A New and Easy Method for Making Well-Organized Micrometer-Sized Carbon Tubes and Their Regularly Assembled Structures

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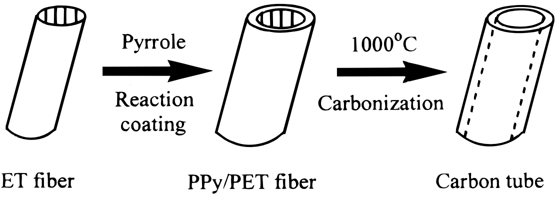
Partially ordered micrometer-sized carbon tubes several centimeters in length have been prepared via a new chemical approach by the pyrolysis of composite fibers consisting of a thermally more stable polypyrrole (PPy) skin layer and a poly(ethylene terephthalate) core. The wall thickness of resultant hollow carbon tubes was found to be directly proportional to the thickness of the original PPy coating. Elemental analysis results indicated that these tubes essentially consisted of pure carbon, accompanied by a small amount of N (<3 wt %) and H (<1 wt %). The use of single-pulse magic-angle-spinning solid-state ^{13}C NMR showed that the carbon of these tubes was unsaturated in nature. The XRD diffraction pattern for the ground-up carbon tubes formed at 1000 °C showed two diffraction bands with the maxima at $2\theta = 25.86°$ and 43.8°, which is equivalent to a d spacing of 3.45 and 2.07 Å, respectively. The Raman spectrum for the same tubes showed two bands at ca. 1354 and 1584 cm^{-1}. This new method enables the control of both the diameter and wall thickness of the carbon tubes. Most interestingly, it also provides a feasible method for the preparation of two- or three-dimensional well-organized carbon tube assembly from suitable woven fabrics or structures.

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 molecular size and their potentials in applications such as electron field emitter,[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 layer.[11] 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. The present paper reports on a new and feasible method for preparing carbon tubes of appreciable length (up to several centimeter long) with a controllable tube wall thickness ranging from less than 100 nm to a few microns. Currently, this method is successful in preparing carbon tubes with diameters in the range of 1−100 μm. However, it is envisaged that with further refinements, this method should provide a good starting point to prepare carbon tubes with much smaller diameter. The combination of these newly

Scheme 1



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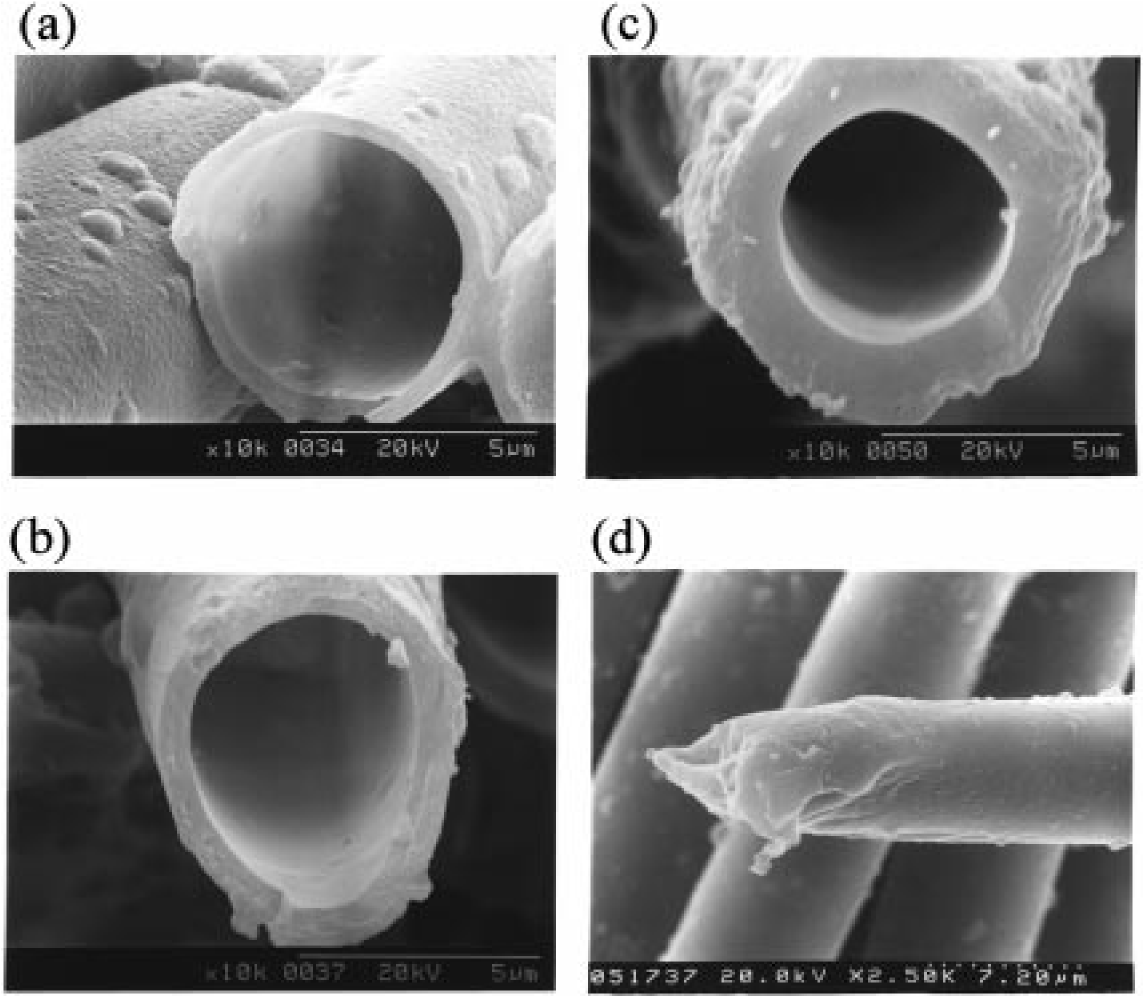

Figure 1. SEM micrographs for (a−c) resultant carbon tubes of similar diameters (ca. 7 μm), but with different wall thickness; (d) PPy/PET composite fibers.

available micrometer-sized carbon tubes and currently available nanotubes should provide a more complete size range of tubes for studies to provide additional information to help clarify or identify the nature of various phenomena that may occur on nanotubes.

As for micrometer-size tubes, with their relatively large inner diameter, it would be easier for reactants to flow through their cavities. If the inner surface is modified via treatment with various chemicals that render the inner surface active with desired affinity, selective separation (or extraction) of interested compounds can occur. Likewise, it would also be easier to embed desired transition metal complexes (with size often larger than 2−3 nm) on the inner surface of micrometer-sized tubes, to impart specific catalytic functions. It is envisaged that, with its larger inner tube diameter, the throughput of micrometer-sized tube microreactors should be acceptable for practical applications. Although hollow carbon fibers of submillimeter size, with 0.4 mm inner diameter and 0.6 mm outer diameter, have been prepared via the carbonization of spun poly(acrylonitrile) hollow fibers,[14] a feasible and reliable method for making thin-walled carbon-tubes with diameter in the range of 1−100 μm has yet to be devised.

The present method can be used to prepare micrometer-sized carbon tubes a few centimeters in length via a chemical strategy[15] as shown in Scheme 1. The basic idea is to utilize a thermally removable polymer fiber, like poly(ethylene terephthalate) (PET), as the growing template for a thermally more stable material such as a conjugated polymer like polypyrrole. The resulting composite fiber was then subjected to a thermal treatment to remove the PET template by thermal degradation, while the polypyrrole skin layer was simultaneously carbonized to form a carbon tube. The study also showed that the diameter and wall thickness of resulted carbon tubes can be conveniently controlled by controlling the diameter of the PET core fiber and the thickness of the polypyrrole skin layer. Most interestingly, this new method also enables the preparation of well-organized two- or three-dimensional structures assembled by carbon tubes several centimeters in length by the use of appropriate woven templates, which should enable easier design and fabrication of actual articles for various practical applications.

Experimental Section

The carbon tubes were prepared from polypyrrole (PPy) coated PET fibers by heating the composite fibers at 1000 °C

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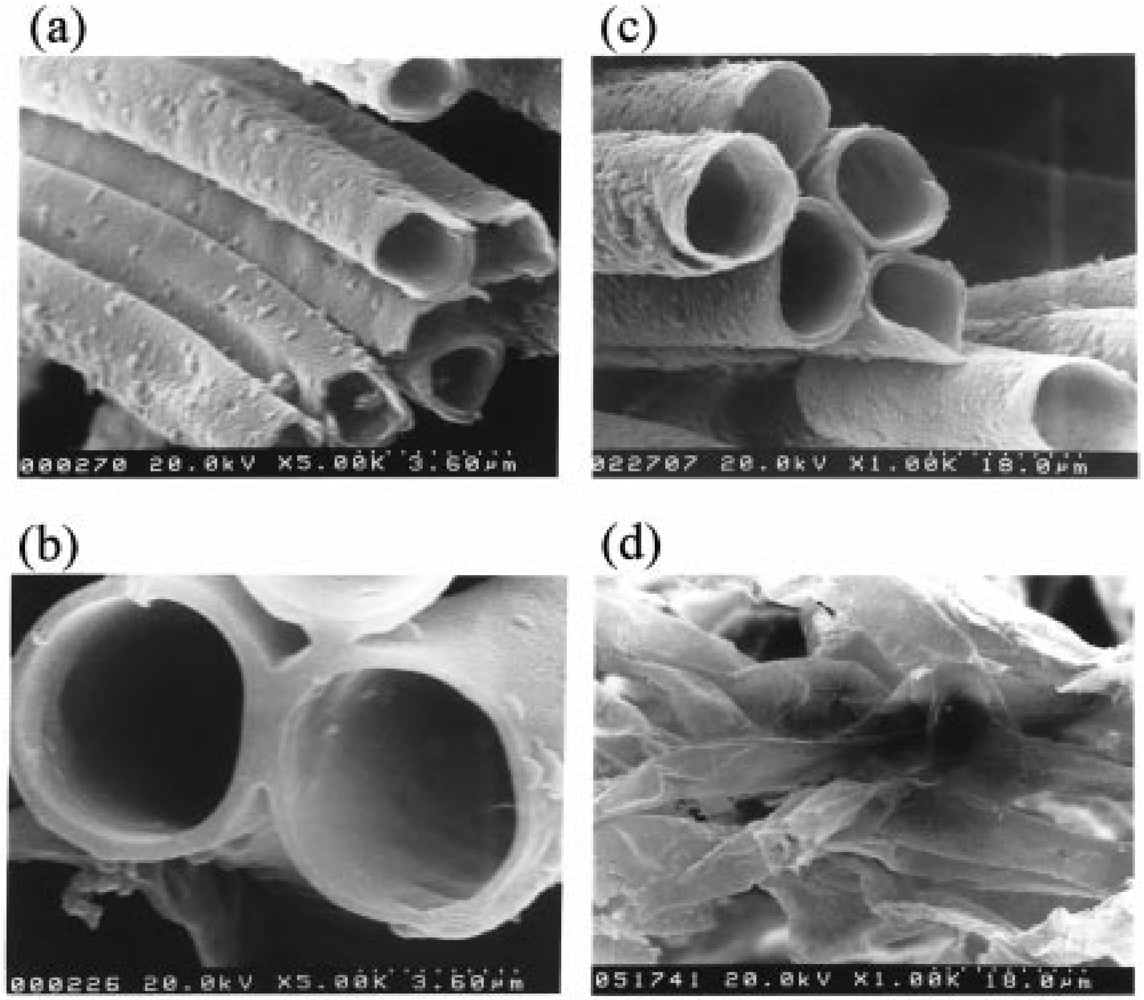

Figure 2. SEM micrographs for resultant carbon tubes with an averaged diameter of about (a) 2, (b) 7, and (c) 15 μm, respectively; (d) collapsed thin-walled carbon tubes.

for 3−24 h under N_2 atmosphere. The PPy coatings were applied via a typical reaction-coating approach,[16] by suspending commercially available PET fibers in a pyrrole aqueous solution that contained 2 equiv of *p*-toluenesulfonic acid, followed by the addition of oxidants to initiate pyrrole polymerization. The resulting PPy presented itself as a homogeneous dark-black coating on the surface of PET fibers. The thickness of such PPy coatings could be controlled by altering the pyrrole concentration of the reaction solution and the number of reaction-coating treatments being conducted. The PPy-coated PET fibers were then slurry-washed with copious amounts of deionized water and air-dried for 48 h. The PPy/PET composite fibers, as shown in Figure 1d, were then placed in a quartz tube oven and heated from room temperature to 1000 °C at a heating rate of 10 °C/min under N_2 atmosphere (N_2 flow rate 0.5 L/min). An annealing time of between 3 and 24 h was employed after the temperature reached 1000 °C.

The chemical nature of the original PET fiber, a control PPy specimen, and the resulted PPy/PET composite fibers was inspected by attenuated total reflection infrared (ATRIR) spectroscopy using a single reflection diamond ATR accessory (Graseby Specac) on a FTIR (Perkin-Elmer 2000) spectrometer, with a resolution of 4 cm^{-1}. The active area of the diamond contact probe is 0.6 × 0.6 mm. To ensure good surface contact, a constant high pressure was applied between the diamond probe head and the sample specimens by using a torque wrench setting of 60 cNm/m.

The thermal stability of the resulted PPy/PET composite fibers was examined by thermogravimetric analysis (TG) with a Seiko Instruments model SSC5000 analyzer. Samples for TG studies were heated from 30 to 1000 °C with a heating rate of 10 °C/min using a nitrogen flow rate of 300 mL/min.

The morphology of the resulted carbon tubes were observed by scanning electron microscopy (SEM) on a Hitachi S-2300 microscope or by field emission scanning electron microscopy (FESEM) using a Hitachi S-4000 equipment. The atomic compositions for the body of the carbon tube and the outer and inner wall surfaces were inspected with scanning Auger microscopy (SAM), utilizing a Physical Electronics 670 X_i PHI instrument. An electron beam with a probing size of about 100 nm in diameter, at a potential of 5 kV and a current of 20 nA, was employed. The chemical nature of the carbon tubes was studied by ATRIR, Raman spectroscopy, and magic-angle-spinning (MAS) solid-state ^{13}C NMR at a spinning rate of 5 kHz using a single pulse mode. The ^{13}C NMR spectra were recorded with a 100.46 MHz NMR instrument (Bruker Avance DSX400 spectrometer). The Raman spectra of the carbon tubes were obtained for a pellet made from a ground-up carbon tube. 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 the Raman spectrum was 5 cm^{-1}. The X-ray diffraction pattern for the ground-up carbon tubes was obtained by a Shimadzu XD-5 X-ray diffratometer with a Cu Kα (λ = 1.541 78 Å) radiation source.

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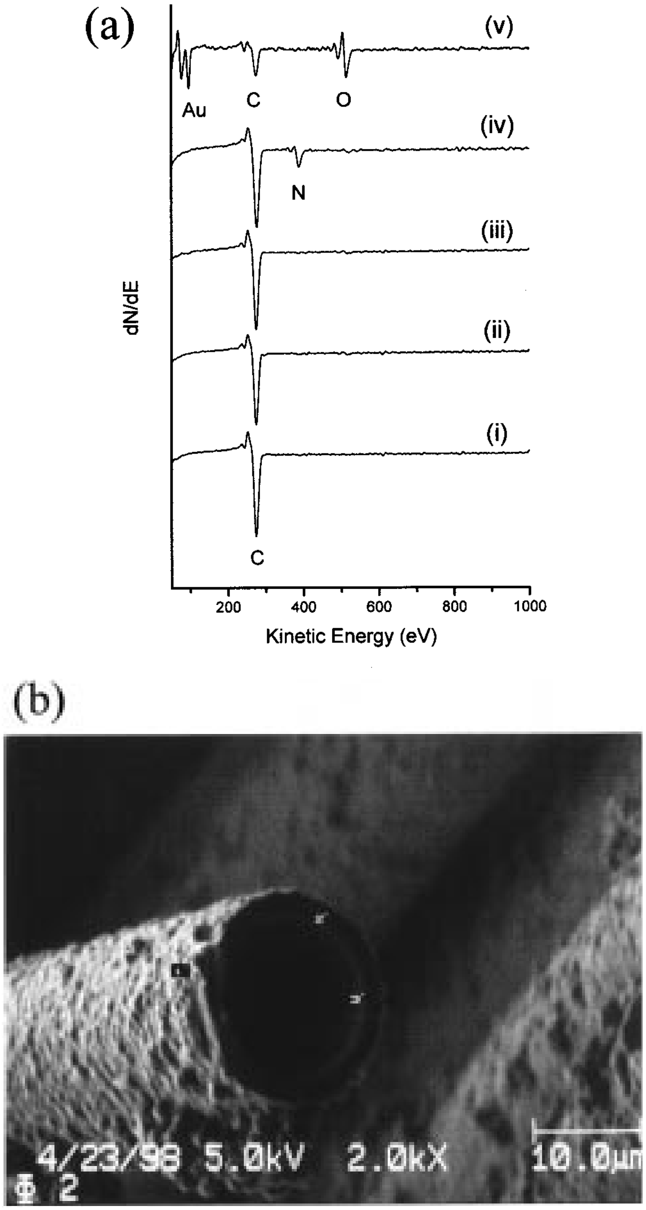

Figure 3. (a) SAM spectra for (i) the outer wall surface, (ii) the body, and (iii) the inner wall surface of the carbon tubes, (iv) polypyrrole coating of composite fibers, and (v) PET fibers. The PET fibers were precoated with a thin layer of Au for discharging purpose. (b) The SEM micrograph of the carbon tube taken during the SAM study; the numbers 1–3 denote the electron beam probing spots (about 100 nm in diameter) for the SAM spectra in i–iii, respectively.

Results and Discussion

Formation and Characterization of Carbon Tubes. The carbon tubes obtained by heating the PPy/PET composite fibers at 1000 °C for 3–24 h were all found to be hollow tubes with very uniform diameter and wall thickness. Figure 1 illustrates the SEM micrographs of tubes obtained after 3 h of 1000 °C treatment. The wall thickness of such carbon tubes was found to be directly proportional to the thickness of the original PPy coating layer. For examples, after 3 h at 1000 °C, composite fibers with PPy coating thickness of 1.2(±0.2) μm, 1.5(±0.3) μm, and 2.0(±0.3) μm yielded carbon tubes with an average wall-thickness of 0.38(±0.05), 0.63(±0.08), and 1.3(±0.2) μm, respectively (Figure 1a–c). The SEM micrograph for the PPy/PET composite fiber before the thermal treatment is found in Figure 1d for comparison.

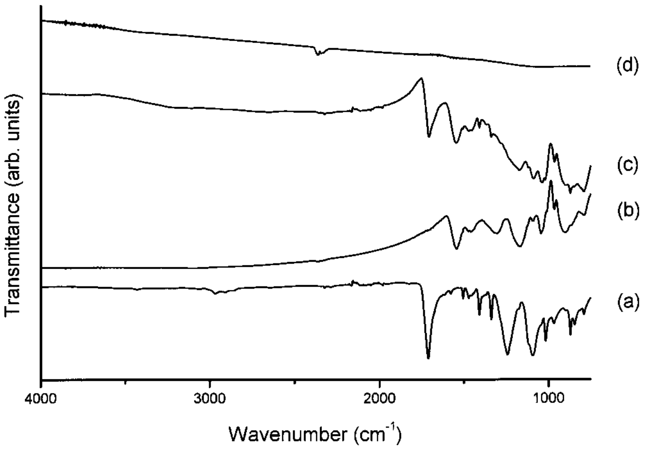

Figure 4. Infrared spectra for (a) PET fiber, (b) PPy powder, (c) PPy-coated PET fiber, and (d) ground-up carbon tube. The IR spectra for PPy powder and ground-up carbon tube (1000 °C, 3 h) were recorded from their KBr pellets, while those for fiber specimens were recorded in an attenuated total reflectance mode using a single reflection diamond ATR accessory.

With the same approach, carbon tubes of different sizes can also be easily prepared from PET fibers with different diameters. For examples, carbon tubes with 2, 7, and 15 μm inner diameter could be prepared from PET fibers with a diameter of 2.5, 7.5, and 16 μm, respectively (Figure 2a–c). Interestingly, it was also found that a minimum thickness of the PPy coating was required to provide sufficient mechanical strength to keep the tubes intact and maintain their round shape during the carbonization process. Figure 2d illustrates that, when the PPy coating was much less than ca.100 nm in thickness, all the resulted carbon tubes collapsed.

All carbon tubes prepared by the present method were found to be highly rich in carbon. Elemental analysis results indicated that these tubes essentially consisted of pure carbon, accompanied by small amount of N (<3 wt %) and H (<1 wt %). Similar results were obtained by scanning Auger microscopy (SAM) on corresponding batches of carbon tubes, as illustrated in Figure 3a. In these SAM studies, the elemental compositions were inspected by an Auger nanoprobe equipped with a SEM. Since the diameter of the electron beam provided by the Auger nanoprobe was only about 100 nm in diameter, the atomic compositions for the outer wall surface, the wall body, and inner wall surface of the carbon tubes can be probed independently. The SAM spectra illustrated in parts i, ii, and iii of Figure 3a are respectively for the outer wall surface, the wall body, and inner wall surface of the carbon tube shown in Figure 3b with the actual probing area labeled as 1, 2, and 3, respectively. The SAM results clearly reveal that only the C peak at 275 eV is present for all probed areas. The N peak of the original PPy coating at 388 eV (part iv in Figure 3a) is hardly noticeable. Such reduction in N was probably caused by denitrogenation of the PPy coating during thermal treatment. Denitrogenation phenomenon had also been reported for the thermal carbonization treatment of poly(acrylonitrile) at ca. 800 °C.[17] The

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Table 1. IR Vibration Peaks

wavenumber (cm^{-1})			
PPy/PET fiber	PET fiber[a]	PPy powder[b]	vibration mode
1707	1712		C═O stretching
	1614		aromatic C═C stretching
	1578		aromatic C═C stretching
1545		1546	C═C and C═N in-plane stretching
1505	1505		aromatic C═C stretching
1470	1471		CH_2 sym deformation in $-O-CH_2-$
1454		1455	C═C and C═N in-plane vibration
1407	1409		C═C stretching in 1,4-ring
1335	1338		
1171−1300		1307	aromatic C−N stretching
1171−1300	1242		C−O−C asymm. stretching
1171−1300		1173	aromatic C−N stretching
1088	1095		C−O−C sym stretching
1037		1044	N−H in-plane deformation
1018	1017		
963	969	965	C−H out-of-plane deformation
896		908	C−H out-of-plane deformation
871	872		C−H out-of-plane deformation of 1,4-ring
	847		
791	792	787	C−H out-of-plane bending

[a] Vibration modes for the bands were assigned according to ref 18. [b] Vibration modes for the bands were assigned according to refs 18 and 19.

denitrogenation reaction for the carbon tubes in this study appeared to have taken place throughout the entire tube, as indicated by the SAM spectra in parts i, ii, and iii of Figure 3a for different parts of the carbon tube. Furthermore, the SAM spectrum (part iii of Figure 3a) for the inner wall surface of the tubes showed hardly any sign of the O peak at 514 eV, due to PET core fiber (part v of Figure 3a). This suggested that the PET core fiber had decomposed completely after 3 h at 1000 °C, and the tube wall was essentially converted from the original PPy skin layer of the composite fiber.

The fact that the PET core fibers have been completely degraded during the thermal treatment is also confirmed by the ^{13}C NMR result of the same carbon tube sample, which shows the lack of any carbonyl carbon that might be due to PET core fibers. The use of single-pulse magic-angle-spinning solid-state ^{13}C NMR showed that the carbon of these tubes was unsaturated in nature, with its spectrum showing a complicated broad band between ca. δ 70−160 and a maximum at ca. δ 120. The excessive peak broadening may be attributed to the slightly different chemical environment for each carbon atom in the matrix and its corresponding pair of spinning sidebands. Neither any saturated sp^3 carbon in the range of δ 0−70 nor a significant amount of carbonyl carbon between δ 160 and 300 was observed.

The ATRIR spectra for PET fiber, PPy powder, and the PPy-coated PET fibers are displayed in Figure 4a−c, respectively. The detailed IR band positions and possible assignments for these three specimens are summarized in Table 1. The results clearly showed that the PPy-coated PET fiber indeed contained the IR characteristic bands for both PPy and PET. The IR spectra for both PPy powder and PPy-coated PET fiber however did not show a discernible N−H stretching band in the region of 3300−3500 cm^{-1}. This might be due to the fact that it is difficult to completely dedope PPy and that the electronic charge-transferring band resulted from the partial doping effect (plus a possible air oxidation effect[20d]) has probably led to a broad tail in this region, which raised the baseline and obscured the already weak N−H bands thereof.[20] All the peaks in the IR spectra, however, disappeared completely after carbonization treatments and left a featureless IR spectrum (Figure 4d) for the formed carbon tubes. This result indicated that all the carbonyl and other characteristic functional groups have been essentially eliminated, and the residual carbons have formed highly symmetrical carbon−carbon bonds that are IR inactive, which further implies the presence of a carbon matrix with an extensive network structure.

The Raman spectrum for a pellet of ground-up carbon tube formed at 1000 °C for 24 h (Figure 5a) shows two vibrational bands at about 1354 and 1584 cm^{-1}, which may be attributed to the disordered structure and graphite-like structure of carbons, respectively. [21] A similar spectrum, as shown in Figure 5b, was obtained from a sample that was heated from 30 to 500 °C at 10 °C/min and cooled naturally. These two bands are, however, much weaker and broader than the corresponding bands illustrated in Figure 5a. The results suggested that thermal treatment at temperatures higher than 1000 °C may further improve both the homogeneity and the structure of the ordered phases.

The XRD diffraction pattern for the ground-up carbon tubes formed at 1000 °C for 24 h (Figure 6a) showed two diffraction bands with maxima at $2\theta = 25.86°$ and 43.8°. The position of the maximum of the lower diffraction angle band is close to the (002) diffraction

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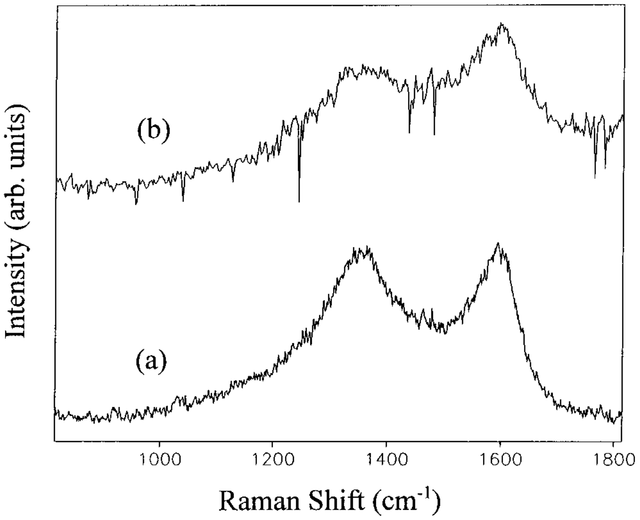

Figure 5. Raman spectra for ground-up carbon tubes formed at (a) 1000 °C and (b) 500 °C, respectively.

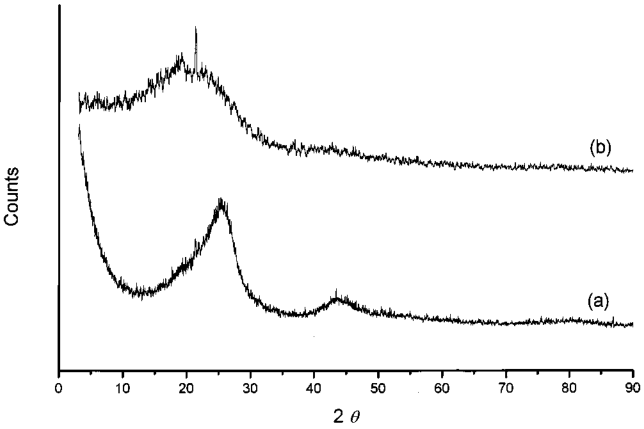

Figure 6. X-ray diffraction spectra for ground-up carbon tubes formed at (a) 1000 °C and (b) 500 °C.

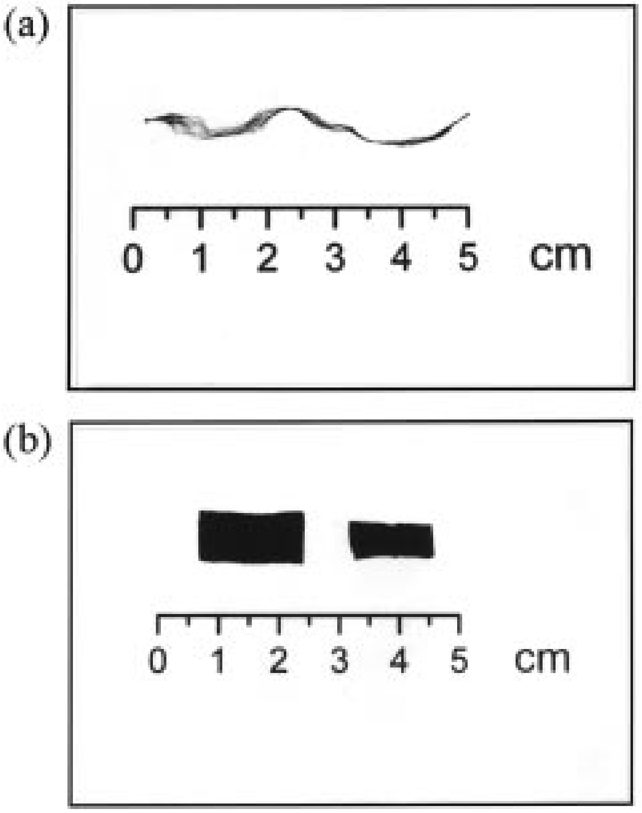

Figure 7. (a) Photograph of a bundle of 5 cm long prearranged carbon-tubes. (b) Photograph for a PPy-coated PET cloth about 2 × 1 cm (left) in size and a carbonized product prepared from another piece of PPy-coated PET cloth of similar size (right).

peak of a 0.2 × 0.2 cm single-crystal graphite plate ($2\theta = 26.52°$), measured under the same conditions. The *d* spacing for the ground-up tubes for the band at $2\theta = 25.86°$ is calculated to be 3.45 Å, which still differs significantly from the d_{002} of 3.354 Å for graphite. It has been reported that carbon with an average *d* spacing of 3.45 Å is typically turbostratic in structure.[22] Although the composite fibers have already transformed to hollow tubing at 500 °C, as determined by SEM, the morphology of the sample specimen formed at 500 °C was still quite amorphous. The XRD spectrum for the 500 °C sample (Figure 6b) showed a rather complicated broad band ranging from $2\theta = 7$ to 35° with a maximum at about 19.3°, which is equivalent to a *d* spacing of about 4.60 Å. The XRD results apparently show that the crystallinity of the resulting carbon tubes increased with annealing temperature, while the average *d* spacing decreased. These results also suggest the possibility of phase transformation from amorphous carbon matrixes to a more ordered form during the thermal annealing process. Our preliminary results from studies at higher treatment temperatures, e.g. 2400 °C for 30 min, produced a sample having a much sharper and stronger peak at $2\theta = 26.36°$ (equivalent to a *d* spacing of about 3.38 Å). An attempt was made to estimate the average crystallite size Lc of the high-temperature sample, using a 0.2 × 0.2 cm single-crystal graphite plate as reference. The average crystallite size (*Lc*) of the high-temperature sample was estimated to be about 170 Å according to the Scherrer equation,[23] basing on the position of the maximum of the lower diffraction angle band of the sample and the corresponding half-maximum widths measured for the sample and the reference graphite plate. The obtained *Lc* value for the high-temperature sample is greater than the typical *Lc* values of 70−80 Å reported for the carbon fibers obtained by graphitizing polyacrylonitrile fibers at a similar temperature, i.e., 2500 °C.[17]

Formation of Well-Organized Carbon-Tube Structures. Using the present new method, carbon tube bundles several centimeters in length have been prepared (Figure 7a) with little difficulty, and SEM inspection of tubes thus prepared confirmed that they were completely hollow. Similarly, a three-dimensional assembly of carbon tubes, as illustrated in Figure 7b, has also been successfully prepared for the first time via the carbonization of a PPy-coated woven PET cloth. During the annealing process, the dimensions of the cloth have been clearly reduced by about 20%, as shown by the photo in Figure 7b. For an example, a sample specimen of PPy-coated PET cloth about 2 × 1 cm in

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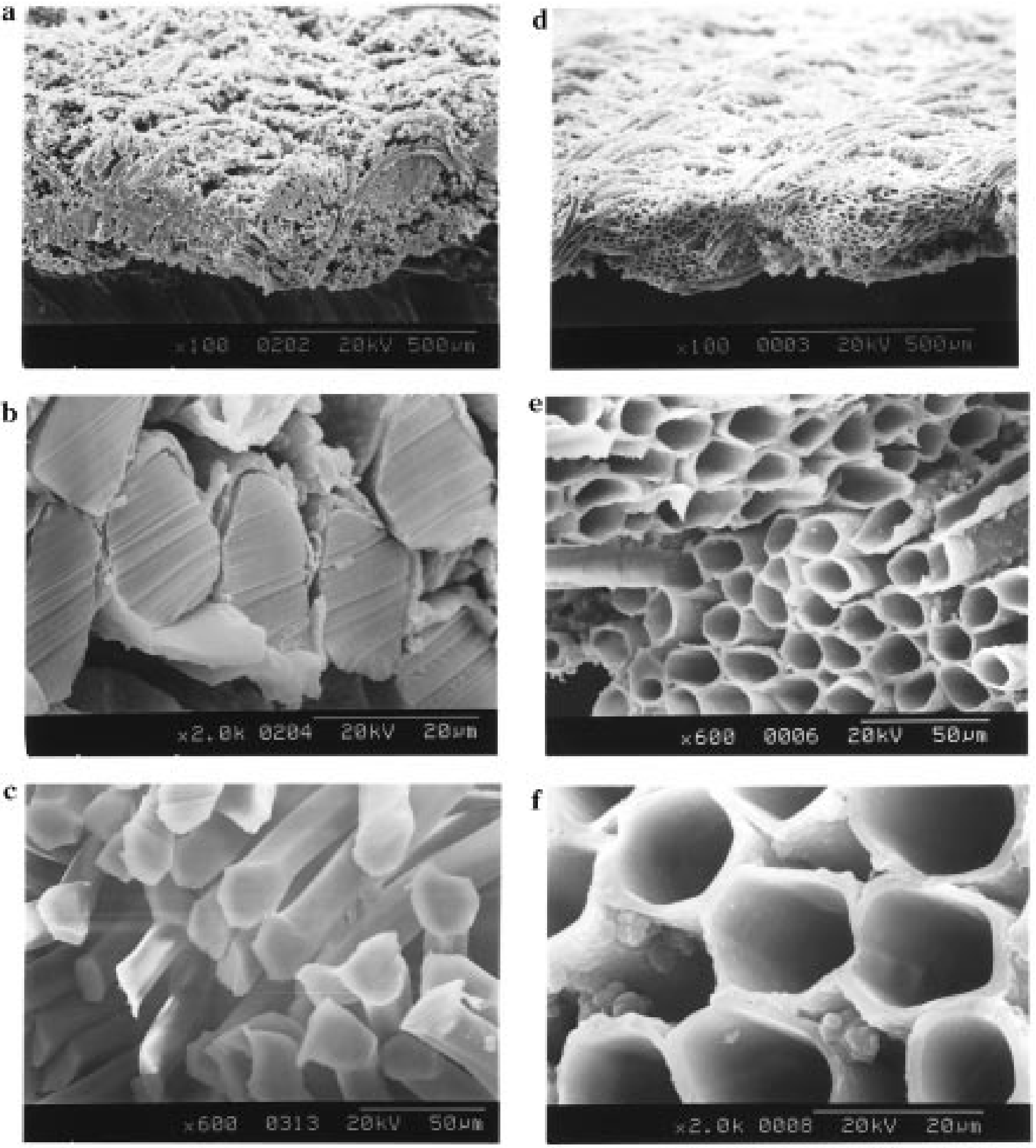


Figure 8. SEM micrographs for a PPy-coated PET cloth magnified (a) 100× and (b) 2000×. (c) SEM micrographs for an uncoated PET cloth magnified 600×; SEM micrographs for a well organized carbon tube assembly, with a magnification of (d) 100×, (e) 600×, and (f) 2000×, respectively.

size has been reduced to a smaller size of about 1.6 × 0.8 cm. Interestingly, the contraction actually happened uniformly along all three axes. The average thickness of the PPy-coated PET cloth has also been reduced by about 20% from ca. 270 to 220 μm, as estimated from SEM micrographs in parts a and d of Figure 8 for the specimens before and after the carbonization treatment, respectively. The SEM micrograph in Figure 8b for the composite fibers in the PPy-coated PET cloth clearly showed that every PET fiber has been homogeneously coated by a skin layer of PPy, as compared with the micrograph in Figure 8c for the uncoated PET cloth. After the carbonization treatment at 1000 °C, all the PPy-coated PET cloths formed a well-organized carbon-tube assembly, as shown by the SEM micrographs in Figure 8d–f. Figure 8e,f also clearly showed that contraction during the carbonization step has led to the formation of tightly packed and highly ordered carbon-tube assembly.

Possible Formation Mechanism of Carbon Tubes. During the carbonization of PPy-coated PET fibers, some white solids sublimed out of the oven and most of the solid appeared at between 400 and 500 °C. The collected solid was identified by NMR, IR, and mass spectroscopy as a mixture of terephthalic acid and 4-(vinyloxycarbonyl)benzoic acid. [For terephthalic acid: ^{1}H NMR (300 MHz, DMSO-d_6): δ 13.4 (s, 2H), 8.15 (s, 4H);^{13}C NMR (75 MHz, DMSO-d_6): δ 166.82, 134.62, 129.62; IR (KBr pellet, cm^{-1}): 3300–2300, 3064, 2670, 2553, 1691, 1576, 1510, 1426, 1295, 939, 782, 733; mass m/z: 166 (M^+), 149 ($M^+ - OH$, 100), 121 ($M^+ - CO_2H$), 104 ($M^+ - CO_2H - OH$), 76 ($M^+ - CO_2H -$

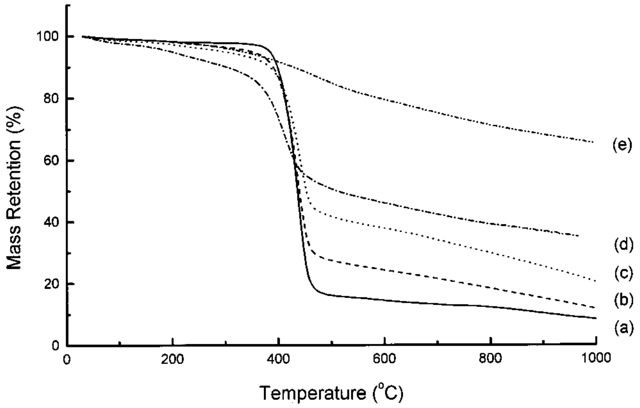
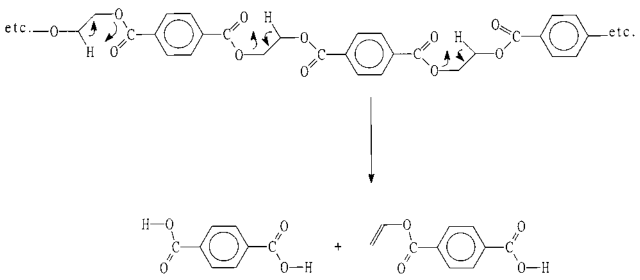


Figure 9. Thermogravimetric analysis traces for (a) PET fiber; (b−d) PPy/PET composite fibers with a progressive increase in PPy coating thickness; (e) undoped PPy powder.

Scheme 2



CO_2H). For 4-(vinyloxycarbonyl)benzoic acid: ^1H NMR (300 MHz, $CDCl_3$) δ 13.4 (s, 1H), 8.20 (s, 4H), 7.50 (dd, 1H, $J_{ab} = 13.9$ Hz, $J_{ac} = 6.3$ Hz), 5.11 (dd, 1H, $J_{ba} = 13.9$ Hz, $J_{bc} = 1.96$ Hz), 4.75 (dd, 1H, $J_{ca} = 6.3$ Hz, $J_{cb} = 1.96$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.08, 162.76, 141.23, 133.55, 133.44, 130.27, 130.03, 99.00; IR (KBr pellet, cm^{-1}): 3300−2300, 3097, 3061, 2671, 2552, 1733, 1686, 1653, 1576, 1506, 1430, 1302, 1283, 951, 932, 804, 725; mass m/z: 192 (M^+), 175 ($M^+ - OH$), 149 ($M^+ - OH - C_2H_2$, 100), 121 ($M^+ - OH - C_2H_2 - CO_2$).] Apparently, both byproducts were the result of the decomposition of PET core fibers. Whereas, no significant amount of decomposed byproducts resulting from polypyrrole, such as oligomeric pyrroles, were found in the sublimed solids.

The observation that polypyrrole is thermally more stable than PET is also confirmed by thermogravimetric analysis (TG) results, as displayed in parts e and a of Figure 9, respectively. The results showed that the mass retention at 1000 °C for undoped PPy powder (65%) was much higher than that for PET fiber (8%). As the thermally less stable PET fiber was coated with PPy, the resulted composite fibers also showed the tendency for higher weight retention. The TG traces in Figure 9 b−d are for a series of composite fibers with an increasing number of PPy coating treatments. The results indicated that the composite fibers with a relatively thicker PPy coating displayed a relatively higher mass retention after annealing at 1000 °C.

A possible carbon-tube formation mechanism is suggested as follows. The core PET fibers first melt at ca. 254 °C when the crystalline melting point of PET was reached. The PET then decomposes into the byproducts terephthalic acid and 4-(vinyloxycarbonyl)benzoic acid via intrachain β-elimination of the ester group (Scheme 2) at between 400 and 500 °C. [The melting point of the PET fibers was measured by DSC (differential scanning calorimetry) to be 254 °C; and their on-set decomposition temperature was measured by TGA to be at 407 °C.] The resultant byproducts sublime at these elevated temperatures, forming the hollow cores. [The sublimation point for terephthalic acid is 402 °C, as reported in the *Merck Index* (12th ed., 1996, Merck & Co., Inc.).] Meanwhile, the PPy skin layer also starts to decompose at its decomposition on-set temperature (i.e. about 310 °C for undoped PPy powder), with the formation of active intermediates. It is believed that these intermediates may induce efficient cross-linking of the highly π-bond-conjugated PPy, thus forming the initial three-dimensional network of the final tube wall.

Conclusion

Partially ordered micrometer-sized carbon tubes have been prepared via a new chemical approach by the pyrolysis of composite fibers consisting of a polypyrrole skin layer and a PET core fiber. The diameter and wall thickness of the resulted carbon tubes can be conveniently controlled by varying the diameter of the PET core fiber and the thickness of the polypyrrole coating, respectively. Most interestingly, this new method also provides a convenient, flexible, and feasible means for the preparation of two- or three-dimensional well-organized carbon-tube assemblies. Work involving the use of other types of core fibers and skin layers is under progress.

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