Characterization of thin multi-walled carbon nanotubes synthesized by catalytic chemical vapor deposition

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Abstract

Thin multi-walled carbon nanotubes (t-MWCNTs) synthesized by catalytic chemical vapor deposition were characterized by transmission electron microscopy (TEM), Raman spectroscopy, and gas adsorption. TEM observations showed that the innermost diameter ranges from less than 1 to 5 nm and the outermost diameter ranges from 4 to 12 nm, which are much smaller than conventional thick MWCNTs. We observed clear radial breathing modes in Raman spectra, which are attributed to the existence of inner nanotubes in small diameters less than 3 nm. We also performed N2 adsorption at 77 K after the tip opening of t-MWCNTs by nitric acid in order to analyze the tube inner diameters. The pores with sizes less than 4 nm corresponding to the inner empty space of t-MWCNTs were largely developed, in good agreement with TEM and Raman observations.

1. Introduction

Carbon nanotubes [1] have attracted much interest due to their unusual one-dimensional structures and peculiar properties [2,3]. In particular, multi-walled carbon nanotubes (MWCNTs) have higher mechanical strength, larger diameters, more rigid properties than single-walled carbon nanotubes (SWCNTs) and therefore can be used as nanoprobes in scanning probe microscope [4], nanotweezers [5], field emitters [6], fuel cell [7], and nanocomposites [8]. To synthesize high-quality MWCNTs, numerous methods have been reported [1,9–11]. However, the application is often limited, since the synthesized MWCNTs have large number of walls with a broad diameter distribution. For instance, the smaller the diameter, the better the field emission due to large field enhancement factor.

Recently, thin-MWCNTs (t-MWCNTs) with small diameters of up to 6 nm have been synthesized in mass quantity by catalytic chemical vapor deposition (CVD) [12]. Therefore, the detailed analysis in the structural properties of t-MWCNTs is necessary prior to the potential applications to several disciplines. In this study, we report the complementary structural properties of t-MWCNTs between SWCNTs and MWCNTs. The inner diameters were analyzed by transmission electron microscopy (TEM), Raman spectra, and N2 adsorption technique at 77 K.

2. Experimental

The t-MWCNTs were synthesized by catalytic CVD on MgO-supported Fe catalyst particles at above 1000 °C with CH4 gas (ILJIN nanotech Co.). Since the as-grown sample contained the transition metals and their oxides, the sample was purified by 6 M hydrochloric acid.
acid (HCl) treatment [13]. Thermogravimetric analysis (TGA) [Seiko Exstar 6000(TG/DTA6100)] was done in air with a heating rate of 5 °C min⁻¹. The Raman spectroscopy measurements were performed using a micro-probe Raman spectrometer (Renishaw, RM1000). The Raman spectra were obtained by using excitation energies of 2.41 eV (514.5 nm), 1.96 eV (632.8 nm), and 1.58 eV (785 nm). We also used FT-Raman (Bruker, IFS-66/S) with an excitation energy of 1.165 eV (1064 nm). Morphology of the nanotube samples was observed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX: JEOL, JSM6700F) and TEM (JEOL, JEM-3011).

In order to open t-MWCNTs tips, the purified t-MWCNTs of 150 mg were refluxed at 110 °C in nitric acid (HNO₃, 60%) of 200 mL for 12 h. The precipitate was filtrated through the membrane filter and then washed with distilled water several times. The samples were dried in vacuum and heated in Ar ambient at 600 °C for an hour. Pore structures of t-MWCNTs were determined by N₂ adsorption isotherm at 77 K using volumetric equipment (Micromeritics, ASAP2020). The pore structure parameters were obtained by subtracting pore effect (SPE) and Brunauer–Emmett–Teller (BET) methods. The SPE method was performed by using high-resolution χ₂-plots. We also introduced Barrett–Joyner–Halenda (BJH) method to determine the mesopore size distribution.

3. Results and discussion

Fig. 1a shows the SEM image of the purified t-MWCNTs. In spite of purification with acid treatments, the t-MWCNTs contained small quantity of transition metals, which can be seen as the white spots on nano-
tube tips. These are visible as the black spots in TEM image, as shown in Fig. 1b. The particle sizes are similar to diameters of individual t-MWCNTs. Fig. 1c shows the individual t-MWCNTs with the number of walls of five and an innermost diameter of about 3.2 nm. It is interesting to see that some individual nanotubes still remained unbundled even after purification by acid treatment. This can be attributed to the toughness of t-MWCNTs, which is in good contrast with floppy SWCNTs that usually formed thick bundles after acid treatment [14]. Inset of Fig. 1c presents t-MWCNTs with large innermost diameter of about 5.2 nm. Fig. 1d shows the thin bundle of a few nanotubes. Some t-MWCNTs revealed small innermost diameters of 0.9 and 1.3 nm (Fig. 1e and f). TEM observations showed that the innermost diameter ranges from less than 1 to 5 nm and the outermost diameter ranges from 4 to 12 nm with an interlayer distance of 0.31–0.35 nm, which is similar to that of graphite (typically 0.34 nm in interlayer spacing) [1]. Most of our samples are individual nanotubes or small-sized bundles, which have the number of walls of five to ten. The distribution of outermost diameters of nanotubes estimated from TEM observations shows that the most probable diameters of nanotubes are below 10 nm. Their diameters are much smaller than those of MWCNTs synthesized by conventional CVD method [15].

The TGA was used to determine the purity of t-MWCNTs (not shown here). The burning temperature (~557 °C) of the t-MWCNTs is higher than that of SWCNTs (~480 °C) [16] but lower than that of the general thick MWCNTs (~700 °C) grown by CVD method [15]. We note that about 13 wt% of the sample still remained even at a burning temperature of 1000 °C in air. The residual material was identified from EDX analysis as the MgO particles in a limited local area and the transition-metal oxides in small quantity.

Fig. 2a shows the radial breathing modes (RBMs) in Raman spectra obtained with several excitation energies. It is well known that the diameter distribution of various nanotubes can be extracted from the RBM of Raman spectra [17]. The expression: \( \omega_{RBM} = \frac{235}{d} + 9 \) cm\(^{-1}\), where 9 cm\(^{-1}\) was attributed to the bundling effect [18], was used to calculate the diameter of t-MWCNTs, since t-MWCNTs presumably resemble SWCNT bundles. In the previous studies, in
order to determine both inner and outer diameters of double-walled carbon nanotubes (DWCNTs), the above formula has been frequently used by assuming that van der Waals interaction between the inner and outer tubes in DWCNTs is similar to intertube interaction in SWCNT bundles [19,20]. This empirical formula is usually valid with diameters up to about 3 nm. The diameters (nm) of nanotubes calculated from the above formula are also shown in Fig. 2a. The RBMs should be mainly attributed to inner diameters in t-MWCNTs. The nanotube diameters calculated from RBMs almost agree with the inner walls of t-MWCNTs observed by TEM. We emphasize that no SWCNTs or DWCNTs were observed by TEM in our samples. The RBM region of t-MWCNTs shows a wide distribution of the tube diameters in the range of 0.74–3.09 nm (corresponding with 329–85 cm$^{-1}$). In general, RBMs were rarely observed in MWCNTs, due to their large diameters and large number of nanotube walls [21]. However, in our sample, the number of walls are small and more importantly some inner diameters are in the range of 0.74–3.09 nm, which is also evidenced by TEM observations. This leads us to conclude that the RBMs are related to the inner walls of t-MWCNTs.

Fig. 2b shows the G-bands near 1580 cm$^{-1}$. The G-band involves the tangential mode vibrating along the tube axis and the circumferential mode vibrating perpendicular to the tube axis that is also diameter-dependent. Peak positions of the G-band are consistently downshifted compared to those of SWCNTs [16], but close to those of thick MWCNTs [15]. The G-band shape is MWCNT-like without small side peak at lower energy side that is typically observed in SWCNTs. The D-band near 1300 cm$^{-1}$ is attributed to the disordered sp$^2$ carbon by the defects in graphitic sheets. The integrated area ratio of D- to G-band is lower than that of conventionally thick MWCNTs [22,23], implying that our t-MWCNTs have less defects or less amorphous carbons on the tube wall than thick MWCNTs. Fig. 2c shows the D-bands of t-MWCNTs at different excitation energies. The D-band was upshifted with increasing excitation energies. The D-band position of t-MWCNTs is linearly dependent on the excitation energies with the similar slope to those of DWCNTs and SWCNTs [19].

The hollow inner space of nanotubes could be estimated by gas adsorption experiment. However, tips of the purified t-MWCNTs are mostly capped such that the excess to the gas adsorption inside the hollow space is limited. In this study, the inner space was estimated by comparing gas adsorption behaviors of samples with/without caps of t-MWCNTs. In order to open t-MWCNTs tips, we refluxed t-MWCNTs in HNO$_3$ solution for 2 h (HNO$_3$-2h) and 12 h (HNO$_3$-12h). As a result, tips of the HNO$_3$-12h were open extensively compared with those of the HNO$_3$-2h. Fig. 3a and b show TEM images of the HNO$_3$-12h at different positions. TEM images show that most of t-MWCNTs tips are opened and cut by an etching effect through severe acid treatments. In addition, the disordered carbons such as amorphous carbons appear on the outer walls and the inner hollow cavities of nanotubes. They might have been produced by the broken nanotubes from longer HNO$_3$ treatment for 12 h. This could be evidenced by the enlarged D-band in Raman spectra (Fig. 3d), where intensities of the D-band increased with increasing treatment times. The peak intensities in the RBM region for HNO$_3$-12h were remarkably decreased compared with those of the purified sample (Fig. 3c). This suggests that even the inner tube walls with smaller diameters were attacked by the strong acid treatment after cap opening.

We next measured N$_2$ adsorption isotherms in order to compare the pore structures of the t-MWCNTs before and after HNO$_3$ treatments. The N$_2$ adsorption isotherm (77 K) of the purified t-MWCNTs shows an intermediate shape between type II and type IV (in IU-PAC classification), as shown in Fig. 4a. This is similar to N$_2$ adsorption isotherms of general thick MWCNTs [25]. The purified t-MWCNTs show a gradual uptake of N$_2$ at the medium relative pressure ($P/P_0$) and also show dramatically predominant adsorption of N$_2$ at higher $P/P_0$, which are associated with multilayer adsorption on the external surface and in larger mesopores or macropores formed at spaces between t-MWCNTs. Fig. 4b and c show N$_2$ adsorption isotherms for the HNO$_3$-2h and the HNO$_3$-12h, respectively. The N$_2$ adsorption amount near $P/P_0 = 1$ progressively decreases with HNO$_3$ treatment time, suggesting a decrease of larger mesopore and macropore volumes due to an agglomeration of t-MWCNTs in HNO$_3$ solution. Therefore, longer HNO$_3$ treatment should promote formation of densely packed t-MWCNT network. The HNO$_3$ treatment for 12 h alters the N$_2$ adsorption isotherm to typical type IV with a clear hysteresis loop (Fig. 4c). Therefore, the appearance of the clear hysteresis loop of N$_2$ isotherm suggests that HNO$_3$ treatment produce the mesopores that are contributed to the interstitial spaces. Type IV isotherm with a hysteresis loop at higher $P/P_0$ have often been reported with the purified SWCNTs [14,26]. Since the internal pore-size of the individual SWCNTs was less than 2 nm, this hysteresis loop should originate from interstitial pores formed at interbundle spaces [14,26]. In case of our sample, the inner hollow cavities of t-MWCNTs observed from TEM were mainly less than 5 nm. In general, the hysteresis loop at $P/P_0 > 0.8$ is contributed to larger mesopores.
Therefore, the hysteresis loop in N$_2$ adsorption isotherm of HNO$_3$-12h should come from not internal spaces but mesopores created by the bundle network. This is confirmed by N$_2$ adsorption isotherm of the pressed t-MWCNTs (Fig. 4d). The t-MWCNTs were compressed by applying the pressure of 20 MPa to reduce spaces formed by the interbundle network. Interestingly, the N$_2$ adsorption isotherm of the pressed t-MWCNTs is similar to that of HNO$_3$-2h.

The pore structure parameters of t-MWCNTs determined by the BET, SPE, and BJH methods are summarized in Table 1. The increase of the BET surface area with HNO$_3$ treatment is mainly contributed by the increase of the micropore surface area. The micropore surface area and the micropore volume increase with HNO$_3$ treatment times. This is probably related to two possibilities: (1) the tips of t-MWCNTs with small inner diameters less than 2 nm are easily etched and opened compared to those with large ones and (2) the inner hollow cavities more than 2 nm (mesopores) are partially filled with disordered carbons, resulting in creation of narrow pores. On the other hand, the mesopore volume and the average mesopore diameter decrease with increasing HNO$_3$ treatment times. This is attributed by the reduction in the amount of mesopores near 20–90 nm that is transformed into narrow mesopores. The mesopore volume and the average mesopore size for the pressed t-MWCNTs decrease compared with those for the purified sample. This diminution in the mesoporosity can be originated from a formation of densely packed t-MWCNTs network by a packing effect. Mesoporosity of the pressed t-MWCNTs is similar to that of HNO$_3$-2h.

Fig. 5 shows the mesopore size distributions calculated by the BJH method. The purified t-MWCNTs show a broad pore size distribution (PSD) from 2 to 100 nm, with a small peak near 2.5 nm and broad peak ranging from 30 to 90 nm, corresponding to mesopores and macropores. The peak position near 40 nm is downshifted to 23 nm in the pressed sample, whereas the peak position near 2.5 nm is not altered after pressing, as expected. The HNO$_3$-treated t-MWCNTs for 2 h show the PSD similar to the pressed t-MWCNTs at larger mesopores, again confirming the formation of densely packed bundle-network. On the other hand, the small mesopores ranging from 2 to 4 nm are heavily developed upon HNO$_3$ treatment for 2 h. This is attributed to the partial opening of t-MWCNT tips, enabling an access of gases.
to the inner empty space. With longer HNO$_3$ treatment for 12 h, the peak intensity of the narrow mesopores ranging from 2 to 4 nm dramatically increases and the large mesopore peak position is shifted from 40 to 15 nm, indicating more abundance of the opened tips and more densely packed bundle-network, respectively. More interestingly, the positions of narrower mesopores are split into two near 2 and 3.5 nm. This strongly suggests that once tips were opened, the HNO$_3$ can be easily diffused into the inner space by the capillarity effect and subsequently attack the inner tube walls. Therefore, the removal of inner walls should enlarge the inner mesopore sizes, which is consistent with the disappearance of smaller diameter peaks in the RBMs (Fig. 3c).

4. Conclusions

The t-MWCNTs have the number of walls of five to ten, and their outermost diameters and burning temperature are intermediate between SWCNTs and typically thick MWCNTs. The RBM region of the t-MWCNTs shows the tube diameters in the range of 0.74–3.09 nm, which are related to the inner walls of t-MWCNTs, in good agreement with TEM observations (from less than 1 to 5 nm). Longer HNO$_3$ treatment not only opens the nanotube tips but also promotes the formation of densely packed t-MWCNT network, resulting in development of pores less than 4 nm, which is evidenced by N$_2$ adsorption measurements. Therefore, TEM, Raman
spectroscopy, and gas adsorption provided reasonable information about innermost diameters of t-MWCNTs. We expect that these t-MWCNTs with complementary structural properties between SWCNTs and MWCNTs can find useful applications.

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References


Fig. 5. BJH mesopore size distributions obtained from N₂ adsorption isotherms of the t-MWCNT samples.

1 10 100

0.00

0.02

0.04

0.06

0.08

0.10

dV/dx (cm³g⁻¹ nm⁻¹)

Pore size, x (nm)

HNO₃-12h

HNO₃-2h

Pressed

Purified


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