Surface Functionalization of Multiwalled Carbon Nanotube with Trifluorophenyl

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Received 21 March 2006; Revised 15 May 2006; Accepted 5 June 2006

Recommended for Publication by Jun Liu

A new approach to dispersion of multiwalled carbon nanotube (MWNT) in common polar solvents was reported. Here, a detailed study of nanotube chemistry by using trifluorophenyl (TFP) to modify the surface of MWNT was discussed, which was not reported before. A characterization of the reaction products using a variety of techniques was provided. The results confirmed that the surface of MWNT was successfully functionalized. Furthermore, trifluorophenyl multiwalled carbon nanotube (TFP-MWNT) was well dispersed in polar solvents, such as tetrahydrofuran (THF), acetic acid (Ac), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), due to the adsorption of trifluorophenyl groups on the surface of raw MWNT. Following chemical modification, dispersed individual nanotube suggests the potentials for wide applications.

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1. INTRODUCTION

Carbon nanotubes (CNTs) show promise for a wide range of applications due to a combination of their novel structural, electronic, mechanical, and nonlinear optical properties [1, 2]. However, the limited ability to process and disperse in organic solvent nanotube hinders the realization of their full potential [3]. To overcome this obstacle, several methods have been developed. For example, CNT could be dispersed in certain solutions via ultrasonication or surfactant treatment [4, 5]. Along with the rapid development of nanotube chemistry, organic modification and *in situ* polymerization of CNTs with specific molecules were also reported [6–11]. Therefore, CNT may be soluble in aqueous and/or nonaqueous solvent to allow homogeneous dispersion. However, the ability to solubilize individual carbon nanotube in solvents is still a great challenge. Moreover, most of the procedures reported are difficult to control and do not provide a clear understanding of CNT chemistry.

Here, we have developed a different approach to disperse multiwalled carbon nanotube (MWNT) in common solvents. Using 3,4,5-trifluoro-bromobenzene (TFBB), a detailed study of nanotube chemistry of MWNT is reported. A detailed characterization of the reaction products

using a variety of techniques is provided. After the functionalization, MWNT was well dispersed in common polar solvents, such as acetic acid (Ac), trifluoroacetic acid (TFAc), N,N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), and so on, due to the adsorption of trifluorophenyl groups.

2. RAW MATERIALS AND EXPERIMENTAL

Multiwalled carbon nanotubes (MWNTs) grown by chemical vapor deposition (CVD) are obtained from Shenzhen Nanotech Port Co., Ltd., China. The MWNT is about 10 ~ 30 nm in diameter and 5 ~ 15 μm in length. The raw MWNT was successfully modified by employing a simple chemical reaction scheme, as illustrated in Figure 1. MWNT was first treated in a mixture of concentrated nitric and sulphuric acids in the volume ratio of 3 : 1. The solvent was agitated by using ultrasonic wave vibration at about 50°C for 4 hours in order to remove the impurity and the amorphous carbon composition, and generate carbonyl ($> \text{C}=\text{O}$) on the surface of MWNT. Then, using an appropriate solvent (diethyl ether), with magnesium (Mg) and 3,4,5-trifluoro bromobenzene, trifluorophenyl functionalization multiwalled carbon nanotube (TFP-MWNT) was obtained

FIGURE 1: Schematic process of functional reaction of raw MWNT.

through reaction with 3,4,5-trifluorobromophenylmagnesium reagent. Finally, the sample was heated to completely evaporate the solvent.

As a comparison, raw MWNT and TFP-MWNT have been characterized by using transmission electron microscopy (TEM, Hitachi H-800), Fourier transform infrared spectra (FTIR, Nicolet 5DX), Raman spectrum (Renishaw RM2000), X-ray photoelectron spectroscopy (XPS, VG Escalab 250), and X-ray diffraction (XRD, D/Max 2500).

3. RESULTS AND DISCUSSION

Transmission electron microscopy revealed that there were some impurities and intertwist clusters in the raw MWNT (Figure 2(a)) and the head of the MWNT was closed (the inset in Figure 2(a)). After the MWNT was treated with TFPB, little impurity could be seen (Figure 2(b)) and the head of the TFP-MWNT was open (the inset in Figure 2(b)). In addition, it might be noticed that some TFP-MWNTs were shortened and the intertwist of MWNT disappeared because the harsh process broke shape and size of MWNT during the functionalization.

The nature of the surface groups was further investigated using FTIR spectroscopy (Figure 3). Both samples have two large peaks, one at 1575 cm^{-1} and another at 1116 cm^{-1} , which are assigned to the CNT skeletal motions [12, 13]. The peak at 1705 cm^{-1} is associated with the stretch vibration of $>\text{C}=\text{O}$. Compared with the corresponding peak in Figure 3(a), the peak at 1705 cm^{-1} is much weaker in Figure 3(b). There are a few $>\text{C}=\text{O}$ groups in the raw MWNT resulting from oxidation and purification, and the number of groups increases after acid treatment. After organometallic reaction, they will be replaced by phenyl groups. Furthermore, the second-order curve displays a broad peak centered at 1168 cm^{-1} (covering the peak at 1116 cm^{-1}), due to the existence of $-\text{F}$ groups [13]. The intensity of the $\nu(\text{C}-\text{H})$ stretch vibration peak (2921 cm^{-1}) decreases significantly, which is related to a decrease of amorphous and impurity carbon after treatment. The results of FTIR spectra confirm the formation of new chemical bonds on the raw MWNT after treatment.

In fact, the surface functionalization on MWNT can be also confirmed using Raman spectroscopy as shown in Figure 4. The first-order spectrum of raw MWNT shows bands around 1350 and 1620 cm^{-1} (the so-called *D* and *D'*

(a)

(b)

FIGURE 2: TEM micrographs of (a) the raw MWNT and (b) TFP-MWNT. The inset in Figure 2 is, respectively, larger magnification micrographs of the raw MWNT and TFP-MWNT.

FIGURE 3: FTIR spectra of the raw MWNT and TFP-MWNT.

bands), and 1585 cm^{-1} (the so-called *G* band). A disorder-induced CNT *D* band is attributed to lattice distortions, or to the presence of structural defects (such as unexpected chemical groups), or both. The peak at 1355 cm^{-1} is higher than that at 1585 cm^{-1} because there is a great deal of amorphous

TABLE 1: Concentration of C, O, and F, in the carbon nanotube samples, as determined by XPS.

	Element	Peak/BE	FWHM/eV	At. %
MWNT	C 1s	284.40	1.08	93.99
	O 1s	535.15	2.19	6.01
	F 1s	—	—	0
TFP-MWNT	C 1s	286.25	1.36	64.61
	O 1s	534.05	2.58	32.20
	F 1s	689.55	2.42	3.19

FIGURE 4: Raman spectra of the raw MWNT and TFP-MWNT.

carbon and impurities in the raw MWNT (Figure 4(a)) [3, 5, 14]. However, after the MWNT was treated with TFBB, only two peaks are observed and the peak at 1348 cm^{-1} is smaller than that at 1577 cm^{-1} (Figure 4(b)), due to the decrease of amorphous carbon and impurities during acid treatment. Both peaks for TFP-MWNT are slightly shifted from that of raw MWNT, which may be ascribed to the presence of fluorophenyl.

In addition, electronic and structural information about carbon atoms and local functionalities may be further deduced from the results of XPS. As shown in Figure 5(a)-2 and Table 1, there is a new minor peak component at the binding energy (BE) of 689.55 eV corresponding to F 1s of the functional reaction on MWNT, which does not exist in the Figure 5(a)-1. As shown in Table 1, the carbon C 1s peak, observed at 284.40 eV in the raw sample, is shifted by 1.85 eV to a higher binding energy following treatment, partly due to the appearance of electrophilic groups. It is well known that the FWHM of C 1s is directly related to the electronic state of the CNT, so the wider FWHM for CNT, as noted in Table 1, indicates a less delocalized electron density compared to raw CNT. This result is consistent with a greater presence of $-F$ and $-OH$ groups in the MWNT, whose presence disrupts electron delocalization. Moreover, the concentration of element O increases after treatment because of the enhancement of the $-OH$ group. Detailed analysis of the XPS spectra

FIGURE 5: (a) XPS and (b) C 1s spectra of MWNT and TFP-MWNT.

FIGURE 6: XRD spectra of the raw MWNT and TFP-MWNT.

FIGURE 7: Photographs of the raw MWNT and TFP-MWNT specimens dispersion in (a) DMSO, (b) DMF, (c) Ac, and (d) THF, respectively.

provides clear evidence that the MWNT has been chemically functionalized by TFP. Peak separations of the C 1s spectra are displayed in Figure 5(b), which clearly reveal at least four components. The carbon C 1s peak, observed at 284.40 eV for sp^2 carbon [15], was reduced following treatment, and the surface of MWNT is covered by other groups, such as $-OH$ and trifluorophenyl groups. The peak at 285.8 eV in raw MWNT, stemming from carbon atoms bound to the $-OH$ group, is shifted by 0.4 eV to higher binding energy after functionalization, owing to the presence of the trifluorophenyl group. And the peak at 287.6 eV is attributed to the $>C=O$ group. Otherwise, as shown in Figure 5(b), the broad peak at a higher binding energy (6-7 eV higher than major peak) is the asymmetrical peak for π electron orbital system. Therefore, the detailed insight into the changes in the electronic and chemical structures has been obtained from XPS spectroscopy, which confirmed that the TFP-MWNT was obtained successfully.

As shown in Figure 6, the XRD results revealed the characteristic microstructure of MWNT. For all specimens, the

XRD patterns indicate the persistence of the main reflection of the original CNT, at $2\theta \approx 26^\circ$ and $2\theta \approx 43^\circ$, assigned to the (002) and (100) reflections of the host lattice (Figure 6(a)). Same results were reported in other studies [16]. Therefore, the structure of cylindrical concentric carbon layers is preserved and that the carbon atoms contain their sp^2 hybridization. Only the surface is modified. Moreover, there are two characteristic peaks at $2\theta \approx 31^\circ$ and $2\theta \approx 45^\circ$ on the second-order curve in Figure 6(b). Some new layered patterns ($56^\circ, 67^\circ$) in Figure 6(b) could also be seen, which are related with formation of other structures of TFP-MWNT. Therefore, all results in FTIR, Raman, XPS, and XRD spectrums illustrate that MWNT was successfully modified with TFPB.

In sharp contrast to the raw MWNT, TFP-MWNT has shown a significantly improved dispersion in polar solvents, such as tetrahydrofuran (THF), acetic acid (Ac), N,N-dimethyl formamide(DMF), dimethyl sulfoxide (DMSO), and so on, due to the appearance of trifluorophenyl groups on the surface of nanotubes. Dispersion of raw MWNT into

DMSO was very difficult even after the nanotubes were sonicated; sedimentation of MWNT from DMSO appeared after centrifuging for 5 minutes. However, dispersion of TFP-MWNT in DMSO and in other polar solvents was very easy, as shown in Figure 7. The solutions of TFP-MWNT in THF, Ac, DMF and DMSO were stable after centrifuging for 5 minutes. Moreover, the solutions showed little precipitation upon prolonged standing. It is clear that TFP-MWNT is dispersed quite well in stronger polar solvents, due to an interaction between trifluorophenyl groups and polar solvent molecules. The solutions of MWNT provide more processes and wider applications for MWNT.

4. CONCLUSIONS

A new approach to disperse multiwalled carbon nanotube in polar solvents was reported. Detailed study of nanotubes chemistry using the chemical treatment was reported. The results in FTIR, Raman, XPS and XRD spectrums confirmed that the surface of MWNT was successfully functionalized by TFP. Furthermore, TFP-MWNT was well dispersed in polar solvents, such as THF, Ac, DMF, DMSO, and so on, due to the appearance of trifluorophenyl groups on the surface of MWNT.

ACKNOWLEDGMENTS

This work was financially supported by the NSF of Beijing City (Grant 2063031) and the Ministry of Education of China through Doctor Project (Grant 20050010010). Z.-M. Dang also acknowledges Humboldt Foundation of Germany for providing fellowship.

REFERENCES

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.
- [2] R. H. Baughman, A. A. Zakhidov, and W. A. De Heer, "Carbon nanotubes-the route toward applications," *Science*, vol. 297, no. 5582, pp. 787–792, 2002.
- [3] L. Wang and Z.-M. Dang, "Carbon nanotube composites with high dielectric constant at low percolation threshold," *Applied Physics Letters*, vol. 87, no. 4, pp. 1–3, 2005.
- [4] A. Koshio, M. Yudasaka, M. Zhang, and S. Iijima, "A simple way to chemically react single-wall carbon nanotubes with organic materials using ultrasonication," *Nano Letters*, vol. 1, no. 7, pp. 361–363, 2001.
- [5] D.-Q. Yang, J.-F. Rochette, and E. Sacher, "Functionalization of multiwalled carbon nanotubes by mild aqueous sonication," *Journal of Physical Chemistry B*, vol. 109, no. 16, pp. 7788–7794, 2005.
- [6] H. Zengin, W. S. Zhou, J. Y. Jin, et al., "Carbon nanotube doped polyaniline," *Advanced Materials*, vol. 14, no. 20, pp. 1480–1483, 2002.
- [7] S. P. Li, Y. J. Qin, J. H. Shi, Z.-X. Guo, Y. F. Li, and D. B. Zhu, "Electrical properties of soluble carbon nanotube/polymer composite films," *Chemistry of Materials*, vol. 17, no. 1, pp. 130–135, 2005.
- [8] R. Czerw, Z. X. Guo, P. M. Ajayan, Y.-P. Sun, and D. L. Carroll, "Organization of polymers onto carbon nanotubes: a route to nanoscale assembly," *Nano Letters*, vol. 1, no. 8, pp. 423–427, 2001.
- [9] C.-Y. Hong, Y.-Z. You, D. C. Wu, Y. Liu, and C.-Y. Pan, "Multiwalled carbon nanotubes grafted with hyperbranched polymer shell via SCVP," *Macromolecules*, vol. 38, no. 7, pp. 2606–2611, 2005.
- [10] M. Holzinger, J. Abraham, P. Whelan, et al., "Functionalization of single-walled carbon nanotubes with (R)-oxycarbonyl nitrenes," *Journal of the American Chemical Society*, vol. 125, no. 28, pp. 8566–8580, 2003.
- [11] K. Balasubramanian and M. Burghard, "Chemically functionalized carbon nanotubes," *Small*, vol. 1, no. 2, pp. 180–192, 2005.
- [12] M. S. P. Shaffer, X. Fan, and A. H. Windle, "Dispersion and packing of carbon nanotubes," *Carbon*, vol. 36, no. 11, pp. 1603–1612, 1998.
- [13] W. Zhao, C. Song, B. Zheng, J. Liu, and T. Viswanathan, "Thermal recovery behavior of fluorinated single-walled carbon nanotubes," *Journal of Physical Chemistry B*, vol. 106, no. 2, pp. 293–296, 2002.
- [14] W. Z. Li, H. Zhang, C. Y. Wang, et al., "Raman characterization of aligned carbon nanotubes produced by thermal decomposition of hydrocarbon vapor," *Applied Physics Letters*, vol. 70, no. 20, pp. 2684–2686, 1997.
- [15] U. Dettlaff-Weglikowska, V. Skákalová, R. Graupner, et al., "Effect of SOCl_2 treatment on electrical and mechanical properties of single-wall carbon nanotube networks," *Journal of the American Chemical Society*, vol. 127, no. 14, pp. 5125–5131, 2005.
- [16] S.-J. Park, H.-J. Jeong, and C. Nah, "A study of oxyfluorination of multi-walled carbon nanotubes on mechanical interfacial properties of epoxy matrix nanocomposites," *Materials Science and Engineering A*, vol. 385, no. 1–2, pp. 13–16, 2004.