Functionalization and Extraction of Large Fullerenes and Carbon-Coated Metal Formed during the Synthesis of Single Wall Carbon Nanotubes by Laser Oven, Direct Current Arc, and High-Pressure Carbon Monoxide Production Methods

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Large fullerenes and carbon-coated metal nanoparticles that are formed during the synthesis of carbon nanotubes have been functionalized by the addition of alkyl radicals and isolated by extraction into chloroform. The soluble, functionalized fullerenes have been isolated from raw single-wall carbon nanotube (SWNT) material prepared by laser oven, direct current arc, and high-pressure carbon monoxide production methods. Analyses of the extracted large fullerenes were carried out by thermogravimetric analysis, UV−vis−near-IR, laser desorption ionization mass spectrometry, and high-resolution transmission electron microscopy.
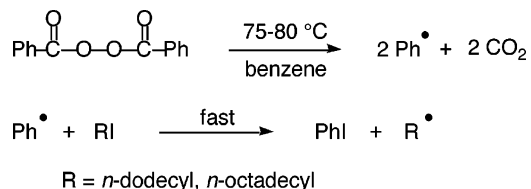
Introduction

Carbon nanotubes[1] have been prepared by laser oven,[2] direct current (DC) arc,[3] and high-pressure carbon monoxide (HiPco)[4] single-wall carbon nanotube (SWNT) production methods using Co/Ni, Ni/Y, and Fe, respectively, as the catalysts. In each instance, the raw (crude) SWNTs contain large fullerenes and carbon-coated metal nanoparticles that are formed in competition with the SWNTs. In addition to the intrinsic interest associated with large fullerenes,[5,6] optimization of the various routes to carbon nanotubes requires a means to determine the yield of the fullerenes. Since these materials are insoluble in most organic solvents, analysis is difficult. In one instance, soluble derivatives of the large fullerenes were isolated after fluorination of the crude SWNTs.[7] However, fluorination reactions are aggressive, and disruption of the carbon skeleton cannot be avoided. Although extraction from fullerene soot using high-boiling solvents has also been reported,[8] we have been unable to extract large fullerenes from HiPco SWNTs. In this paper, we report a method to functionalize the large fullerenes by alkyl radicals and to affect a separation from the SWNTs by extraction of the soluble fullerene derivatives into chloroform.

Experimental Section

In a general procedure, 100 mg (8.3 mmol of carbon) of the raw nanotubes suspended in 120 mL of benzene was added to a 250 mL round-bottom flask and mixed using a Polytron homogenizer (Poly Science 50/60 Hz, 120 V) for 30 min, followed by sonication for 30 min (Cole Palmer, 55 kHz). *n*-Octadecyl iodide (6.4 g, 16.7 mmol) and benzoyl peroxide (2.0 g, 8.3 mmol) were then added to the flask, and the contents were heated at 78 °C (351 K) for 12 h under argon. After being

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SCHEME 1

$$Ph{-}C({=}O){-}O{-}O{-}C({=}O){-}Ph \xrightarrow[\text{benzene}]{75\text{-}80\ °C} 2\ Ph^{\bullet} + 2\ CO_2$$

$$Ph^{\bullet} + RI \xrightarrow{\text{fast}} PhI + R^{\bullet}$$

R = *n*-dodecyl, *n*-octadecyl

cooled, the benzene was removed in vacuo, and the organic byproducts were extracted into ethanol (100 × 5 mL). Chloroform (50 mL) was then added, and the solution was sonicated for 30 min. After sonication, the solution was filtered through a 0.2 μm polytetrafluoroethylene (PTFE) membrane filter. The reaction mixture was then processed in the same way two more times. The combined filtrates were concentrated using a rotary evaporator, and the black residue was washed with dry ethanol
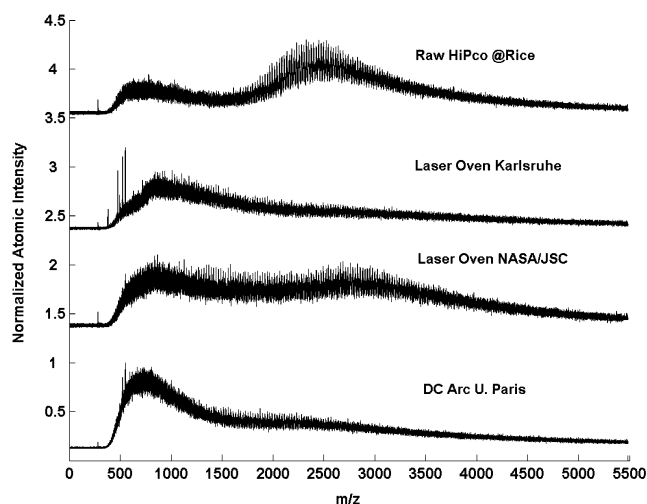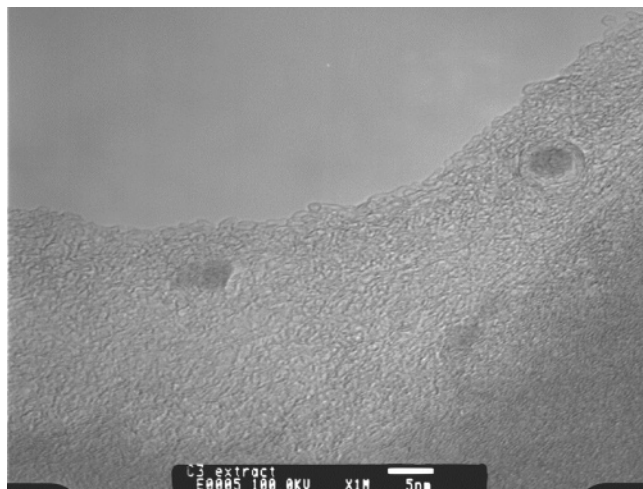
Figure 1. LDI-TOF mass spectra of extracted large fullerenes from different raw nanotube samples.

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Figure 2. HRTEM image of large fullerenes extracted from the DC arc Université Paris sample.
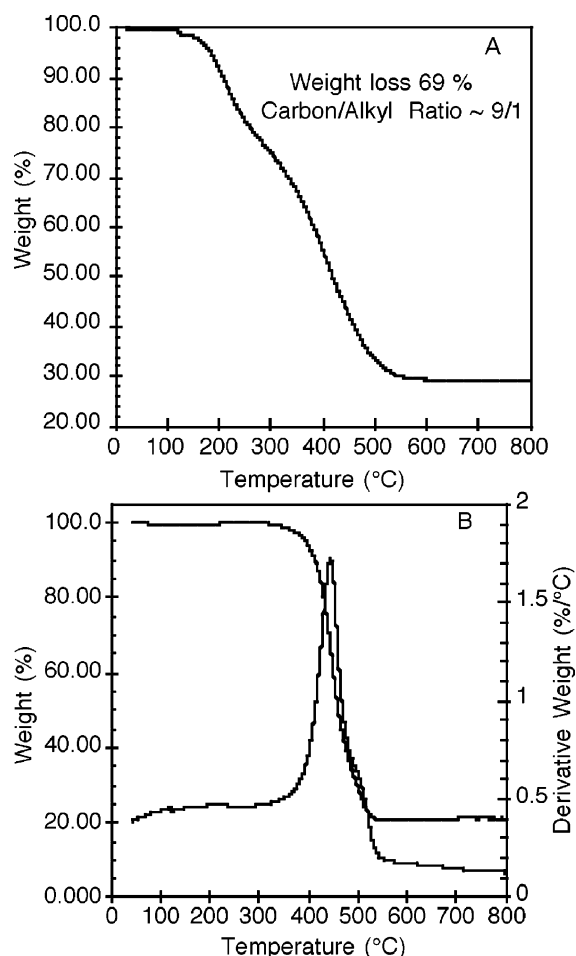

Figure 3. (A) TGA analysis of octadecylated HiPco extract showing the extent of functionalization. (B) DTA-TGA analysis in air of dealkylated HiPco extract showing the ash content as Fe_2O_3. Differential thermal analysis of defunctionalized HiPco extract showing a sharp transition indicating rapid combustion of carbonaceous species in the extract.

to remove traces of byproducts. The resulting black powder was used for spectroscopic measurements.

Results and Discussion

The alkyl radicals used for these studies were prepared by decomposing benzoyl peroxide in the presence of alkyl iodides
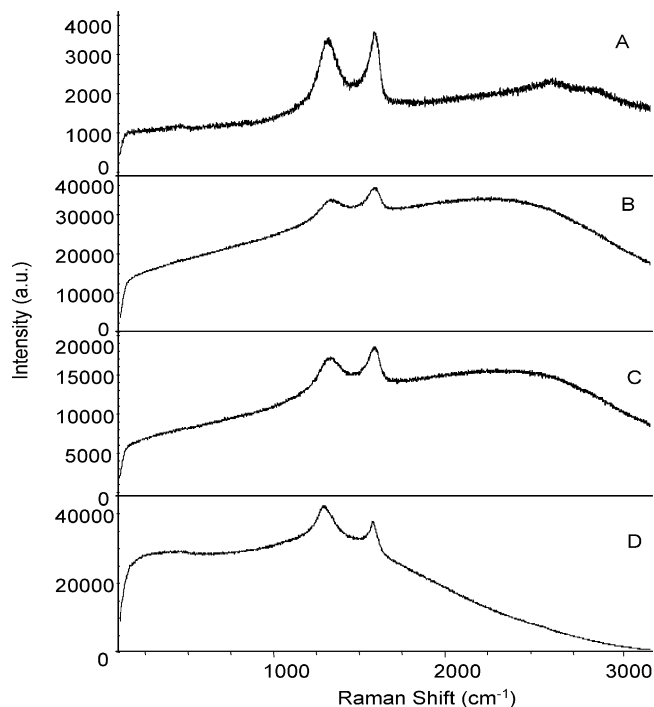
Figure 4. Raman spectra (He−Ne laser 633 nm) of the extracts isolated from different samples of carbon nanotubes. (A) HiPco; (B) Laser oven Karlsruhe; (C) Laser oven NASA−Johnson Space Center; (D) DC arc Université Paris.

TABLE 1: Percent by Weight of Extracted Large Fullerenes in Different Carbon Nanotubes Samples as Determined by TGA and UV−Vis−near-IR Analyses

	raw HiPco	laser oven Karlsruhe	laser oven NASA−JSC	DC arc Université Paris
wt % (TGA and UV−vis−nIR)	5.2	32	33	20

as illustrated in Scheme 1.[9] Studies using both *n*-dodecyl iodide and *n*-octadecyl iodide have been carried out. Although alkylation by both radicals leads to products that are soluble in common organic solvents (chloroform, tetrahydrofuran, and benzene), solubility was enhanced, as expected, when the octadecyl radicals were bound to the fullerenes. The optimal stoichiometry was determined by carrying out a series of reactions using different concentrations of the reagents. The SWNTs would also be expected to experience alkylation under these conditions, but the nanotubes are not soluble in chloroform. Large fullerenes substituted by phenyl radicals, generated by decomposition of benzoyl peroxide, could not be dissolved in chloroform.

LDI-TOF (laser desorption ionization time-of-flight) mass spectrometry experiments were carried out by depositing a chloroform extract onto a stainless steel substrate plate by successive dropwise addition and evaporation. Several runs showed a mass spectral range from 600 to 4500 amu (Figure 1). The masses were evenly separated at a spacing of 24 amu, a well-known feature of fullerenes arising from the loss of C_2.[10,11]

High-resolution transmission electron microscopy (HRTEM) experiments were carried out by placing a drop of the yellowish black $CHCl_3$ extract onto a TEM grid. TEM of all samples exhibited characteristic fullerene morphology. Metal particles are also visible but not amorphous carbon (Figure 2).

Thermogravimetric analyses (TGA) were carried out in air/argon (flow rate 100 cm³/min; heating rate 5 °C/min) using a
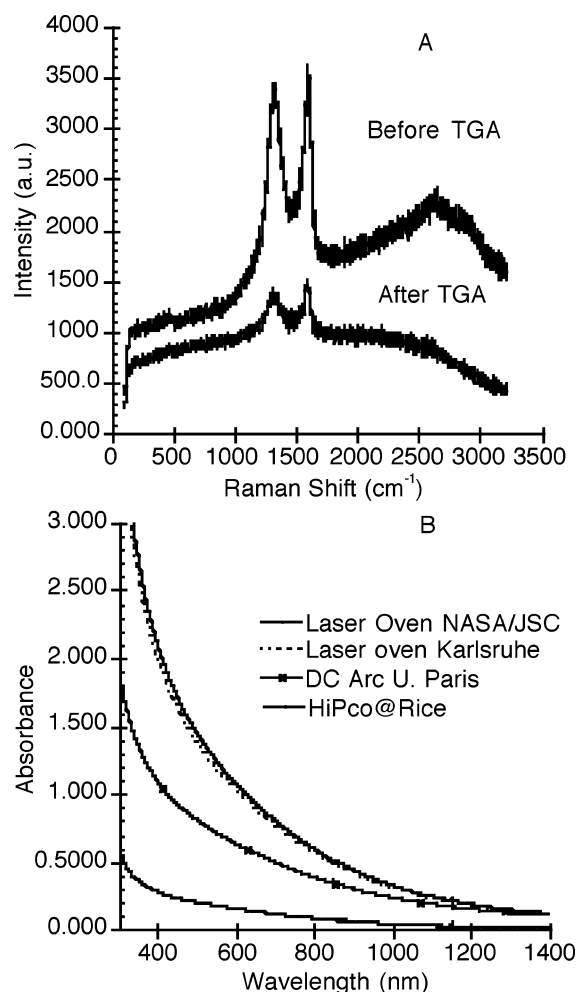
Figure 5. (A) Raman spectra of HiPco extract before and after TGA analysis. (B) UV−vis−near-IR of extracts from different samples of raw nanotubes in CHCl₃.

TA-SDT-2960 differential thermal analysis (DTA)-TGA analyzer. The HiPco SWNTs functionalized by octadecyl groups gave a carbon/octadecyl ratio of ~9:1 (Figure 3A). The material extracted from the laser oven and DC arc routes gave a similar carbon/octadecyl ratio.

The percentage of large fullerenes extracted from each sample is given in Table 1. In the case of the HiPco sample, the residual metal was first determined by combustion of the carbonaceous material (Figure 3B). By subtraction of the weight of the residual metal from the fullerenes prepared by dealkylation under argon, the percentage of large fullerenes was found to be 5.2%. The percentage of large fullerenes in the remaining samples was calculated on the basis of comparative UV−vis−near-IR

absorption data. Thus, extracts from different samples were diluted with chloroform to the same concentration, and absorption values at 500 nm were taken for comparison (Figure 5 B).

The extent of functionalization can also be inferred from the exceptional disorder peak in the Raman spectra of each sample (Figure 4). As expected, the large fullerenes that are formed after dealkylation are no longer soluble in organic solvents. The Raman spectra exhibit the same features before and after dealkylation (Figure 5A).

In conclusion, an efficient method for the extraction of large fullerenes from raw carbon nanotubes has been developed. A small amount of carbon-coated metal is also extracted along with the large fullerenes. Experiments to isolate large fullerenes from other sources are in progress.

References and Notes

(1) (a) Iijima, S. *Nature* **1991**, *354*, 56. (b) *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*; Dresselhaus, M. S., Dresselhaus, G., Avouris, Ph., Eds.; Springer-Verlag: Berlin, Germany, 2001.

(2) (a) Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tomanek, D.; Fischer, J. E.; Smalley, R. E. *Science* **1996**, *273*, 483. (b) Rinzler, A. G.; Liu, J.; Dai, H.; Nikolaev, P.; Huffmann, C. B.; Rodriguez-Macias, F. J.; Boul, P. J.; Lu, A. H.; Heymann, D.; Colbert, D. T.; Lee, R. S.; Fischer, J. E.; Rao, A. M.; Eklund, P. C.; Smalley, R. E. *Appl. Phys. A* **1998**, *67*, 29.

(3) (a) Bethune, D. S.; Kiang, C. H.; de Vries, M. S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. *Nature* **1993**, *363*, 605. (b) Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; Lamy de la Chapelle, M.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* **1997**, *388*, 756.

(4) (a) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91. (b) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *J. Vac. Sci. Technol., A* **2001**, *19*, 1800.

(5) For isolation of large fullerenes from meteorites see: (a) Becker, L.; Poreda, R. J.; Bunch, T. E. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 2979. (b) Becker, L.; Poreda, R. J.; Hunt, A. G.; Bunch, T. E.; Rampino, M. *Science* **2001**, *291*, 1530.

(6) For fullerenes in carbon blacks see: (a) Pontier Johnson, M.; Donnet, J. B.; Wang, T. K.; Wang, C. C.; Locke, R. W.; Brinson, B. E.; Marriott, T. *Carbon* **2002**, *40*, 189. (b) Donnet, J. B.; Johnson, M. P.; Norman, D. T.; Wang, T. K. *Carbon* **2000**, *38*, 1885. (c) Lee, T. H.; Yao, N.; Chen, T. J.; Hsu, W. K. *Carbon* **2002**, *40*, 2275.

(7) Ramesh, S.; Brinson, B.; Pontier Johnson, M.; Gu, Z.; Saini, R. K.; Willis, P.; Marriott, T.; Billups, W. E.; Margrave, J. L.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2003**, *107*, 1360.

(8) Beer, F.; Gügel, A.; Martin, K.; Räder, J.; Müllen, K. *J. Mater. Chem.* **1997**, *7*, 1327.

(9) Ying, Y.; Saini, R. K.; Liang, F.; Sadana, A. K.; Billups, W. E. *Org. Lett.* **2003**, *5*, 1471.

(10) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220.

(11) Ulmer, G.; Campbell, E. E. B.; Kuehnle, R.; Busmann, H. G.; Hertel, I. V. *Chem. Phys. Lett.* **1991**, *182*, 114.