg sample was fixed in a 25 mm × 20 mm × 1.5 mm sample holder. Raman spectra (Jobin Yvon LabRam HR-800) were obtained with excitation source 514nm Ar-ion laser line. FE-SEM (JEOL JSM-6700F) and TEM observations (Hitachi) were also carried out to investigate the microstructure of annealed tubes.

3. Results and discussion

3.1 Effect of annealing temperature

Recent studies on the bio-compatibility of carbon nanotubes revealed that the remained metal particles cause toxicity [14]. Thus, it is very important to evaluate the type and also the retained amount of catalytic compounds in carbon nanotubes by thermal annealing. As shown in Fig. 1, continuous decrease in iron content with increase in temperature indicates that thermal annealing is the powerful tool for

removing metal impurities. Interestingly, when annealed above 2500°C, no large changes in iron contents are observed. On the aspect of residual sulfur content, it starts to reduce rapidly above 1500°C and becomes below 100ppm (the measurable limit for the instrument in this study) after annealing above 2000°C. It should be noticed that both iron and sulfur reduce rapidly above 1500°C, although it is reported that iron catalyst begins to remove at 1800°C, the vaporization temperature of iron [10]. According to the results of ^{57}Fe TMS, the iron phases are found to exist as γ-iron, α-iron, and compound with sulfur or carbon with iron, and more than 50% $Fe_{1-x}S$ has been detected for as-grown MWNTs. Therefore, it is reasonable to consider that the removal of catalyst would involve the vaporization of different iron phase and the decomposition of iron compound with sulfur. The decomposition of iron compound with sulfur is thought to start at 1500°C.

Figure 2 shows the Raman spectra of our tubes annealed at different temperature for 20 minutes. The effective removal of the structural defects with increase in annealing temperatures is strongly supported by the low intensity and narrow full-width at half-maximum (FWHM) of D-band (defect-mode) at 1350 cm^{-1}, when compared with the increased intensity and narrow FWHM of G-band (E_{2g2} mode) at 1582 cm^{-1}.

Interestingly, no large change in Raman spectra for tubes annealed at temperatures above 2200°C is surely ascribed to the saturated structural development on the near-surface of the carbon nanotube. Thus, this result suggests that electrical conductivity in a single tube does not vary a lot because the degree of structural order (including the amount of defects) of the outermost shell of the MWNTs is known to be determining factor [15].

Figure 3 (a) shows the XRD patterns around the range of peak C (002), C (100) and C (004) for the as-grown and thermally annealed tubes at various temperatures from 1200 to 2800°C for 20 minutes. The peak C (002) becomes sharp and symmetrical after annealing above 1800°C. Similarly, peak C (004) become visible at 1800°C and stronger above 2200°C. In the range of C (100), below 2200°C there is a peak around 44.4°, but it disappears after annealing above 2400°C. This peak is thought to correspond to the residual catalyst, which is well consistent with the changes in the residual content of catalyst (Fig. 1). Around 42.3°, there is an asymmetrical peak appeared above 1800°C. Usually, the asymmetrical peak C (10) around 42.3° develops into two symmetrical C (100) and C (101) peaks when a turbostratic structure is evolved into a graphitic structure [16]. In this study, no separation of C (100) and C (101) after

annealing at 2800°C gives us structural information regarding no three-dimensional stacking order. By the accurate determination of diffraction (002) peak position and FWHM, the (002) interlayer spacing d_{002} and the crystallite dimension L_c are determined, shown as the function of annealing temperature in Fig. 3 (b). The d_{002} has continuous reduction in the range from 1200 to 1800°C and from 2200 to 2800°C, however little change from 1800 to 2200°C. Similar trend has been reported [10] although the range with little variation is from 1600 to 2250°C. When looking at the changes in the crystallite dimension L_c, below 1500°C and above 2200°C, there is no obvious variation. On the contrary, there are the abrupt changes in L_c in the range from 1500 to 2200°C. The relationship between d_{002} and L_c as a function of annealing temperatures shows that the structural evolution of our MWNTs proceeds in a stepwise manner. Besides, even after annealing at 2800°C, the value of d_{002} is 3.386 Å, which is larger than that of graphite (3.354Å). All results mentioned above indicate that the structural order are improved effectively by increasing the annealing temperatures, however the three-dimensional ordering seems to be lack even after annealing at 2800°C. Considering the small diameter of MWNTs (ranging from 20 to 60 nm) in this study, the large curvature of the graphene sheet could might one of reason for the lack of three-dimensional stacking fidelity [17].

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In detail, to understand the morphological variation and the microstructural changes including defects by thermal annealing, the detailed TEM observations have carried out for thermally annealed our tubes. Figure 4 (a) shows a highly disordered microstructure of as-grown MWNTs with ca. 5nm inner diameter and 50nm outer diameter. The as-grown tubes contain relatively straight fibrous morphology and also constant outer and inner diameter along the tube length (Fig. 4 (b)). For tubes annealed at 1800°C (Fig. 4 (c) and (d)), we observed short and undulated fringes (indicated by white arrow), a rough surface and bent tube (indicated by black arrow). For tubes at 2000°C (Fig. 4 (e) and (f)), even though rough surface was not changed, we could observe long but undulated fringes and decreased amount of chasm-like voids (indicated by white arrow). After annealing at 2600°C, a highly ordered microstructure with straight and smooth fringes is achieved accompanying with the smooth surface of straight tube (Fig. 4 (g) and (h)). As reported in other studies [10, 11], some "gross defects" cannot be removed by thermal annealing (Fig. 4 (h), (i) and (j)). From the detailed TEM studies, it is assumed that the accumulation of the internal stress by radical morphological changes occur in the range from 1800 to 2200°C. The abrupt reduction in the residual catalyst content (Fig. 1) in this region contributes to the creation of internal stress in the wall of MWNTs, because the vaporization of catalyst

would result in the remarkable change of density [11]. After annealing at higher temperature, the stress can be released. However there are still some "gross defects" in the wall, even further annealing at still higher temperature (>2800℃) would not eventually remove them because of the limited release of strain energy due to confined space [12]. It could be considered to be one of the reasons for the lack of 3-dimensional ordering, corresponding to the results of XRD shown in Fig.3 (b), both the crystallite dimension L_c and the (002) interlayer spacing d_{002} have little variation above 2600℃.

3.2 Isothermal treatment

In order to understand the structural evolution isothermally, duration times varied from 2 to 60 minutes at 1800, 2000, 2400 and 2600°C. At all annealing temperatures the interlayer spacing d_{002} decreases rapidly at first 10 minutes, and no obvious decrease is observed even though nanotubes are thermally treated for longer time (Fig. 5 (a)). On the contrary, in the high temperature range (2400 and 2600°C), little change in crystallite dimension L_c means the saturated growth of graphene sheets along the tube length. For samples heat treated at 2000°C, crystallite size (L_c) abruptly increase linearly, and approach those of samples annealed at 2400 and 2600°C for longer time. For

samples annealed at 1800°C, little increase in L_c is observed for the first 10 minutes, but saturate soon even after annealing for longer time.

By plotting all L_c data in this study as a function of d_{002} (Fig. 6), the structural evolution of our tubes proceeds in three distinct stages. The first region ($d_{002} > 3.43$Å) could be characterized by their low degree of structural order and continuous structural improvements (< 1800°C). Secondly, for the range of 3.42 Å $< d_{002} < 3.43$Å, there is a little reduction of d_{002}, but an abrupt increase in crystallite dimension L_c (1800～ 2200°C). Thirdly, for the range of $d_{002} < 3.42$ Å, L_c is almost unchanged while the interlayer spacing d_{002} is obviously contracted, which is correspond to the sample heat treated at high temperature range (> 2200°C). This result strongly supports the structural order occur in a stepwise manner from disordered to highly ordered carbon nanotubes via the thermal annealing as following [11]: (1) straightening and rearrangement of distorted small graphene layers, (2) fusion between graphene layers, (3) growth to larger graphene layer along the tube axis and then removal of stacking faults between graphene layers within a confined space.

Therefore the structural evolution is considered to be a crystallite growth process, thus its kinetics can be discussed with the time dependence of a given structural parameter. According to our data, general evaluation could not be done with only d_{002} or

L_c because of their variation in stages. Furthermore, the much great curvature of the graphene sheet in MWNTs results in somewhat difference when evaluating the structural ordering with XRD data. On the other hand, the Raman spectra are applied to structural evolution, especially suitable to analyze the structure of graphene. For example the intensity ratio of D-band and G-band (R value = I_D/I_G), is often used as a disorder parameter of conventional carbon materials [18, 19]. It is reasonable to discuss isothermal study (such as rate constant and aviation energy) using R value. As shown in Fig. 7 (a), an obvious decrease in R value was observed for samples annealed at 2000°C. However for samples annealed at 1800, 2400 and 2600°C, no changes in R value is observed even annealing for more than 10 minutes. Plots of the *ln(R value)* versus isothermal annealing time at 1800, 2000, 2400 and 2600°C reveal the linear relationship, which provide the rate constant k at each annealing temperature from the slopes of these lines shown in Fig. 7 (b) (k=dln(*R value*)/dt). Application of the Arrhenius equation written as in following [20], the apparent activation energy for graphitization of MWNTs could be estimated.

k=A exp(-E/RT)

In the Arrhenius equation, k is the rate constant, E the energy of activation, A the frequency factor, T the absolute temperature of heat treatment and R is the gas constant.

The resultant linear relation of the plot *ln(k)* as a function of *1/T* (Fig. (8)) provides the estimation of the apparent activation energy as the order of 90 kJ/mol for graphitization of our MWNTs in the temperature range from 1800 to 2600°C. This value is significantly lower than those of various carbon fibers (from 100 to 250 kcal/mol) [21]. However, it corresponds to the activation energy for bulk diffusion of carbon through solid metal catalysts [22, 23].

4. Conclusions

We have carried out the systematic thermal annealing on the CVD-derived highly disordered MWNTs at various temperatures from 900 to 2800°C for different duration times from 2 to 60 minutes. By examining the structural changes for tubes annealed at various temperatures for different duration time, it is confirmed that the effect of annealing temperature is much greater than that of duration time. Even though the residual catalytic compounds and nano-sized fibrous morphology makes it difficult to understand the structural changes by thermal annealing, it is possible to divide into three distinct stages for our tubes: (a) The first region was below 1800°C, and no substantial change was observed. (b) Radical structural enhancement in the temperature range from 1800 to 2200°C (the second region) occur due to the high graphitizabiltiy of our tubes

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(e.g., partially aligned small-sized fringes along the tube length) and partially the catalytic effect of the residual metal compounds. (c) The third region above 2200°C was characterized by the saturation in structural development for samples annealed at temperatures above 2200°C. Thus, when getting high purity and high crystalline MWNTs economically, the optimized annealing temperature is found to be below 2400°C for disordered tubes. Finally, we proposed that Raman value (e.g. R value) is more effective than other data for kinetic studies of our tubes. The calculated apparent activation energy for our tubes is estimated to be 90kJ/mol in the temperature ranges from 1800 to 2600°C.

Acknowledgements

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Figure captions

Figure 1 Variation of the residual catalyst content with annealing temperature

Figure 2 First-order Raman spectra for the CVD-derived disordered nanotubes annealed at various temperatures.

Figure 3 (a) X-ray diffraction patterns, (b) their calculated interlayer spacing d_{002} and crystallite dimension L_c as a function of annealing temperatures.

Figure 4 TEM images of our MWNTs annealed at different temperatures: (a-b) as-grown, (c-d) $1800^{\circ}C$, (e-f) $2000^{\circ}C$ and (g-j) $2600^{\circ}C$. We can see the sequential structural transformation from a disordered fringe to highly ordered tubes via thermal annealing.

Figure 5 Changes of (a) interlayer spacing d_{002} and (b) crystallite dimension L_c as a function of duration time.

Figure 6 Correlation of interlayer spacing d_{002} and crystallite size L_c.

Figure 7 Changes in (a) *R value* and (b) *ln(R value)* for samples heat treated at different

duration time.

Figure 8 Plot of *ln[dln(R value)/dt]* versus 1/T, the estimation of activation energy for

the structural changes in the temperature range from 1800 to 2600°C.