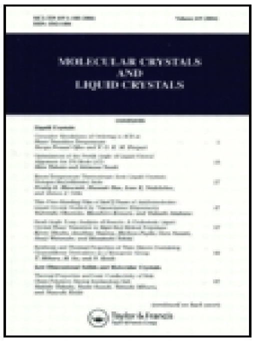

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Preparation of Aspect Ratio-Controlled Carbon Nanotubes

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Commercial methods for producing multiwalled carbon nanotubes (MWCNTs), such as chemical vapor deposition (CVD), employ transition metal catalysts. Therefore raw MWCNTs usually contain metal catalysts and other carbon impurities. Acid treatments are commonly used to eliminate these impurities, which can reduce the length of the MWCNTs, thereby controlling their aspect ratio. These aspect ratio controlled MWCNTs can have many applications as electrode materials, biological imaging and sensing, etc. In this study, the aspect ratio of MWCNTs was controlled by an acid treatment with a 3:1 mixture of concentrated H_2SO_4/HNO_3 *for various treatment times. The results show that the acid treatment can control the aspect ratio of the MWCNTs. The aspect ratio controlled MWCNTs were observed by TEM, TGA and Raman spectroscopy.*

Keywords: carbon nanotubes; aspect ratio; electrical conductivity; oxidation

1. INTRODUCTION

Carbon nanotubes (CNTs) have been used extensively for applications in many areas on account of their unique physical and chemical properties [1]. Since Iijima first reported their production in 1991, many methods for synthesizing CNTs have been demonstrated [2–4]. Currently, CNT production methods, such as chemical vapor deposition (CVD), employ transition metal catalysts. Therefore, raw CNTs contain impurities, such as amorphous carbon, nanocrystalline graphite and metallic catalysts. A common way of eliminating these impurities is chemical oxidation, which is generally achieved by acid treatments

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[5,6]. Acid treatments can reduce the length of CNTs, which can be used to control their aspect ratio. Many of the methods reported for cutting the CNTs begin with the chemical oxidation of CNTs [6,7]. In addition, CNTs with different lengths may be used in a variety of fields, such as electronic, biological and composite materials [6,8–10].

Recently, the potential toxicity of CNTs has attracted attention because of their apparent similarity to asbestos and other carcinogenic fibers. However, C. A. Poland *et al.* reported that short tangled CNTs have lower toxicity than long straight CNTs [11,12]. For this reason, length controlled CNTs have been prepared by chemical oxidation for many applications with reduced toxicity.

Chemical oxidation causes structural changes to the CNTs, such as defects, which can cause considerable changes to their thermal, mechanical and electrical properties. Since the structure of CNTs is similar to that of graphite, it is reasonable that a theoretical model developed for graphite would also be applicable to CNTs. Consequently, many researchers have examined the repair of defects in CNTs by high-temperature annealing [13–15].

In this study, multiwalled carbon nanotubes (MWCNTs) were prepared with a controlled length but little change in their inherent properties, such as purity, crystallinity and electrical conductivity.

2. EXPERIMENTAL

2.1. Materials

The MWCNTs (95% purity, supplied by Iljin Nanotech, Korea) were produced by thermal chemical vapor deposition (CVD).

2.2. Purification and Cutting of MWCNTs

The MWCNTs were suspended in a mixture of condensed H_2SO_4 and HNO_3 (3:1, vol/vol), and then heated at 60°C under reflux for 2, 12 or 24 h were named I, II and III, respectively. Subsequently, the CNTs were washed several times with deionized water until the pH of the rinsing water became neutral and then dried in a vacuum oven at 25°C for 48 h.

2.3. High-Temperature Annealing of MWCNTs

The acid-treated MWCNTs were placed in the center of a horizontal electric resistance tube furnace (High Temp. Furnace, Ajeon Heating

Industrial Co., Ltd., Korea) and heated to 1600°C at a rate of 10°C/min. The samples were held at this temperature for 3 h under pressures <10 Pa. The lowest pressure was 10^{-3} Pa to prevent oxidation. The resulting high-temperature annealed samples I, II and III were named I-A, II-A and III-A, respectively.

2.4. Characterization

The morphology and average length of the MWCNT samples were characterized by transmission electron microscopy (TEM, Philips, CM200, 200 kV accelerating voltage, USA). The thermal stability and mass loss of the MWCNT samples was estimated by thermogravimetric analysis (TGA, TA instruments, Q50, UK), with a heating rate of 20°C/min from room temperature to 800°C in air. Raman spectroscopy (BRUKER, RFS-100/S, 1064 nm excitation, Germany) was used to determine the presence of sp^2 hybridized carbon in the MWCNT samples through an examination of the E_{2g} mode or G band (stretching vibrations in the basal plane of crystalline graphite), so-called D band (indicating the level of defects in the graphitic material) and I_G/I_D ratio (the intensity ratio of the D band to the G band, which is usually used to assess the purity and crystallinity of CNTs). In order to measure the electrical conductivity, the samples were prepared in the form of disc-type pellets with a thickness of 0.3 mm by applying a pressure of 1 ton at room temperature using a Carver laboratory press (Model #3912, Carver Inc., Wabash, IN, USA). The electrical conductivity of the samples was measured using a four-probe method with a resistivity meter (Mitsubishi chemical co., Hiresta-up MCP-HT450, Japan).

3. RESULTS AND DISCUSSION

Figure 1 shows that the raw MWCNTs synthesized by CVD are several micrometers in length and have a bent and twisted structure. This structure results from defects, such as pentagons, heptagons and vacancies created on the surface of the CNTs [16,17]. These defect sites produce a variety of relatively active chemical structures. Therefore, the CNTs can be functionalized chemically. The sp^3 carbon atoms of defects in the MWCNTs are first attacked by oxidation, which ultimately etches the MWCNTs. Finally, an acid treatment can be used to control the aspect ratio of the MWCNTs. In addition, this method can eliminate impurities, such as metal catalysts and other forms of carbon. This method has more advantages than other methods because of its simplicity. For this reason, a 3:1 concentrated H_2SO_4:HNO_3

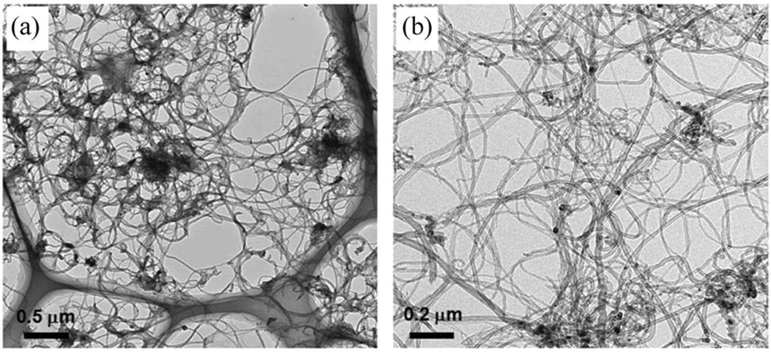


FIGURE 1 TEM image of the Raw MWCNTs.

solution was prepared to cut the MWCNTs in an attempt to control the aspect ratio.

It was expected that the length of MWCNTs would change with acid treatment time. Figure 2 shows TEM images of the aspect ratio controlled MWCNTs, and Table 1 shows the corresponding average length, average diameter and I_G/I_D ratio of the MWCNTs before and after the acid treatment for various times. The average lengths of the acid-treated MWCNTs were <4 μm. As previously mentioned, short tangled CNTs have lower toxicity than long straight CNTs. Therefore, it was expected that the aspect ratio controlled MWCNTs would have low toxicity [11,12].

TEM confirmed that the length and average diameter of the MWCNTs decreased with increasing acid treatment time. In addition, the I_G/I_D ratio in Raman spectra of the acid treated MWCNTs was significantly lower than the raw MWCNTs, which was attributed to

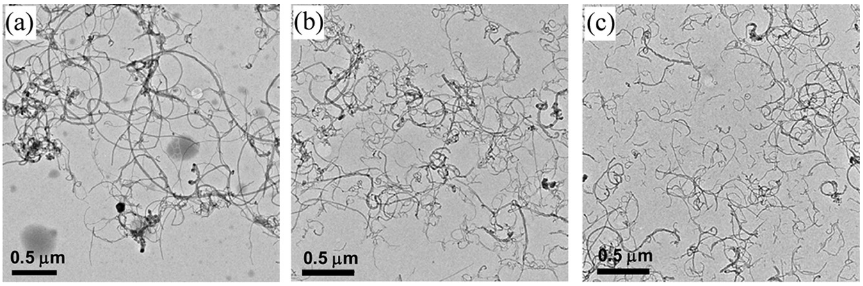
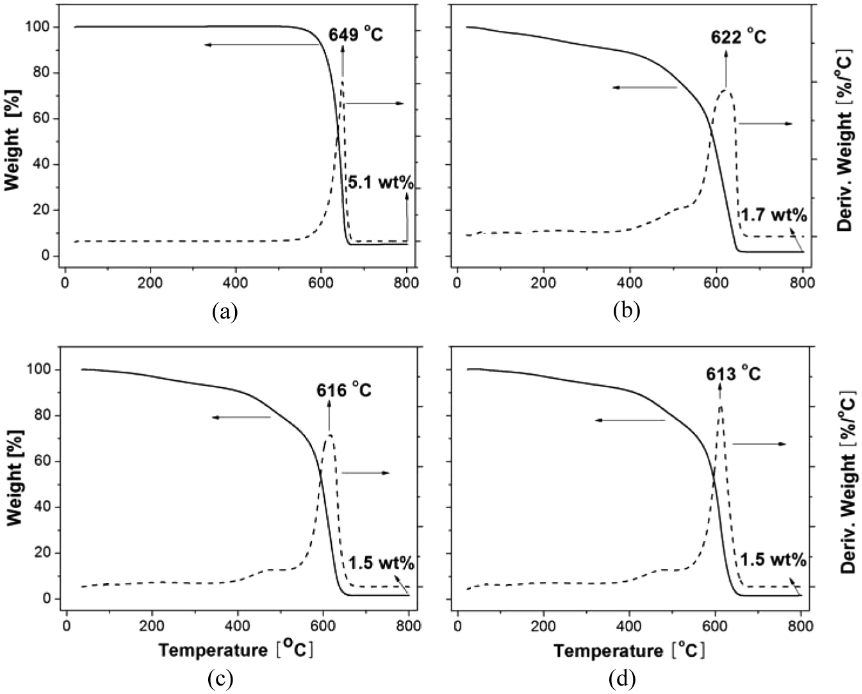


FIGURE 2 TEM images of the MWCNTs acid-treated for (a) I (b) II (c) III.

TABLE 1 Average Length, Diameter, I_G/I_D Ratio and Electrical Conductivity of the Acid-Treated and MWCNTs

	Raw	I	II	III
Average Length [μm]	7.0 ± 2	3.0 ± 0.6	2.1 ± 0.8	0.9 ± 0.6
Average Diameter [nm]	13 ± 3	13 ± 3	11 ± 3	8 ± 2
I_G/I_D ratio	0.85	0.76	0.76	0.72
Electrical Conductivity [S/cm]	8.56×10^2	1.52×10^1	2.72×10^1	2.45×10^1

the increased number of defects induced by the acid-treatment. One of the most common defects in MWCNTs that can have a significant effect on the I_G/I_D ratio is an open end as a result of cutting the MWCNTs. TGA demonstrated the changes in length of the MWCNTs. Figure 3 shows the maximum decomposition temperatures (MDT) and metal catalyst residues of the acid-treated MWCNTs, which have



(a) (b)

(c) (d)

FIGURE 3 TGA and DTG curves (in air) of (a) Raw MWCNTs and (b) I, (c) II and (d) III.

different values according to the samples. The MDTs decreased with decreasing MWCNT length. Moreover, the amount of metal catalyst residue decreased with increasing acid treatment time. This shows that the acid treatment causes structural alterations to the MWCNTs, particularly reductions in length, which can be used to control the aspect ratio of MWCNTs. Table 1 shows the electrical conductivity of the acid-treated MWCNTs. The electrical conductivity of the acid-treated MWCNTs was lower than the raw MWCNTs because the electrical conductivity of the MWCNTs depends strongly on their structure. In particular, the electrical conductivity of the MWCNTs increased with increasing crystallinity [15]. Therefore, the acid treatment damaged the structure of the MWCNTs.

For confirmation, the MWCNTs were annealed at high temperatures, and disc-type pellets with a thickness of 0.3 mm were prepared. This process can reduce the number of defects in the MWCNTs [13–15]. The change in electrical conductivity of the MWCNTs before and after high-temperature annealing MWCNTs was examined. Table 2 shows the change in the I_G/I_D ratio and electrical conductivity of the high-temperature annealed MWCNTs without a change in the average length or diameter. The I_G/I_D ratio and electrical conductivity of the high-temperature annealed MWCNTs was higher than the acid-treated MWCNTs.

Figure 4 shows the MDT and metal catalyst residues of the high-temperature annealed MWCNTs which have different values according to the samples. It was confirmed that the MDT of the high-temperature annealed MWCNTs was higher than that of the acid-treated MWCNTs. In addition, the quantity of metal catalyst residue of the high-temperature annealed MWCNTs was lower than that of the acid-treated MWCNTs. This was attributed to high-temperature annealing removing amorphous carbon or other carbon fragments. These results demonstrate that the defects in the MWCNTs had been removed. Therefore, the influence of the MWCNT structure on the electrical conductivity was reduced.

TABLE 2 Average Length, Diameter, I_G/I_D ratio and Electrical Conductivity of the High-Temperature Annealed MWCNTs

	Raw-A	I-A	II-A	II-A
Average Length [μm]	6.8 ± 1	3.1 ± 0.8	2.1 ± 0.7	0.9 ± 0.6
Average Diameter [nm]	13 ± 3	13 ± 3	11 ± 2	8 ± 3
I_G/I_D ratio	1.06	0.81	0.81	0.81
Electrical Conductivity [S/cm]	2.23×10^2	7.25×10^2	2.12×10^2	8.43×10^2

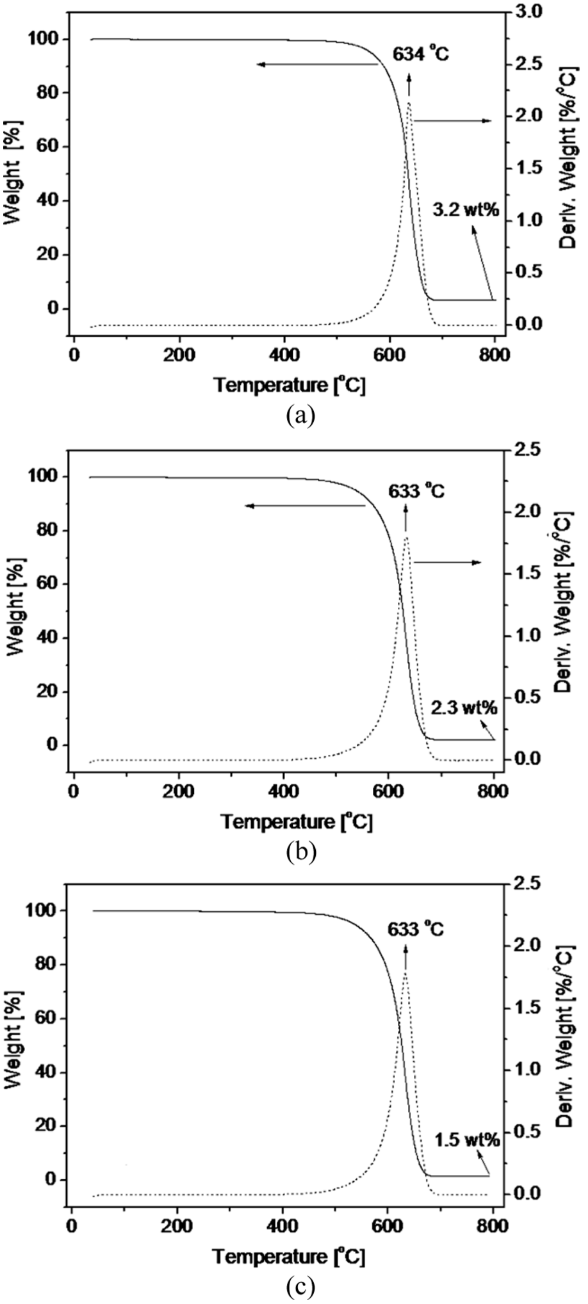


FIGURE 4 TGA and DTG curves (in air) of (a) I-A, (b) II-A and (c) III-A.

4. CONCLUSION

An acid treatment for various times can control the aspect ratio of the MWCNTs. Furthermore, aspect ratio-controlled MWCNTs with fewer changes in their inherent properties, such as electrical conductivity, were obtained using a high-temperature annealing method. Aspect ratio controlled MWCNTs with novel properties might have a variety of applications, such as electronic, biological and composite materials with reduced toxicity.

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