Thermal Annealing Effects on Structure and Morphology of Micrometer-Sized Carbon Tubes

Chien-Chung Han,* Jyh-Tsung Lee, and Hua Chang

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

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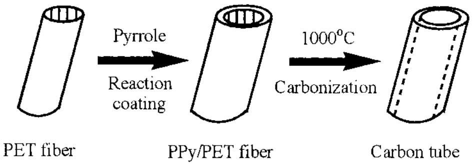
Micrometer-sized carbon tubes can be conveniently prepared via a new chemical approach by pyrolyzing the composite fibers consisting of a polypyrrole skin layer and a PET core fiber at 1000 °C under a N_2 atmosphere. The resultant carbon tubes were found to be amorphous carbon. After further annealing at 1000−2400 °C, the carbon tube structure was found, on the basis of XRD, Raman, and TEM studies, to change gradually from a disordered amorphous phase to a highly ordered graphitic phase with preferred orientation. As the annealing temperature increased from 1000 to 2400 °C, the graphitic crystallites of carbon tubes not only increased their sizes considerably but also tilted their stacking planes gradually toward the tube axis. Both SEM and SAD results implied that the 2400 °C annealed sample may have a cylindrical layer-stacking structure similar to those of carbon nanotubes. Accompanying these enhancements of structural ordering and orientational preference of the graphitic planes, the conductivity along the tube axis of the corresponding carbon tubes was also found to increase significantly.

Introduction

Studies on the formation and growth mechanism[1] of nanosized carbon tubes have attracted a lot of research interest in recent years, due to the interesting properties that arise from their size being comparable to that of a molecule and their potential for use in applications such as electron field emitters,[2] nanowires,[3] nanometer-sized probes,[4] natural gas storage, possible catalytic microreactors, and biosensors.[5] Various methods have been reported for the preparation of carbon tubes; these include carbon-arc discharge,[6] laser ablation,[7] condensed-phase electrolysis,[8] and the catalytic pyrolysis of hydrocarbons on various substrates such as porous anodic aluminum oxide,[9] fine metal particles,[10] and patterned cobalt layers.[11] Furthermore, it has also been demonstrated that various metal oxides,[12] and some molecules such as small proteins,[13] can be introduced into the cavity of nanotubes, followed by different reactions. Recently, we have also developed a novel method[14] for making carbon tubes (via the chemical strategy in Scheme 1) by thermal pyrolysis of composite fibers that contained a thermally removable polymer core, like poly(ethylene terephthalate) (PET), and a thermally more stable skin, such as one made from a conducting polymer like polypyrrole (PPy). The present method can be used to prepare micrometer- or submicrometer-sized carbon tubes a few centimeters in length with a controllable tube wall thickness ranging from less than 30 nm to a few micrometers, by varying the thickness of the PPy skin layer. Furthermore, the tube diameter can also

Scheme 1



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* To whom correspondence should be addressed. E-mail: cchan@mx.nthu.edu.tw. Tel.: 886-3-5724998. Fax: 886-3-5711082.

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be varied by changing the diameter of the PET core fiber. Most interestingly, this new method enables the preparation of well-organized two- or three-dimensional structures assembled by carbon tubes several centimeters in length via the use of appropriate woven templates,[14b] which should enable easier design and fabrication of actual articles for various practical applications.

Regarding the morphology of the tube wall, these micrometer-sized carbon tubes (obtained by pyrolysis of PPy/PET composite fibers at 1000 °C) were found to be mostly amorphous in structure, whereas the carbon nanotubes produced by a carbon-arc discharge method,[6] which created an interelectrode plasma with a temperature believed to be close to ca. 4000 K,[16] showed a highly ordered cylindrical layer-stacking structure.[6] It has been previously reported that, after thermal treatment at higher than ca. 2200 °C, the amorphous carbons resulting from the carbonization (at 1000 °C) of a typical graphitizing carbon source (e.g. poly(vinyl chloride), petroleum coke, and pitch coke) could be transformed to highly ordered graphitic carbons, whereas those amorphous carbons resulting from the nongraphitizing carbon sources (e.g. poly(vinylidene chloride), sugar charcoal, hexachlorobenzene) could not.[17] A typical graphitizing carbon matrix was found to have a relative compact structure, whereas a typical nongraphitizing carbon matrix was rather porous.[15,17] On the basis of these findings[15,17] together with our SEM and TEM observations that the micrometer-sized carbon tubes have a very compact structure, it is believed that these micrometer-sized amorphous carbon tubes could also be transformed to highly ordered graphitic carbon tubes after a typical graphitization treatment. Therefore, by preparation of carbon tubes with different sizes, wall thicknesses, and compositions, the present results can also be extended to study the influence of these factors on the graphitization behavior of various carbon sources.

The present paper is directed at understanding, with the aid of various spectroscopic and analytical methods, the structural and morphological changes of these novel carbon tubes when annealed at temperatures typically used for graphitization studies, such as 1600−2400 °C. The results clearly revealed that the initial isotropic amorphous carbon phase changed to a much more ordered graphitic phase at 2400 °C with a preferred orientation, possibly having a cylindrical layer-stacking structure with the concentric tube axis approximately parallel to the axis of carbon tube.

Although the current study is focused on micrometer-sized carbon tubes as prepared from the micrometer-sized PPy/PET composite fibers that utilized commercially available micrometer-sized and submicrometer-sized PET as the core fibers, it is envisaged that such annealing effects and chemical insights for controlling carbon-tube structures will also be applicable for future preparation of nanometer-sized carbon tubes using the recently developed nanometer-sized fibers[18] as the core fibers.

Experimental Section

Materials. The poly(ethylene terephthalate), PET, fibers (16.7, 7.5, 2.5, and 0.8 μm in diameter) were obtained from Far Eastern Textile Co. Ltd. (Hsinchu County, Taiwan) and Union Chemical Laboratories, Industrial Technology Research Institute (Hsinchu, Taiwan). Pyrrole was obtained from Aldrich and distilled under vacuum to remove brown decomposition products before use. *p*-Toluenesulfonic acid monohydrate (Aldrich, 98%) and ammonium persulfate (Aldrich, 98%) were used without further purification. The resistance of the deionized water used was 18.2−18.3 MΩ.

Preparation of PPy/PET Composite Fibers. The PPy-coated PET fibers were prepared via a typical reaction-coating approach[19] by first suspending commercially available PET fibers (1 g) in a 0.02 M pyrrole aqueous solution (120 mL) containing a 2 equiv amount of *p*-toluenesulfonic acid, followed by the addition of 0.025 M APS aqueous solution (120 mL). A reaction coating time of 30 min was used, and the resulting PPy presented itself as a homogeneous black coating on the surface of PET fibers. Such formed composite fibers were first washed with copious amounts of deionized water and collected by filtration; washing was continued until the filtrate was clear, and then the fibers were washed with methanol, followed by drying in an vacuum oven at ambient temperature overnight or until constant weight. The thickness of such PPy coatings can be further controlled by the number of coating treatment cycles. The typical PPy/PET composite fiber in this work employed 4 cycles of PPy coating treatment.

Formation of Carbon Tube. The above PPy/PET composite fibers were placed in a quartz tube oven and then purged with N_2 (0.5 L/min) for 6 h. The fibers were then heated from room temperature to 1000 °C at a heating rate of 10 °C/min under a N_2 atmosphere (N_2 flow rate 0.5 L/min). An annealing time of 3 h was employed after 1000 °C was reached, before the carbon tubes were allowed to cool to ambient temperature.

Graphitization. The above carbon tubes were heat-treated in an electric graphite furnace under a He atmosphere. The temperature was raised at a heating rate of 3 °C/min to a predetermined temperature and held there for 0.5 h, before cooling to ambient temperature.

Instrumentation. The morphology and shape of various samples were observed by scanning electron microscopy (SEM) on a Hitachi S-2300 microscope or by field emission scanning electron microscopy (FESEM) using Hitachi S-4000 equipment, both using an accelerating voltage of 20 kV. The surface of samples was typically coated with a thin film of Pt/Pd (4/1) or Au (ca. 50−200 Å thick) for SEM studies, to facilitate charge dissipation. The X-ray powder diffraction for the ground-up carbon tubes was obtained by a Shimadzu XD-5 X-ray diffractometer with a Cu Kα ($\lambda = 1.541\,78$ Å) radiation source. The diffractogram in the 2θ range of 3−90° was recorded at a step size of 0.02°. The corresponding *d*-spacing was calculated on the basis of Bragg's equation, $n\lambda = 2d \sin \theta$, where n is the order of diffraction, λ is the wavelength of X-rays used, d is the interplanar spacing, and θ is the diffraction angle. The corresponding crystallite size was estimated by using Scherrer's equation, $L = (K\lambda/\beta \cos \theta)$, where K is 0.9 and β is the half-maximum line width in radians. The Raman spectra of the carbon tubes were obtained for a pressed pellet of neat ground-up carbon tubes. The excitation source was 60 mW with a wavelength of 514.5 nm from an argon ion laser (Spectra Physics). The scattered light was dispersed by a spectrometer (Spex, 0.85 m), detected by a photomultiplier (RCA, C31014A), and amplified by a photon counting system (SSR). The resolution of Raman spectrum was 5 cm^{-1}. The structural details of the carbon tubes were obtained from transmission electron microscopy (TEM, JEOL JEM-2010) and high-resolution transmission electron microscopy (HRTEM,

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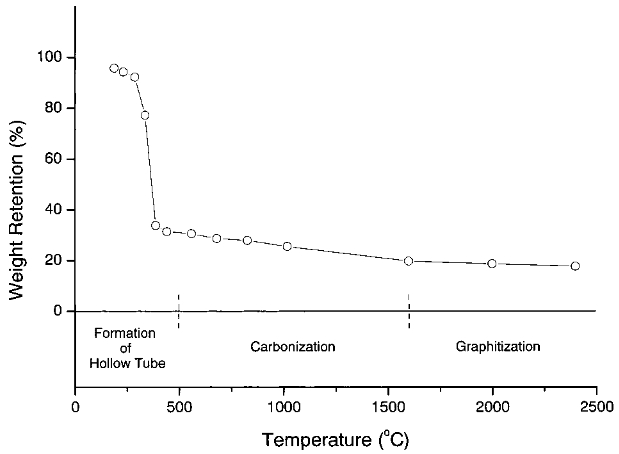

Figure 1. Weight retention for a PPy/PET composite fiber after being thermally treated at different temperatures.

JEOL JEM-4000EX), with an accelerating voltage of 200 and 400 kV, respectively. The TEM specimens were typically prepared by ultrasonic dispersion of the carbon tubes in anhydrous ethanol and then transfer of a drop of the supernatant onto a copper grid. The conductivity measurement was performed using a standard four-in-line probe method with a constant current source (Keithley 220) and a multimeter (Keithley 196).

Results and Discussion

Weight and Morphology Changes. The percent weight retention of the carbon tubes from annealing at between 1600 and 2400 °C was calculated, on the basis of the weight of the corresponding original PPy/PET composite fiber, and summarized in Figure 1. For a more complete understanding of the carbon tube formation process, the percent weight retention of the samples being heated at a predetermined temperature between room temperature and 1000 °C for 3 h was also included in Figure 1. The results indicated that the weight loss of the composite fiber occurred most rapidly between 300 and 500 °C, then moderately between 500 and 1600 °C, and insignificantly between 1600 and 2400 °C. The weight loss between ca. 300−500 °C was found, in our other related study, to be mainly due to the decomposition of the core PET fiber, forming various gaseous byproducts (such as carbon monoxide, carbon dioxide, acetylene, ethanal, and H_2O) and some solid sublimates (including terephthalic acid, 4-((vinyloxy)carbonyl)benzoic acid, and bis((vinyloxy)carbonyl)benzene).[20] The same work[20] also showed that most of the PET core had already decomposed and disappeared at temperatures above ca. 400 °C, leaving only hollow tubes. Thus, the range of temperature from ambient to about 500 °C is therefore best characterized as the hollow tube formation stage. The same related work also found that the weight loss between ca. 500 and 1000 °C was mainly caused by the decomposition of the PPy skin layer to form various N-containing byproducts (such as HCN, NH_3, and N_2), thus leading to the reduction of N/C atomic ratio in the resultant pyrolyzed tubes.[20] The main activity that occurred within this temperature range can be best described as carbonization. Similar carbon-enriching behavior has also been observed during the carbonization of polyacrylonitrile.[21]

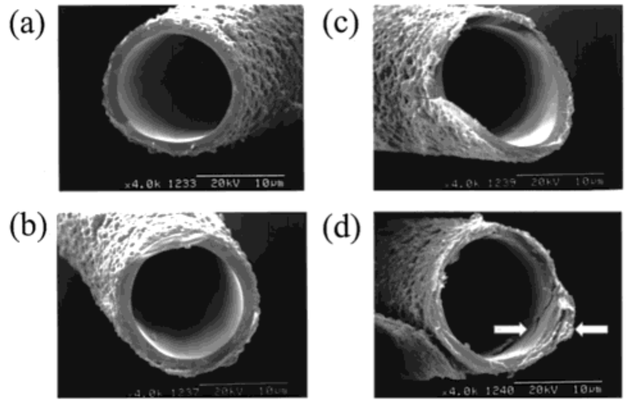

Figure 2. SEM micrographs for the carbon tubes after being annealed at (a) 1000 °C, (b) 1600 °C, (c) 2000 °C, and (d) 2400 °C.

The current study indicated that although the weight loss between 1000 and 1600 °C continued in a similar trend like that between 500 and 1000 °C, it apparently leveled off above ca. 1600 °C. The percent weight retention between 1600 and 2400 °C was found, within experimental error, to be almost unchanged (i.e., 18.7 ± 0.7%). However, results from various analytical studies indicated that the structure and morphology of the resultant hollow carbon tubes has changed dramatically with the annealing temperature. Therefore, this temperature range, i.e., between ca. 1600 and 2400 °C, can be best described as the graphitization stage.

Figure 2 shows the SEM micrographs of the cross-sectioned carbon tubes after the heat-treatment at temperatures between 1000 and 2400 °C. The results indicated that the carbon tubes maintained their round shape throughout the whole temperature range. Interestingly, while all samples obtained at below 2000 °C (Figure 2a−c) showed a similar smooth structural feature in their cross sections, the carbon tubes that resulted at 2400 °C (Figure 2d) however showed a clear cylindrical layer-stacking structural feature (depicted by the region marked between two arrows in Figure 2d). This result suggests the possible formation of a graphitic carbon tube at 2400 °C, which might have a cylindrical layer-stacking structure similar to that reported for multiwalled carbon nanotubes.[6] The SEM results thus showed that the tube wall structure has been significantly changed when annealed between 1600 and 2400 °C, even though no significant weight loss was observed.

X-ray Diffraction Patterns and Raman Spectra. The X-ray powder diffraction (XRD) patterns for ground-up samples of the carbon tubes annealed between 1000 and 2400 °C are displayed in Figure 3. The results indeed showed a very clear structural transition from the disordered amorphous carbon phase at 1000 °C to a highly ordered graphitic phase at 2400 °C. The XRD pattern for the 1000 °C sample (Figure 3a) showed a rather complicated broad band ranging from $2\theta = 13-32°$ with a maximum at about 22.5°, which is equivalent to a *d* spacing of about 3.951 Å as calculated according

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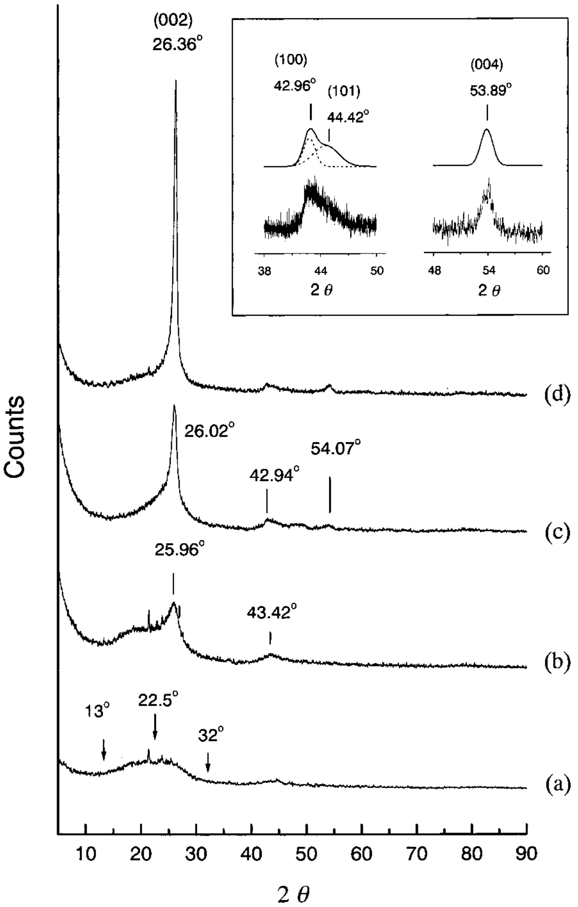

Figure 3. XRD patterns for ground-up samples of the carbon tubes after being annealed at (a) 1000 °C, (b) 1600 °C, (c) 2000 °C, and (d) 2400 °C. The insert for (d) showed the enlarged diffraction peaks (bottom) and their corresponding fitting curves (top) in the 2θ range of 38−50° and 48−60°.

to Bragg's equation.[22] As the sample was further annealed at 1600 °C for 0.5 h, a higher ordered carbon phase started to form, showing a new XRD peak (Figure 3b) with a maximum at $2\theta = 25.96°$, which is equivalent to a d spacing of about 3.432 Å. Such transition to higher ordered structure was even more obvious for the sample being annealed directly at 2000 °C for 0.5 h. The peak maximum for the ordered carbon phase appeared at $2\theta = 26.02°$, which corresponds to a d spacing about 3.424 Å. Such increase in structural orderliness continued as the annealing temperature was further raised to 2400 °C, with the corresponding XRD pattern (Figure 3d) showing a very strong and sharp peak at $2\theta = 26.36°$, which is very close to the (002) diffraction peak of a 0.2 × 0.2 cm single-crystal graphite plate ($2\theta = 26.56°$) measured under the same conditions. The d spacing for a ground-up sample of the 2400 °C tube at $2\theta = 26.36°$ is calculated to be 3.3810 Å, which is significantly smaller than the average d spacing of 3.45 Å for a typical turbostratic carbon structure[23] but is closer to the average d spacing of 3.354 Å for an ideal graphitic structure (theoretical $2\theta = 26.58°$, if measured with the same instrument). In addition to the strong (002) peak, the same XRD pattern also showed three much smaller peaks (as displayed in the insert of Figure 3) at $2\theta = 42.96$, 44.42, and 53.89°, which may be ascribed to the diffraction peaks for the corresponding (100), (101), and (004) planes of graphite, respectively.

The average crystallite size (L_c) of the 2400 °C annealed samples is estimated to be 155 ±15 Å according to Scherrer's equation,[24] using the positions and the half-maximum widths (fwhm) of the (002) peak measured on the sample and the reference graphite plate. The obtained L_c value for the 2400 °C sample is greater than the typical L_c values of 70−80 Å reported for carbon fibers obtained by graphitizing polyacrylonitrile fibers at a similar temperature, i.e., 2500 °C.[25]

The graphitization index can be determined from the average d_{002} spacing, or the interplanar d spacing between two graphitic layers, according to the following equation:[26]

$$g_p = (3.440 - d_{002})/(3.440 - 3.354)$$

The graphitization index g_p for the 1600, 2000, and 2400 °C samples was calculated to be 9.2%, 18.2%, and 68.7%, respectively. The results indicated that the 2400 °C annealed carbon tube was indeed highly graphitic, in agreement with the layer-stacking features observed under SEM.

The above structural transformation on annealing, from a disordered amorphous carbon phase to a highly ordered graphitic phase, can also be clearly observed by means of their corresponding Raman spectra as displayed in Figure 4, using ground-up samples of carbon tubes ca. 2 μm in diameter as examples. All of the samples showed a typical two-band Raman spectrum in the range of 800−1800 cm^{-1} similar to other carbonaceous or graphite-like materials, with the vibrational bands appearing at ca. 1354 cm^{-1} (generally referred as the disorder-induced D band) and at 1584 cm^{-1} (i.e. the Raman-allowed G band), which may be ascribed to the disordered and graphite-like structure of carbons, respectively.[27] As the annealing temperature was increased from 1000 to 2400 °C, both broad bands of the 1000 °C sample (Figure 4a) became narrower and sharper. Meanwhile, the originally weaker G band of the 1000 °C sample (Figure 4a) also showed increased intensity relative to that of the D band as the annealing temperature was raised through 1600 and 2000 °C (Figure 4b,c) and eventually became the stronger band at 2400 °C (Figure 4d). The detailed Raman spectroscopic information, including Raman shift and area ratio, is summarized in Table 1. The results indicated that as the annealing temperature was increased from 1000 to 2400 °C, the wavenumber of the D band shifted from 1326 to 1342 cm^{-1}, while that of the G band shifted from 1588 to 1574 cm^{-1}. The area ratio of the G band

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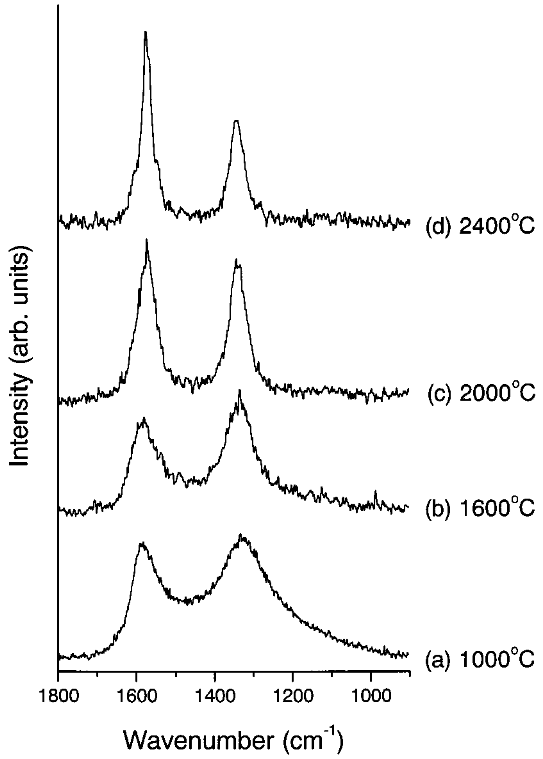

Figure 4. Raman spectra for ground-up samples of the carbon tubes after being annealed at (a) 1000 °C, (b) 1600 °C, (c) 2000 °C, and (d) 2400 °C.

Table 1. Raman Results for Thermally Annealed Carbon Tubes

	G-band[a]		D-band[a]			
annealing temp (°C)	peak max (cm^{-1})	fwhm[b] (cm^{-1})	peak max (cm^{-1})	fwhm[b] (cm^{-1})	I_G/I_D[c]	L_a (Å)[d]
1000	1588	81	1326	224	0.32	38.4
1600	1584	74	1336	106	0.58	69.6
2000	1576	51	1340	53	1.05	126.0
2400	1574	33	1342	43	1.34	160.8

[a] G-band, Raman-allowed band; D-band, disorder-induced band. [b] fwhm: full width at half-maximum of peak. [c] I_G/I_D: integrated intensity ratio of G-band vs D-band. [d] L_a: in-plane crystallite size.

relative to the D band increased from 0.32 at 1000 °C to 1.34 at 2400 °C, confirming the structural transformation from a disordered amorphous carbon phase to a more ordered graphitic carbon phase. The corresponding in-plane crystallite size L_a was estimated, on the basis of the ratio of the integrated intensity I_D/I_G of D band vs G band, to increase from 38.4 to 160.8 Å, if the empirical relation in eq 1, as being validated for 632.8 nm HeNe laser line,[28] was applied herewith.

$$L_a = 120(I_G/I_D) \qquad (1)$$

Electron Microscopy Observations. Figure 5a presents the TEM bright-field image for a 2400 °C annealed carbon tube (ca. 2 μm in diameter). The corresponding selected area diffraction (SAD) patterns for the tube wall edge (area B) and the tube wall center part (area C) is displayed in Figure 5b,c, respectively. The SAD pattern for area B (Figure 5b) showed a pair of small but strong arcs for 002 and 004, plus another pair of weak arcs for 006, along the direction generally perpendicular to the tube axis. Furthermore, this result also showed a very weak pair of 10 and 11 arcs, along the direction generally parallel to the tube axis. This SAD result suggests that the 002 planes near the edge of the tube wall are preferentially oriented in the direction approximately parallel to the incident electron beam (as sketched in Figure 5d). The SAD pattern for area C (Figure 5c), on the other hand, showed strong 10 and 11 diffraction rings together with a weak 002 ring. This SAD result suggests that the 002 planes at the center part of the tube wall are preferentially oriented in the direction approximately perpendicular to the incident electron beam (as sketched in Figure 5d). The overall SAD results seem to suggest that the tube wall consists of cylindrically stacked 002 planes and that our 2400 °C treated micrometer-sized carbon tubes have indeed revealed a graphitization behavior similar to other graphitizing carbons[17] and may have already transformed to a structure in closer resemblance to that of a multiwalled carbon nanotube.[6]

The lattice images of the tube wall for the thermally annealed carbon tubes (ca. 2 μm in diameter) were further studied with high-resolution TEM (HRTEM). The HRTEM images for the edge areas of the tube walls are displayed in Figure 6 with the horizontal direction of the photographs being approximately parallel to the axis of the corresponding carbon tubes. The HRTEM image for the 1000 °C annealed carbon tube (Figure 6a) showed that the tube wall consists of many small crystallites with the axis of their crystallite domain randomly oriented in all directions, showing a typical structure for an amorphous carbon matrix. As the annealing temperature increased to 1600 °C, these crystallites (Figure 6b) clearly grew larger, which is consistent with the XRD result (Figure 3b). Furthermore, the planes of these crystallite domains had clearly inclined toward the direction of the carbon tube axis. The average *d* spacing for this 1600 °C sample was found by XRD to be 3.43 Å (Figure 3b), which is very close to 3.45 Å as typically reported for a turbostratic carbon matrix.[23] As the annealing temperature increased to 2000 °C, the crystallites had grown significantly larger (with $L_c = 70$ Å), showing a long range of ordering having a layer-stacking structure within the crystalline domain (Figure 6c). Moreover, the layer planes were found to be approximately parallel to the direction of the carbon tube axis. The HRTEM image however also indicated that these roughly parallel crystallite planes did have many layer-stacking dislocations. As the annealing temperature was raised to 2400 °C, most of the above dislocations had disappeared, showing the typical graphitic layer structure with the planes of the layers being parallel to the tube axis. Apparently, the TEM results suggested that as the annealing temperature was increased from 1000 to 2400 °C, the randomly distributed small crystallites not only grew larger but also gradually titled their *ab* planes toward the axis of the inner tube and eventually merged with each other to form more extensive graphene sheets. Such structural ordering behavior has also been recently observed for the carbon nanotubes prepared from the

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(28) Endo, M.; Kim, C.; Karaki, T.; Kasai, T.; Matthews, M. J.; Brown, D. M.; Dresselhaus, M. S.; Tamaki, T.; Nishimura, Y. *Carbon* **1973**, *11*, 1633.

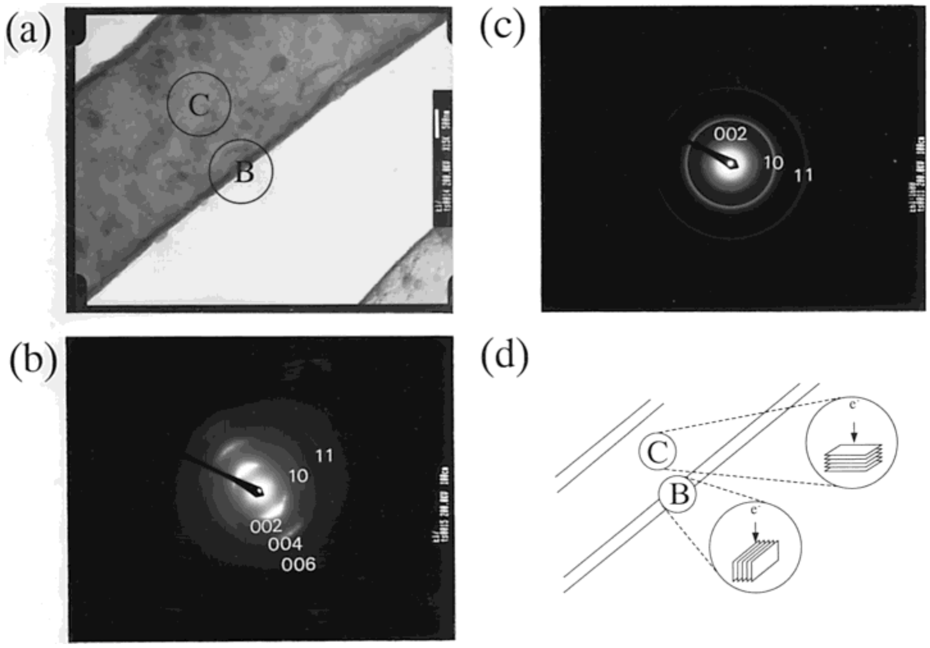

Figure 5. TEM results for the 2400 °C annealed carbon tube: (a) bright-field image; selected area diffraction patterns for (b) edge area B and (c) center area C; (d) the sketched orientation relationships between the incident electron beam and the corresponding 002 planes in areas B and C, respectively.

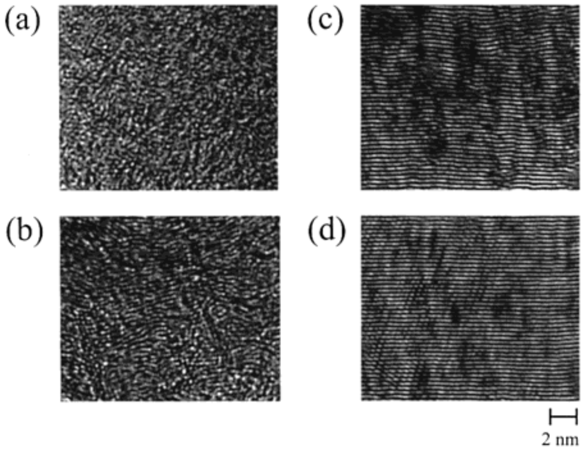

Figure 6. HRTEM images for the carbon tube walls after being annealed at (a) 1000 °C, (b) 1600 °C, (c) 2000 °C, and (d) 2400 °C.

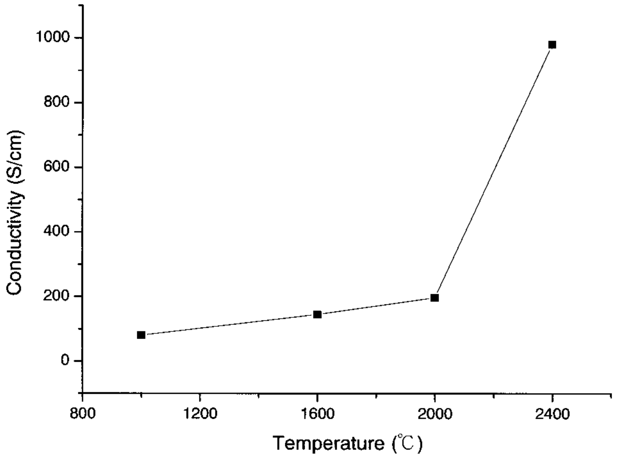

Figure 7. Conductivity for the carbon tube samples after being annealed at 1000, 1600, 2000, and 2400 °C, respectively.

catalytic pyrolysis method basing on the thermal decomposition of acetylene over silica-supported cobalt catalysts at 700−1100 °C, which yielded a large fraction of carbon nanotubes having a less ordered carbon structure with the stacked aromatic layers (in a noncylindrical fashion) oriented at ca. 30° with respect to the tube axis.[10b] After being thermally annealed at 2800 °C, all the disordered carbon structures were found to be completely transformed into a highly ordered concentric cylindrical stacking layer structure, whose axis was parallel with the inner tube axis.[10b]

The above HRTEM imaging results clearly revealed the structural change from amorphous carbon phase at 1000 °C to the graphitic layer-stacking structure at 2400 °C; they also indicated that the 2400 °C annealed sample might have actually developed a cylindrical stacking layer structure similar to that of the carbon nanotubes.[6] Although the mechanism of carbon tube graphitization is not yet understood, the present results still hinted that the morphological change during graphitization appeared to be independent of carbon tubes sizes.

Conductivity. Furthermore, as the structure of the carbon tubes changed with the annealing temperature from the disordered amorphous carbon phase to the highly ordered and oriented graphitic phase, the conductivity along the tube axis of the corresponding carbon tubes also increased. The conductivity along the axis of the resultant carbon tubes of ca. 15 μm in diameter was measured using the typical four-in-line probe method[29] and summarized in Figure 7. The results indicated that the conductivity along the tube axis seemed to increase linearly with the treatment temperatures of the corresponding carbon tubes from 1000 °C until 2000 °C. The conductivity for tube samples annealed at 1000, 1600, and 2000 °C was 81, 145, and 197 S/cm, respectively. Such an increase in conductivity along the tube axis is

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[29] Wieder, H. H. *Laboratory Notes on Electrical and Galvanomagnetic Measurements*; Elsevier Scientific Publishing Co.: Amsterdam, 1979.

attributable to the gradually improved structural order and the increased orientation of conducting paths (i.e. the graphitic crystallite planes) along the tube axis. Most interestingly, the conductivity showed an abruptly sharp increase from 197 S/cm to 980(±100) S/cm as the annealing temperature was elevated from 2000 to 2400 °C. This result is in agreement with the above HRTEM observation that as the annealing temperature was raised from 2000 to 2400 °C, the layer-stacking dislocations (equivalent to the conducting path defects) that existed in the crystallites had also been significantly reduced.

Conclusion

The annealing treatment at elevated temperatures, ranging from 1600 to 2400 °C, was shown to have a significant influence on the morphology and structure of the micrometer-sized carbon tubes. As the annealing temperature was increased from 1000 to 2400 °C, the structure of the annealed carbon tubes changed gradually from a disordered amorphous carbon phase to a more ordered and preferentially oriented graphitic phase, as evidenced by results from Raman spectroscopy, XRD, and TEM studies. Accompanied with the improvement of structural ordering and orientation preference with annealing temperature, the conductivity along the tube axis of the corresponding carbon tubes was also enhanced. Most interestingly, the abruptly sharp increase in conductivity for the 2400 °C sample (980 S/cm) relative to that of the 2000 °C sample (197 S/cm) was found to be in good agreement with the HRTEM observations, which indicated that the large number of layer-stacking dislocations (i.e. equivalent to the conducting path defects) that originally existed in the 2000 °C sample were mostly absent from the 2400 °C sample. Thus, the conductivity result further supported the relationship between structural change of carbon tube wall with annealing temperatures as observed by XRD, Raman, and TEM.

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