A new and easy method for making micrometer-sized carbon tubes

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Highly crystalline and single-walled micrometer-sized carbon tubes several centimeters in length have been prepared *via* the pyrolysis of composite fibers consisting of a thermally stable polypyrrole skin layer and a thermally degradable PET core fiber.

Studies on the formation and growth mechanism[1] of nano-size carbon tubes have attracted a lot of research interest in recent years, due to their potential in applications like electron field emitters,[2] nanowires,[3] catalytic micro-reactors and natural gas storage. Various methods have been reported for the preparation of carbon tubes; these include carbon-arc discharge,[4] laser ablation,[5] condensed-phase electrolysis,[6] and the catalytic pyrolysis of hydrocarbons on various substrates such as porous anodic aluminium oxide,[7] fine metal particles[8] and patterned cobalt layers.[9] Regarding nano-tubes, their potential as micro-reactors might be significantly limited due to their relatively small inner diameters, which could preclude the entry of large reactive species or reactants. However, for micrometer-sized carbon tubes, with their relatively larger inner diameter, it would be easier to perform inner surface modifications *via* treatment with various chemicals and render the inner surface active, thus enabling selective separation (or extraction) of interested compounds. Likewise, it would also be easier to embed desired transition metal complexes (with sizes often larger than 2–3 nm) on the inner surface of micrometer-sized tubes, to impart specific catalytic functions. It is envisaged that, with their larger inner tube diameter, the throughput of micrometer-sized tube micro-reactors should be acceptable for practical applications. Similarly, it should also be relatively easier to activate chemically both the inner and outer surfaces of micrometer-sized tubes to facilitate the formation of micro- or meso-porous features, making them suitable for natural gas storage. Although hollow carbon fibers of sub-millimeter size, with 0.4 mm inner diameter and 0.6 mm outer diameter, had been prepared *via* the carbonization of spun poly(acrylonitrile) hollow fibers,[10] there is still a lack of a feasible and reliable method for making thin-walled carbon tubes with diameters in the range of 1–100 μm.

Here, a new and feasible method for the preparation of micrometer-sized single-walled carbon tubes is proposed. The method also enables convenient control of both the diameter and wall thickness of the resultant carbon tubes. Tubes several centimeters in length and pre-organized in one- or two-dimensional matrices have been obtained experimentally.

These carbon tubes were prepared from polypyrrole (PPy)-coated poly(ethylene terephthalate) (PET) fibers by heating the composite fibers at 1000 °C for 3–6 h under an N_2 atmosphere. The PPy coatings were applied *via* a typical reaction-coating approach,[11] by suspending commercially available PET fibers in an aqueous pyrrole solution that contained 2 equiv. of toluene-*p*-sulfonic acid, followed by the addition of oxidants to initiate the polymerization of pyrrole. The resulting PPy thus formed presented itself as a homogeneous black coating on the surface of the PET fibers. The thickness of such PPy coatings could be controlled by altering the pyrrole concentration of the reaction solution, and by the number of reaction-coating treatments conducted. The resulting PPy-coated PET fibers were then slurry-washed with copious amounts of de-ionized water and air-dried for 48 h. The PPy/PET composite fibers, as shown in Fig. 1(*a*), were then placed in a quartz oven and heated from room temperature to 1000 °C at a heating rate of 10 °C min^{-1} under an N_2 atmosphere. An annealing time of between 3 to 6 h was employed after the temperature reached 1000 °C. During the heating and annealing process, some white solid sublimed out of the oven and was identified as a mixture of terephthalic acid and 4-(vinyloxycarbonyl)benzoic acid.§ Most of this solid was collected at between 400 and 500 °C, consistent with the decomposition temperature of the PET fibers. All the carbon fibers obtained after the thermal treatment were found to be hollow tubes with uniform diameters and wall thicknesses, as illustrated by the SEM micrographs in Fig. 1. The wall thickness of such carbon tubes was found to be directly proportional to the thickness of the original PPy coating layer. For example, composite fibers with PPy layer thicknesses of 1.2 (±0.2), 1.5 (±0.3) and 2.0 (±0.3) μm yielded carbon tubes with an average wall thicknesses of 0.38 (±0.05), 0.63 (±0.08) and 1.3 (±0.2) μm, respectively. The electron micrographs of these carbon tubes are illustrated in Fig. 1(*b*)–(*d*). Thermogravimetric analysis of the same composite fibers also showed similar trends on mass retention, with composite fibers having thicker PPy layers displaying higher mass retention after annealing at

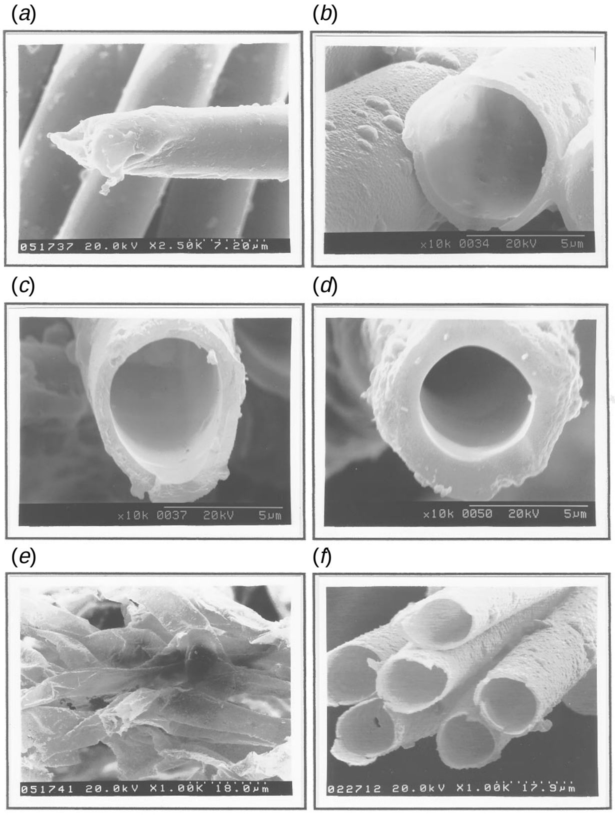

Fig. 1 SEM micrographs for (*a*) PPy/PET composite fibers, (*b*)–(*d*) resultant carbon-tubes of similar diameter (*ca.* 7.5 μm), but with different wall thickness, (*e*) collapsed thin-walled carbon tubes and (*f*) carbon tubes of *ca.* 15 μm diameter

1000 °C. Interestingly, it was found that a minimum thickness of the PPy layer was required to provide sufficient mechanical strength to keep the tubes intact and maintain their round shape during the carbonization process. Fig. 1(*e*) illustrates that, when the PPy layer was less than *ca*. 100 nm in thickness, all the resulted carbon tubes collapsed. Carbon tubes of different sizes can also be prepared from PET fibers with different diameters. For example, carbon tubes with 15 μm in inner diameter [Fig. 1(*f*)] were prepared from PET fibers with a diameter of 16 μm.

All the carbon tubes prepared by the present method were found to be rich in carbon. Elemental analysis results indicated that these tubes consisted essentially of pure carbon, accompanied by small amount of N (<3 wt%) and H (<1 wt%). Similar results were obtained by scanning auger microscopy (SAM). A typical SAM spectrum for the outer wall of the carbon tubes clearly reveals that only the C peak at 275 eV is present. The N peak of the original PPy layer at 388 eV had almost completely disappeared. The reduction in N was probably caused by de-nitrogenation of the PPy coating during thermal treatment. Similar de-nitrogenation phenomena had also been reported for the thermal carbonization treatment of poly(acrylonitrile) at *ca.* 800 °C.[12] The de-nitrogenation reaction for the carbon tubes in this study appeared to have taken place throughout the entire tube, as indicated by the SAM spectra for the cross-section and the inner wall of the tubes. Furthermore, the SAM spectrum for the inner wall of the tubes showed hardly any sign of the O peak at 514 eV due to PET core fiber. This suggested that the PET core fiber had decomposed completely, and the tube wall was essentially converted from the original PPy skin layer of the composite fiber.

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 δ 70–160 and a maximum at *ca.* δ 120. The unusual peak broadening may be attributed to the slightly different chemical environment of each carbon atom in the network and its corresponding pair of spinning side-bands. No saturated sp^3 carbons in the range δ 0–70 nor any significant amount of carbonyl carbons between δ 160–300 were observed. The infrared spectra of ground-up carbon tubes as KBr pellets were completely featureless, probably due to the highly symmetric bonding nature of the tubes, as in the case of a carbon matrix with an extensive network. The Raman spectrum for the ground-up carbon tubes showed two bands at *ca.* 1354 and 1584 cm^{-1}, similar to those bands for graphite.

The most intriguing finding in the present study is that, although the carbonized product of PPy powder [annealed at 1000 °C for 3 h] was totally amorphous, the carbon tubes prepared in this study from PPy/PET composite fibers were highly crystalline. The X-ray diffraction spectrum for the ground-up carbon tubes, obtained using a Shimadzu X-ray diffractometer XD-5 with a Cu-Kα radiation source, showed two rather strong and sharp peaks at 2θ = 21.4 and 23.8°, equivalent to a *d*-spacing of 4.15 and 3.74 Å, respectively. Although the X-ray diffraction results indicated the presence of highly crystalline carbons in the tube wall, the lattice structure appeared to be different from the sheet-like morphology of graphite,¶ as the strongest diffraction peak for graphite is at 2θ = 26.6°. Further exploration of the crystalline nature of these carbon tubes with high resolution transmission electron microscopy (TEM) is in progress. It is believed that the surface of the highly stretch-oriented PET fibers might have acted as a template for the arrangement of deposited PPy chains during the polymerization coating process. The formation of more ordered and pre-arranged PPy matrices could increase the possibility of crystalline carbon formation during the carbonization process. The formation of induced structural order in carbon layers on fibres has also been observed for resin-based matrices in carbon–carbon composites.[13]

Using the present new method, carbon tube bundles several centimeters in length have been prepared with little difficulty, and SEM inspection of tubes thus prepared confirmed that they were completely hollow. Similarly, a two-dimensional matrix of carbon tubes has also been successfully prepared for the first time *via* the carbonization of a PPy-coated PET cloth.

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 is reached. The PET then decomposes into terephthalic acid and 4-(vinyloxycarbonyl)-benzoic acid by-products *via* intra-chain β-elimination of the ester group between 400 to 500 °C.‖ The resultant by-products then sublime at these elevated temperatures, forming the hollow cores.** Meanwhile, the PPy skin layer also starts to decompose at its decomposition on-set temperature (*i.e.* 310 °C for undoped PPy powder), with the resulting active intermediate species very likely to induce efficient cross-linking of the highly π-bond-conjugated PPy, thus setting up the three-dimensional network of carbon tubes.

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Notes and References

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§ *Selected data* for terephthalic acid: δ_H (300 MHz, [^{2}H$_6$]DMSO) 13.4 (s, 2H), 8.15 (s, 4H); δ_c (75 MHz, [^{2}H$_6$]DMSO) 166.82, 134.62, 129.62. For 4-(vinyloxycarbonyl)benzoic acid: δ_H (300 MHz, CDCl$_3$) 13.4 (s, 1H), 8.20 (s, 4H), 7.50 (dd, 1H, J_{ab} 13.9, J_{ac} 6.3), 5.11 (dd, 1H, J_{ba} 13.9, J_{bc} 1.96), 4.75 (dd, 1H, J_{ca} 6.3, J_{cb} 1.96); δ_C (75 MHz, CDCl$_3$) 170.08, 162.76, 141.23, 133.55, 133.44, 130.27, 130.03, 99.00.

¶ The carbon fibers prepared from poly(acrylonitrile) also did not form the graphitic structure until the annealing temperature was raised up to 2500 °C (ref. 12).

‖ The melting point of the PET fibers was measured by DSC (differential scanning calorimetry) to be 254 °C, and their decomposition on-set temperature was measured by TGA to be at 407 °C.

** The sublimation point for terephthalic acid is 402 °C, as reported in the Merck index (12th edn. 1996, Merck and Co., Inc.).

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