Chem. Mater. **2001,** *13,* 3823−3824

Highly Functionalized Carbon Nanotubes Using in Situ Generated Diazonium Compounds

Jeffrey L. Bahr and James M. Tour*

Department of Chemistry and Center for Nanoscale Science and Technology, MS 222, Rice University, 6100 Main Street, Houston, Texas 77005

Received July 16, 2001
Revised Manuscript Received September 14, 2001

There is presently great interest in chemical functionalization of single-wall carbon nanotubes, in particular, to improve solubility[1,2] and to enhance compatibility in composite materials. Some progress has been made on functionalization of the ends of oxidatively etched nanotubes.[3−5] Additionally, both covalent[6−8] and noncovalent[9−12] sidewall functionalization has been explored. As part of the ongoing efforts in our laboratory, we recently reported on the functionalization of single-wall carbon nanotubes (SWNTs) by electrochemical reduction of aryl diazonium salts using a bucky-paper electrode.[6] In this manner, we were able to achieve functionalization of up to 1 in 20 carbons in the nanotube framework. We describe here our finding that derivatization with aryl diazonium salts is not limited to the electrochemically induced reaction. That is, both direct treatment of SWNTs with aryl diazonium tetrafluoroborate salts in solution and in situ generation of the diazonium with an alkyl nitrite are effective means of functionalization. In some cases, direct treatment with preformed diazonium salts is observed to be effective at moderate or even room temperature. We focus here on in situ generation of the diazonium species because this method avoids the necessity of isolating and storing often unstable and light-sensitive aryl diazonium salts.

The SWNTs used in this investigation were produced by a gas-phase catalytic process developed by Smalley et al.[13] and are now commercially available (Carbon Nanotechnologies Inc., HiPco material).[14] The production material was purified by oxidation in wet air at 250 °C for 24 h and then stirring in concentrated hydrochloric acid at room temperature for 24 h. The resulting material was washed with copious amounts of water, then with 10% aqueous sodium bicarbonate, and finally with additional water.[15] After drying under vacuum, the material was used for the functionalization reactions. The residual iron (catalyst) content was ≈0.2 at. %. The reaction sequence is depicted in Figure 1. In a typical experiment, ≈8 mg of SWNTs was sonicated for 10 min in 10 mL of 1,2-dichlorobenzene (ODCB).[1] To this suspension was added a solution of the aniline derivative (2.6 mmol, ≈4 equiv/mol of carbon) in 5 mL of acetonitrile. After transfer to a septum-capped reaction tube (Ace Glass, #8648-03) and bubbling with nitrogen for 10 min, 4.0 mmol of isoamyl nitrite was quickly added. The septum was removed and replaced with a Teflon screw cap, and the suspension was stirred at 60 °C for ≈15 h. (*CAUTION! Considerable pressure was attained in the vessel due to the evolved nitrogen. This was alleviated by partially unscrewing the cap for venting every ≈30 min for the first 3 h.*) After cooling to ≈45 °C, the suspension was diluted with 30 mL of dimethylformamide (DMF), filtered over a PTFE (0.45 μM) membrane, and washed extensively with DMF. Repeated sonication in and further washing with DMF constituted purification of the material.

Functionalized materials **1−4** display significantly altered spectroscopic properties, akin to those reported for materials derivatized via the electrochemical method.[6] Thus, the UV/vis/NIR absorption spectra (Figure 2) show an almost complete loss of the van Hove singularities. This loss of structure is characteristic of the disrupted π system and indicates covalent modification of the nanotubes. In the Raman spectra (Figure 3) the overall intensity of the scattered light is lower, and the relative intensities of the three main modes are altered. Relative to the tangential mode at ≈1590 cm^{-1}, the intensity of the radial breathing mode (≈250 cm^{-1}) is decreased, and the intensity of the disorder mode (1290 cm^{-1}) is significantly increased. The increase in the relative intensity of the disorder mode can be attributed to an increased number of sp^3-hybridized carbons in the nanotube framework and can be taken as a crude measure of the degree of functionalization. Additionally, we previously showed that the functionalized phenyl moieties attached to the nanotubes can be removed by heating in an argon atmosphere and that thermal gravimetric analysis (TGA) consequently provides a

---

* To whom correspondence should be addressed. Tel.: 713-348-6246. Fax: 713-348-6250. E-mail: tour@rice.edu.

(1) Bahr, J. L.; Mickelson, E. T.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *Chem. Commun.* **2001**, 194−195.

(2) Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S. *J. Phys. Chem. B* **2000**, *104*, 8911−8915.

(3) Chen, J.; Hamon, M. A.; Hu, H.; Chen, Y.; Rao, A. M.; Eklund, P. C.; Haddon, R. C. *Science* **1998**, *282*, 95−98.

(4) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525−2528.

(5) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879−5880.

(6) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 6536−6542.

(7) Boul, P. J.; Liu, J.; Mickelson, E. T.; Huffman, C. B.; Ericson, L. M.; Chiang, I. W.; Smith, K. A.; Colbert, D. T.; Hauge, R. H.; Margrave, J. L.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *310*, 367−372.

(8) Haddon, R. C.; Chen, Y.; Fang, S.; Rao, A. M.; Eklund, P. C.; Lee, W. H.; Dickey, E. C.; Grulke, E. A.; Pendergrass, J. C.; Chavan, A.; Haley, B. E.; Smalley, R. E. *J. Mater. Res.* **1998**, *13*, 2423−2431.

(9) O'Connell, M. J.; Boul, P. J.; Ericson, L. M.; Huffman, C. B.; Huang, Y.; Haroz, E. H.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265−271.

(10) Star, A.; Stoddart, J. F.; Steuerman, D.; Diehl, M.; Boukai, A.; Wong, E. W.; Yang, X.; Chung, S.-W.; Choi, H.; Heath, J. R. *Angew. Chem.* **2001**, *113*, 1721−1725.

(11) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001**, *123*, 3838−3839.

(12) Dalton, A. B.; Stephan, C.; Coleman, J. N.; McCarthy, B.; Ajayan, P. M.; Lefrant, S.; Bernier, P.; Blau, W. J.; Byrne, H. J. *J. Phys. Chem. B* **2000**, *104*, 10012−10016.

(13) Nikolaev, P.; Bronikowski, M. J.; Bradley, R. K.; Rohmund, F.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *Chem. Phys. Lett.* **1999**, *313*, 91−97.

(14) Carbon Nanotechnoligies Inc.: http://www.cnanotech.com.

(15) Chiang, I. W.; Brinson, B. E.; Huang, A. Y.; Willis, P. A.; Bronikowski, M. J.; Margrave, J. L.; Smalley, R. E.; Hauge, R. H. *J. Phys. Chem. B* **2001**, *105*, 8297−8301.

10.1021/cm0109903 CCC: $20.00 © 2001 American Chemical Society
Published on Web 10/24/2001

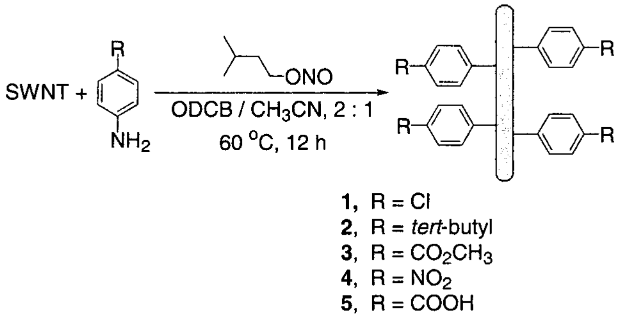

Figure 1. Reaction sequence for derivatization of SWNTs by in situ generation of the diazonium species and the functionalized phenyl moieties employed.

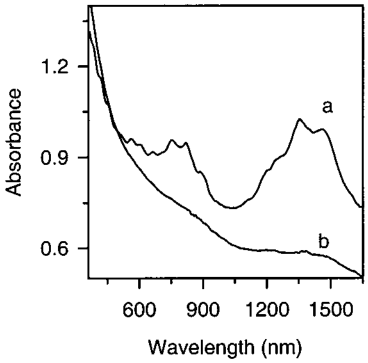

Figure 2. Absorption spectra in dimethylformamide showing the loss of band structure on functionalization: (a) pristine, unfunctionalized material; (b) **3**. The spectra of **1**, **2**, and **4** are similar, with little or no visible structure. The spectrum of the material from the sequence to produce **5** was essentially equivalent to that shown for the pristine material.

quantitative estimate of the degree of functionalization. Upon heating of **1**–**4** to 600 °C in an argon atmosphere, the observed weight loss values were as follows, with the value previously reported for similar materials prepared via the electrochemical technique in parentheses: **1**: 26% (30%); **2**: 25% (27%); **3**: 26% (31%); **4**: 23% (26%). Material **5** did not display similar changes in the spectroscopic properties or significant mass loss in TGA, indicating a lack of significant functionalization, even though this moiety can be successfully attached by the electrochemical technique. Nonetheless, the ester-bearing material **3** was successfully prepared, in principle giving access to the carboxylic acid moiety via hydrolysis.

It is of primary interest to compare the degree of functionalization achievable by this thermal technique to that obtained by the previously reported electrochemical method. The present experiments were performed with a large excess of the aniline derivative, thatis, sufficient to provide the diazonium species in amounts equivalent to the amount of diazonium tetrafluoroborate salts used in the previously reported electrochemical experiments. For material **1**, a straightforward comparison is available through electron microprobe analysis. This analysis gave a value of 2.2 at. % chlorine, relative to 97 at. % carbon. Further sonication and washing of the material did not significantly affect this value. Similar material prepared by the electrochemical technique was analyzed to have 2.7 at. % chlorine, relative to 96 at. % carbon.[6] The TGA data give additional insight into the relative efficiency of the thermal method. For example, the mass loss for **4** corresponds to an estimated 1 in 37 carbons in the nanotubes being functionalized, versus the 1 in 34 ratio achieved by the electrochemical method. The thermal technique is then comparable in its effectiveness to the electrochemical method. We fully expect that the conditions described here can be optimized to provide a higher degree of functionalization. However, the observed efficacy is sufficient to significantly alter the properties of the SWNTs and will likely be satisfactory for numerous applications, such as cross-linked materials and composite formation, routes we are currently pursuing.

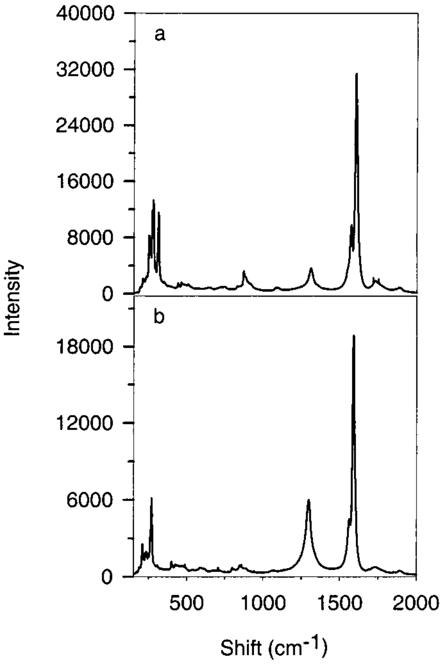

Figure 3. Raman spectra from solid samples, with excitation at 782 nm: (a) pristine, unfunctionalized material; (b) **2**. The Raman spectra of **1**, **3**, and **4** are similar, but with differing ratios of the peak intensities. In all these cases, the relative intensity of the disorder mode is increased. The spectrum of the material from the sequence to produce **5** was essentially equivalent to that shown for the pristine material.

In summary, the thermally induced reaction of single-wall carbon nanotubes with diazonium compounds, generated in situ by action of isoamyl nitrite on aniline derivatives, is an effective means of functionalization. This thermal reaction is potentially more scaleable and offers a more traditional alternative to the previously reported electrochemical method.

Acknowledgment. Financial support for this work was provided by NASA (NASA-JSC-NCC 9-77, OSR 99091801) and the NSF (NSF-DMR-0073046). We express our gratitude to Professor Richard E. Smalley and Dr. Peter Willis for providing the HiPco-produced nanotubes.

CM0109903