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A Facile, Solvent-Free, Noncovalent, and Nondisruptive Route To Functionalize Single-Wall Carbon Nanotubes Using Tertiary Phosphines

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Received June 12, 2007. Revised Manuscript Received August 14, 2007

A facile, solvent-free, low-level noncovalent method for the modification of single-wall carbon nanotubes (SWNTs) by tertiary phosphines is described. The modified SWNTs show greater ease of exfoliation into common organic solvents (such as dichloromethane, dimethylformamide, ethanol, and 1,2-dichlorobenzene) than unmodified nanotubes which is important for enhanced processability. AFM analysis shows a significant debundling of the SWNTs upon phosphine treatment. Interestingly, Raman spectroscopy and absorption spectroscopy in the near-infrared region indicate that the disruption of the intrinsic electronic structure of the nanotubes upon modification is minimal. X-ray photoelectron spectroscopy (XPS) data obtained from the modified nanotubes suggest that the tertiary phosphines interact chemically, presumably via the lone pair of electrons on the phosphorus, with the "electron-deficient" nanotubes.

Introduction

Carbon nanotubes (CNTs) are known to have impressive electrical, thermal, and mechanical properties and have attracted interest and excitement across a broad range of disciplines including engineering, materials, physics, chemistry, and biosciences. Many potential applications for CNTs have been envisaged ranging from composite materials, energy storage, sensors, and field emission devices to nanoscale electronic components.[1] In attempts to realize the full potential of CNTs in nanoscale materials and devices a problem of solubility is frequently encountered. CNTs have a tendency to aggregate together into bundles, resulting in very low solubility in common solvents making their handling and processing difficult. It is no surprise therefore that considerable efforts have focused on producing stable dispersions of CNTs in both aqueous and organic solvents. Solubilizing CNTs in water is often achieved by wrapping the nanotube in water-soluble polymers such as poly(vinylpyrrolidone)[2] and poly(acrylic acid)[3] or by the π-stacking of ionic pyrenes (or other polycyclic aromatic compounds) onto the nanotube surface.[4–6] The same methodology, using appropriate polymers and polycyclic aromatic molecules, can be used

to solubilize CNTs in organic solvents.[7,8] Similarly, stable CNT dispersions in aqueous media can be achieved using anionic (sodium dodecyl sulfate, SDS), cationic (dodecyltrimethylammonium bromide, DTAB), or nonionic (Triton X) surfactants.[9] Alternatively, CNTs can be solubilized in both organic and aqueous solvents by employing synthetic strategies that use covalent chemistry. Common reactions that result in the covalent attachment of functional groups to a nanotube surface include radical,[10,11] cycloaddition,[12,13] and oxidation reactions.[14,15] The noncovalent and covalent chemical modification of carbon nanotubes has been extensively reviewed recently.[16]

However, while noncovalent routes, such as the use of surfactants, polymer wrapping, and π-stacking of molecules, can have a dramatic effect on solubility they have the obvious disadvantage of rendering the CNT surface less accessible, therefore inhibiting further chemistry or interactions, whereas covalent functionalization can disrupt the intrinsic electronic structure of the CNTs, thereby compromising their exciting

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(1) Dresselhaus, M. S., Dresselhaus, G., Avouris, Ph., Eds.; *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*; Springer: Berlin, 2001.
(2) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J. M.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001,** *342,* 265.
(3) Liu, A. H.; Honma, I.; Ichihara, M.; Zhou, H. S. *Nanotechnology* **2006,** *17,* 2845.
(4) Tomonari, Y.; Murakami, H.; Nakashima, N. *Chem.—Eur. J.* **2006,** *12,* 4027.
(5) Paloniemi, H.; Ääritalo, T.; Laiho, T.; Liuke, H.; Kocharova, N.; Haapakka, K.; Terzi, F.; Seeber, R.; Lukkari, J. *J. Phys. Chem. B* **2005,** *109,* 8634.
(6) Chen, R. J.; Zhang, Y.; Wang, D.; Dai, H. *J. Am. Chem. Soc.* **2001,** *123,* 3838.

(7) Star, A.; Liu, Y.; Grant, K.; Ridvan, L.; Stoddart, J. F.; Steuerman, D. W.; Diehl, M. R.; Boukai, A.; Heath, J. R. *Macromolecules* **2003,** *36,* 553.
(8) Yuan, W. Z.; Sun, J. Z.; Dong, Y. Q.; Haussler, M.; Yang, F.; Xu, H. P.; Qin, A. J.; Lam, J. W. Y.; Zheng, Q.; Tang, B. Z. *Macromolecules* **2006,** *39,* 8011.
(9) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hague, R. H.; Smalley, R. E. *Nano Lett.* **2003,** *3,* 1379.
(10) Price, B. K.; Tour, J. M. *J. Am. Chem. Soc.* **2006,** *128,* 12899.
(11) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003,** *125,* 14893.
(12) Tagmatarchis, N.; Prato, M. *J. Mater. Chem.* **2004,** *14,* 437.
(13) Azamian, B. R.; Coleman, K. S.; Davis, J. J.; Hanson, N.; Green, M. L. H. *Chem. Commun.* **2002,** 366.
(14) Coleman, K. S.; Bailey, S. R.; Fogden, S.; Green, M. L. H. *J. Am. Chem. Soc.* **2003,** *125,* 8722.
(15) Coleman, K. S.; Chakraborty, A. K.; Bailey, S. R.; Sloan, J.; Alexander, M. L. H. *Chem. Mater.* **2007,** *19,* 1076.
(16) Tasis, D.; Tagmatarchis, N.; Bianco, A.; Prato, M. *Chem. Rev.* **2006,** *106,* 1105.

properties.[17,18] The challenge, therefore, is to achieve sufficient modification of the CNT surface to ensure ease of processing, while avoiding significant degradation of electronic structure. Here we report a simple, solvent-free, low-level noncovalent and nondestructive modification of SWNTs by triphenylphosphine [P(C$_6$H$_5$)$_3$] and tri-*n*-octylphosphine [P(C$_8$H$_{17}$)$_3$]. X-ray photoelectron spectroscopy (XPS), ultraviolet–visible−near-infrared (UV–vis−NIR) spectroscopy, Raman spectroscopy, thermogravimetric analysis (TGA), and atomic force microscopy (AFM) have been employed to characterize the functionalized material.

Experimental Details

Materials Preparation. SWNTs produced by the HiPco method and supplied by Carbon Nanotechnologies, Inc., were purified by heating in air at 400 °C and then soaking in 6 M HCl overnight, followed by filtration over a polycarbonate membrane (0.2 *μ*m, Whatman) and washing with copious amounts of high-purity water until pH neutral. The purified SWNTs were annealed under vacuum (10^{-2} mbar) at 900 °C to remove residual carboxylic acid functional groups and any adsorbed gases or solvents. The purified and annealed SWNTs (SWNT-PA) were then treated with the tertiary phosphines as follows: 5 mg of SWNTs was stirred in 5 g of molten triphenylphosphine, PPh$_3$ (Avocado, 99%), or 5 mL of tri-*n*-octylphosphine, P(C$_8$H$_{17}$)$_3$ (Avocado, 90%), at 90 °C under nitrogen for 48 h. The SWNT products were then washed repeatedly with dichloromethane to remove excess phosphine to afford SWNT-PPh$_3$ and SWNT-POc$_3$, respectively.

Characterization. *AFM.* Samples of SWNT-PA, SWNT-PPh$_3$, and SWNT-POc$_3$ for AFM analysis were produced by drop deposition onto mica of the corresponding solution of SWNTs (concentration of ca. 0.005 mg/mL) in dimethylformamide produced by sonication in an ultrasonic bath (Ultrawave U50, 30–40 kHz) for 15 min. Samples were dried in air before imaging in tapping mode using a Digital Instruments Multimode AFM with a Nanoscope IV controller.

XPS. XPS studies were performed at NCESS, Daresbury Laboratory, using a Scienta ESCA 300 hemispherical analyzer with a base pressure under 3 × 10^{-9} mbar. The analysis chamber was equipped with a monochromated Al Kα X-ray source (*hν* = 1486.6 eV). Charge compensation was achieved (if required) by supplying low-energy (<3 eV) electrons to the samples. XPS data were referenced with respect to the corresponding C 1s binding energy of 284.5 eV, which is typical for carbon nanotubes.[19] Photoelectrons were collected at a 45° takeoff angle, and the analyzer pass energy was set to 150 eV, giving an overall energy resolution of 0.4 eV.

TGA. Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer Pyris I system in a He environment. Samples were first heated to 100 °C and held at this temperature for 30 min to remove residual solvent and then heated to 900 °C at a rate of 10 °C/min.

UV–Vis−NIR. The UV–vis−NIR absorption spectra were recorded on a Perkin-Elmer Lambda 900 spectrometer. The samples were prepared by dispersing the nanotube material in 1,2-dichlorobenzene (concentration ca. 0.03 mg /mL) by sonication in an ultrasonic bath (Ultrawave U50, 30–40 kHz) for 15 min followed by filtration through a plug of cotton wool to remove particulates.

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

(18) Kamaras, K.; Itkis, M. E.; Hu, H.; Zhao, B.; Haddon, R. C. *Science* **2003**, *301*, 1501.

(19) Dyke, C. A.; Stewart, M. P.; Tour, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 4497.

Scheme 1. Reaction Scheme for the Modification of SWNTs Using Tertiary Phosphines
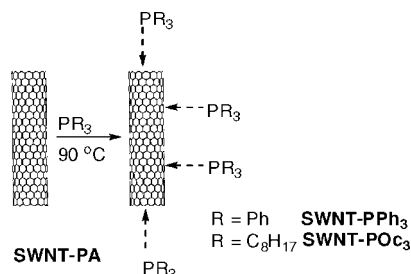
Solubility studies were carried out on the supernatant of dimethylformamide solutions of SWNT-PA, SWNT-PPh$_3$, and SWNT-POc$_3$ (of initial concentration ca. 0.03 mg) /mL which were allowed to stand for 2 months.

Raman Spectroscopy. Raman spectra were recorded using a Jobin Yvon Horiba LabRAM spectrometer in a back scattered confocal configuration using He/Ne laser excitation (632.8 nm, 1.96 eV). All spectra were recorded on solid samples over several regions and were referenced to the silicon line at 520 cm^{-1}.

Results and Discussion

Purified SWNTs (SWNTs-PA), where the residual metal catalyst particles have been removed and the material heated at 900 °C under vacuum, were treated with either triphenylphosphine (PPh$_3$) or tri-*n*-octylphosphine (POc$_3$) and heated at 90 °C under nitrogen to produce SWNT-PPh$_3$ and SWNT-POc$_3$, respectively (Scheme 1). Interestingly, the treatment of SWNTs with the tertiary phosphines resulted in significant improvements in the dispersion of the carbon nanotubes in organic solvents such as dichloromethane, dimethylformamide, ethanol, and 1,2-dichlorobenzene. The improved solubility of SWNT-PPh$_3$ and SWNT-POc$_3$ in ethanol, typically a poor solvent for dispersing CNTs, can be readily observed in the optical photographs, taken after 2 days, displayed in Figure 1. It is clear that while the SWNT-PA material starts aggregating shortly after sonication, the phosphine-treated samples form stable suspensions for several days. In order to further support the enhanced dispersion properties of the phosphine-treated SWNTs in organic solvents, an AFM analysis of the dilute solutions of nanotube samples (in dimethylformamide) on a mica surface was carried out. Figure 2 shows two representative AFM images of (a) SWNT-PA and (b) SWNT-POc$_3$ samples. It is evident that the untreated nanotubes, SWNT-PA, are present as larger bundles when compared with SWNT-POc$_3$ (a similar trend was observed for SWNT-PPh$_3$). Histograms showing the diameter distribution, determined by measuring the heights of the individual bundles observed in the AFM height images shown in Figure 2, are plotted in Figure 3. The mean diameters of the bundles in the two samples are calculated to be 15.1 and 6.5 nm for SWNT-PA and SWNT-POc$_3$, respectively, clearly demonstrating a significant de-bundling in phosphine-treated SWNTs which is presumably responsible for the improved dispersion of the material observed in dichloromethane, dimethylformamide, ethanol, and 1,2-dichlorobenzene. The mean diameter of the bundles found in SWNT-PPh$_3$ was calculated to be 6.9 nm (see Figure S1 of the Supporting Information for details).

Single-Wall Carbon Nanotubes

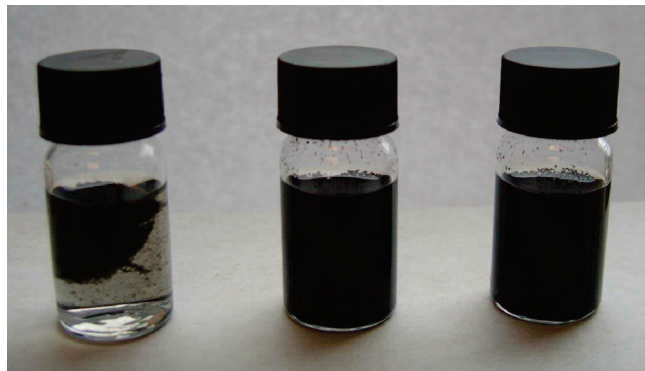*Chem. Mater., Vol. 20, No. 5, 2008* 1707

Figure 1. Optical photographs of SWNT suspensions (ca.1 mg/mL) in ethanol taken after 48 h. From left to right: SWNT-PA, SWNT-PPh₃, and SWNT-POc₃.

In order to probe the interaction of the tertiary phosphines with SWNTs, the reacted material was studied by XPS. XPS data recorded on SWNT-PPh₃ show the presence of a broad peak associated with P 2p core electrons at a binding energy of ∼133.5 eV (Figure 4a). This value is ∼2.6 eV shifted from the P 2p peak position expected for pure triphenylphosphine (130.9 eV).[20–22] This indicates that the phosphorus atoms present in the nanotube material are in a different chemical environment than those in the pure phosphine reagent. The binding energy is in line with that expected for a simple phosphine adduct such as PPh₃·BF₃, where the 2p₃/₂ binding energy has been reported to have values between 132 and 133.2 eV.[20–22] The broad nature of the P 2p peak can be understood by considering that the P 2p peak consists of two closely spaced (∼1.3 eV apart) lines due to 2p₃/₂ and 2p₁/₂ electrons (which are unresolved in the current data) and may contribute, along with other factors such as inhomogeneity and the presence of more than one phosphorus environment, to the peak broadening. Deconvolution of the peaks into its components shows the presence of two main doublets at 132.7 and 133.4 eV, respectively, indicating (see Figure S2 of the Supporting Information for details) signatures of a simple phosphine adduct or phosphorus(V)-like state.[21] While it is not possible to comment on the exact chemical nature of the interaction, the upward shift in the 2p₃/₂ binding energy of the phosphorus indicates that charge transfer between the electron-donating phosphorus atoms and the carbon nanotubes may have taken place. Similar results were found for SWNT-POc₃, with the presence of a broad peak associated with P 2p core electrons at a binding energy of ∼133.0 eV (Figure 4b). The large upward shift in 2p binding energy also rules out other interactions such as π–π for SWNT-PPh₃ and van der Waals for SWNT-POc₃ which would be expected to give binding energies closer to the parent phosphine. Elemental composition analysis of the XPS data for SWNT-PPh₃ and SWNT-POc₃ show that the phosphorus content is ∼0.1 at. % for both materials. However, the TGA data for SWNT-PPh₃ and SWNT-POc₃

(see Figure S3 of the Supporting Information) show a weight loss of up to ca. 20 and 25 wt %, respectively, when compared to SWNT-PA, indicating the desorption of organic groups could correspond to as many as 0.9 and 0.8 tertiary phosphines per 100 carbon atoms for SWNT-PPh₃ and SWNT-POc₃, respectively.

UV–vis–NIR spectroscopy has been used extensively to follow functionalization of SWNTs with the loss of the characteristic absorption bands corresponding to the electronic transitions between the van Hove singularities a consequence of their chemical modification.[17,18,23–26] The normalized absorption spectra obtained from the SWNT-PA, SWNT-PPh₃, and SWNT-POc₃ samples, recorded in 1,2-dichorobenzene, are shown in Figure 5. Only a small suppression of the absorption bands of the phosphine-treated SWNTs can be seen, which is indicative of a low level of functionalization. Importantly, the electronic structure of the SWNTs has not been perturbed significantly by the tertiary phosphine treatment. Solubility studies in dimethylformamide, a good solvent for dispersing unmodified SWNTs, of the supernatant of SWNT-PA, SWNT-PPh₃, and SWNT-POc₃ solutions that have been allowed to stand for 2 months afforded concentrations of 0.006, 0.011, and 0.013 mg/mL, respectively. These values were calculated using the Beer–Lambert law and an extinction coefficient (α) of 30.0 mL mg^{-1} cm^{-1} and absorption values at $\lambda = 700$ nm (see Figure S4 of the Supporting Information).[27] It is clear from these values that phosphine treatment of SWNTs had a dramatic effect on the solubility of the carbon nanotubes, almost doubling the amount of material that can be dispersed in the solvent.

Raman spectra of SWNT-PPh₃ and SWNT-POc₃ show an expected enhancement in intensity of the disorder related D band (ca. 1330 cm^{-1}) compared to the SWNT-PA sample. This Raman mode, linked to an increase in scattering sites and a lowering of the symmetry of the SWNT structure,[28] indicates that groups have been introduced on to the walls of the nanotube material (Figure 6). Importantly, however, the increase in the D band intensity reported here is well below those reported for other functional groups covalently attached to carbon nanotubes,[23–26] which is in keeping with the low levels of functionalization determined by XPS and TGA, thus confirming the integrity of the samples. Similarly, only a small variation in the relative intensities of the radial breathing modes (RBMs) of SWNT-PPh₃ and SWNT-POc₃ was evident upon comparison with the SWNT-PA material, indicating that there is little perturbation of the electronic structure upon modification.

The best comparison for the phosphine-treated SWNTs discussed here is the interaction of amines, particularly

(20) Hoste, S.; Van de Vandel, D. F.; Van der Kelen, G. P. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *17*, 191.
(21) Moulder, J. F.; Stickle, W. F.; Soble, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Physical Electronics: Chanhassen, MN, 1995.
(22) Fluck, E.; Weber, D. *Z. Naturforsch. B* **1974**, *29*, 603.

(23) 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.
(24) Kazaoui, S.; Minami, N.; Jacquemin, R.; Kataura, H.; Achiba, Y. *Phys. Rev. B* **1999**, *60*, 13339.
(25) Kazaoui, S.; Minami, N.; Kataura, H.; Achiba, Y. *Synth. Met.* **2001**, *121*, 1201.
(26) Hu, H.; Zhao, B.; Hamon, M. A.; Kamaras, K.; Itkis, M. E.; Haddon, R. C. *J. Am. Chem. Soc.* **2003**, *125*, 14893.
(27) Landi, B. J.; Ruf, H. J.; Worman, J. J.; Raffaelle, R. P. *J. Phys. Chem. B* **2004**, *108*, 17089.
(28) Dresselhaus, M. S.; Eklund, P. C. *Adv. Phys.* **2000**, *49*, 705.
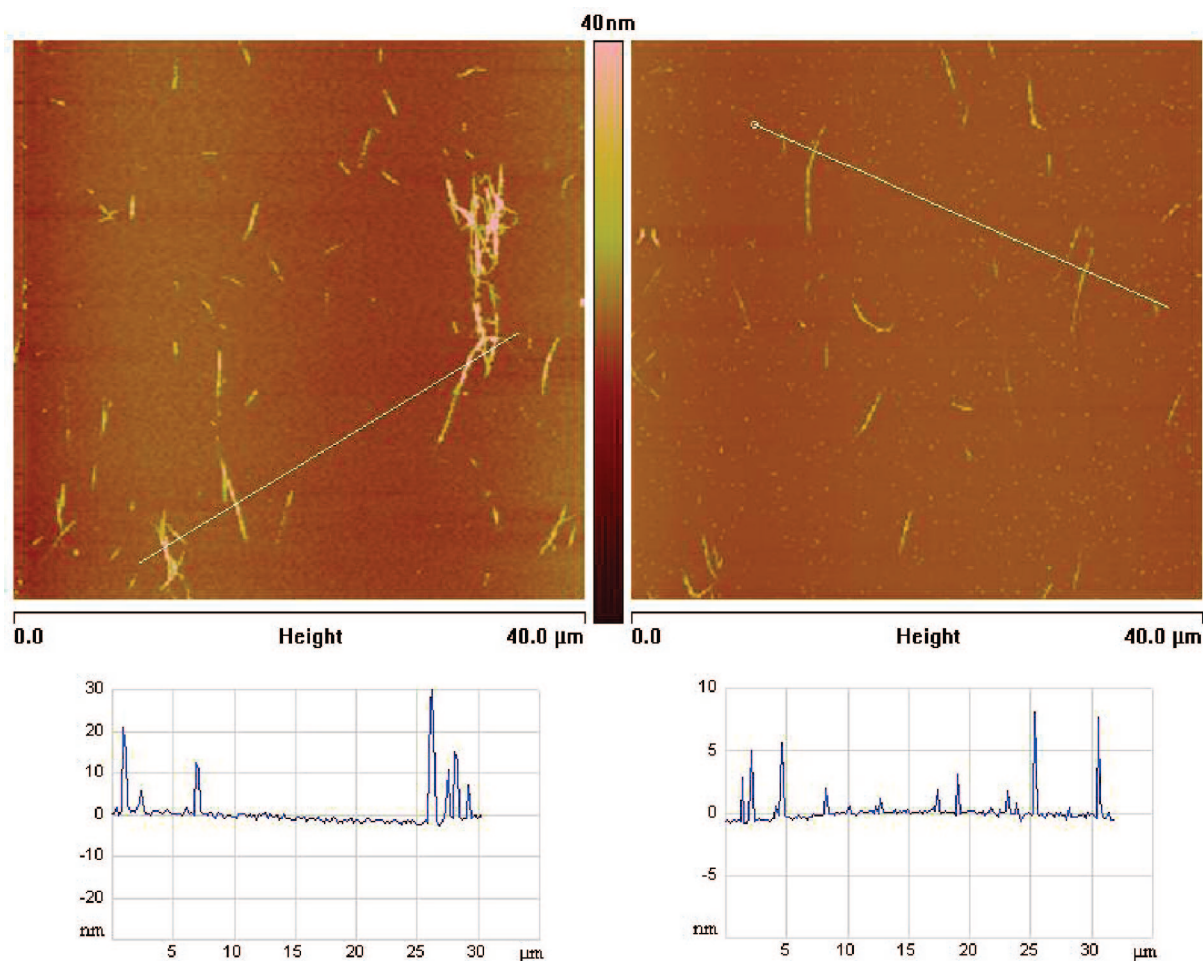
Figure 2. Tapping mode AFM height images of SWNT-PA (left) and SWNT-POc₃ (right) showing the distribution of SWNT bundles on a mica surface. Bottom panels show the corresponding height profiles of the white lines shown in the image.
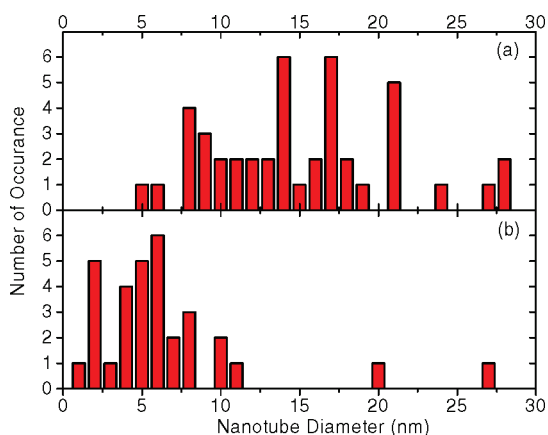

Figure 3. Histograms showing the diameter distribution of the nanotubes (shown in Figure 2) for (a) SWNT-PA (mean diameter 15.1 nm, $\sigma = 5.7$) and (b) SWNT-POc₃ (mean diameter 6.5 nm, $\sigma = 5.2$).
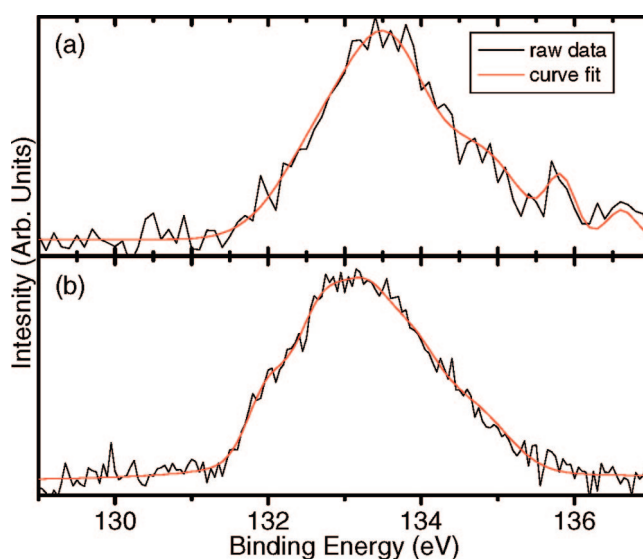

Figure 4. P 2p photoelectron spectra of SWNT samples treated with (a) triphenylphosphine (SWNT-PPh₃) and (b) tri-*n*-octylphosphine (SWNT-POc₃). The red line represents the fitted curve to the experimental data (black).

octadecylamine (ODA), with carbon nanotubes which is well documented.[29–33] The nature of this amine interaction is predominantly physisorption although some degree of non-

covalent functionalization, with the formation of zwitterions from the interaction of the amine with residual carboxylic

(29) Kong, J.; Franklin, N.; Zhou, C.; Chapline, M.; Peng, S. *Science* **2000**, *287*, 622.
(30) Kong, J.; Dai, H. *J. Phys. Chem. B* **2001**, *105*, 2890.
(31) Basiuk, E. V.; Monroy-Pelaez, M.; Puente-Lee, I.; Basiuk, V. A. *Nano Lett.* **2004**, *4*, 863.
(32) Chattopadhyay, D.; Galeska, I.; Papadimitrakopoulos, F. *J. Am. Chem. Soc.* **2003**, *125*, 3370.

(33) Choi, N.; Kimura, M.; Kataura, H.; Suzuki, S.; Achiba, Y.; Mizutani, W.; Tokumoto, H. *Jpn. J. Appl. Phys.* **2002**, *41*, 6264.
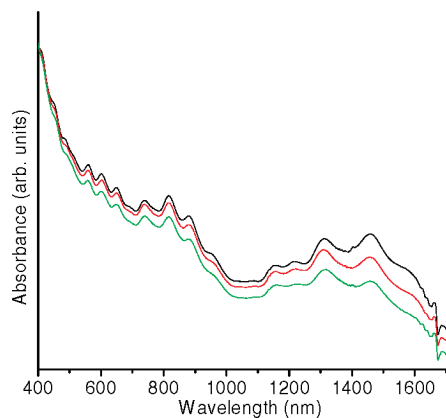
Single-Wall Carbon Nanotubes

Chem. Mater., Vol. 20, No. 5, 2008 1709

Figure 5. Normalized (at 400 nm) UV–vis–NIR spectra, recorded in 1,2-dichlorobenzene, of SWNT-PA (black), SWNT-PPh$_3$ (red), and SWNT-POc$_3$ (green).
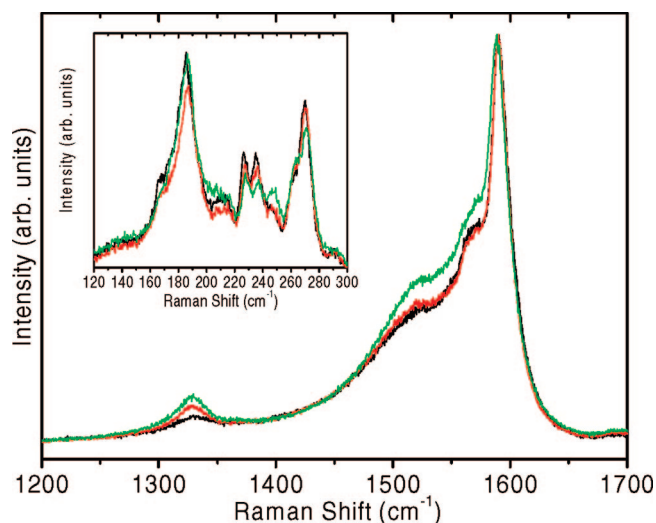

Figure 6. Normalized Raman spectra of SWNT-PA (black), SWNT-PPh$_3$ (red), and SWNT-POc$_3$ (green). The inset shows the corresponding radial breathing modes (RBM).

acid groups, is possible.[29,30,32] It has also been shown that under suitable conditions amination of the nanotubes (the activation of an N–H bond over a nanotube π-bond) can occur in an analogous manner to that found in C$_{60}$ chemistry.[31] In the case of the phosphine-treated SWNTs described here the physisorption of the phosphine can be ruled out as the attachment of the tertiary phosphines to the SWNTs is not reversed even after repeated ultrasonication and washing with solvent (dichloromethane). Interaction of the tertiary phosphines with defect sites, while possible, is thought unlikely as a similar degree of functionalization was observed upon reaction with SWNTs that were known to contain a greater number of oxygen-containing defects (i.e., SWNTs that had not been subjected to annealing at high temperature under vacuum). It is worth noting that a tertiary amine (triethylamine) has been shown to untangle bundled SWNTs and stabilize nanotube dispersions.[33]

Conclusion

Tertiary phosphines (triphenyl- and tri-*n*-octylphosphine) have been shown to interact with SWNTs using a simple and robust solvent-free route. XPS data recorded in the P 2p region clearly show that the phosphorus atoms present in the phosphine-treated nanotube material are in a different chemical environment than found in pure phosphine, indicating that charge transfer between the electron-donating phosphorus atom and the carbon nanotube may have taken place. Modification with phosphines resulted in significant debundling of the SWNTs, allowing stable dispersions in common organic solvents to be prepared. Although the modified material disperses readily the electronic properties of the nanotube are not perturbed, and the surface of the nanotube is thought to be still accessible as the degree of functionalization is low (ca. 1 at. %). The effect of the tertiary phosphines on the electrical conductivity of SWNTs is currently under investigation.

Supporting Information Available: AFM image of SWNT-PPh$_3$ dispersion (Figure S1), fitted and deconvoluted components of the XPS data for SWNT-PPh$_3$ and SWNTs-POc$_3$ (Figure S2), TGA data for SWNT-PPh$_3$ and SWNTs-POc$_3$ (Figure S3), and UV–vis–NIR spectra of SWNT-PA, SWNT-PPh$_3$, and SWNTs-POc$_3$ in DMF (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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