

Articles

Amino-Functionalized Carbon Nanotubes for Binding to Polymers and Biological Systems

T. Ramanathan, F. T. Fisher, R. S. Ruoff, and L. C. Brinson*

Department of Mechanical Engineering, Northwestern University, Evanston, Illinois 60208

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Single-walled carbon nanotubes (SWCNT) functionalized with amino groups were prepared via chemical modification of carboxyl groups introduced on the carbon nanotube surface. Two different approaches (amide and amine-moieties) were used to produce the amino-functionalized nanotubes. The amino-termination allows further chemistry of the functionalized SWCNTs and makes possible covalent bonding to polymers and biological systems such as DNA and carbohydrates. The functionalization of the SWCNTs was characterized in detail using FTIR and XPS.

Introduction

Research on carbon nanotubes (CNTs) has focused on exploiting the wide range of outstanding mechanical, electronic, and thermal properties of these materials.^{1,2} However, many of these interesting and unique properties can only be realized once the CNTs are integrated into more complex assemblies.^{3,4} A common technique to incorporate SWCNTs into such assemblies is through chemical functionalization of the SWCNTs, which enables chemical covalent bonding between the SWCNTs and the material of interest.^{5–8} Examples of such covalent linkages achieved through chemical functionalization have been utilized in SWCNT-reinforced polymer composites^{9–12} and biological systems.^{13–15} In SWCNT–polymer composites, chemical functionalization

is used to enhance the nanotube–polymer interface. Increasing the interfacial binding between SWCNTs and the polymer will improve the interfacial strength and thus load transfer to the SWCNTs, with the goal of improving the macroscopic mechanical properties of the composite. Functionalized nanotubes are also typically easier to disperse in organic solvents¹⁶ and water,^{17,18} which can improve the dispersion and homogeneity of the SWCNTs within the polymer. While property improvements based on carboxylated functionalized MWCNTs in a polymer⁹ and SWCNT in epoxy¹⁹ have been obtained, results for amino ($-\text{NH}_2$) functionalized SWCNT composites have yet to be reported. In one study, amino-terminated MWNT/epoxy showed improved dispersion and increased interfacial interaction between nanotubes and polymer but no quantitative thermomechanical or chemical results are provided.²⁰ The use of covalent chemistry to link DNA to SWCNTs is also expected to provide excellent stability, accessibility, and selectivity compared to noncovalent bonding.²¹

Here, the preparation of amino-functionalized SWCNTs by two different approaches is described. Both protocols are based on chemical manipulation of carboxylic acid residues, easily introduced onto the SWCNTs by chemical oxidation. The first approach involves a direct coupling of ethylenediamine with the carboxylic groups to introduce amino groups via amide formation. The second approach first involves reduction of the carboxyl group to hydroxymethyl, followed by transformation into aminomethyl groups. The

* Corresponding author. Phone: 847-467-2347; fax: 847-491-3915; e-mail: cbrinson@northwestern.edu.

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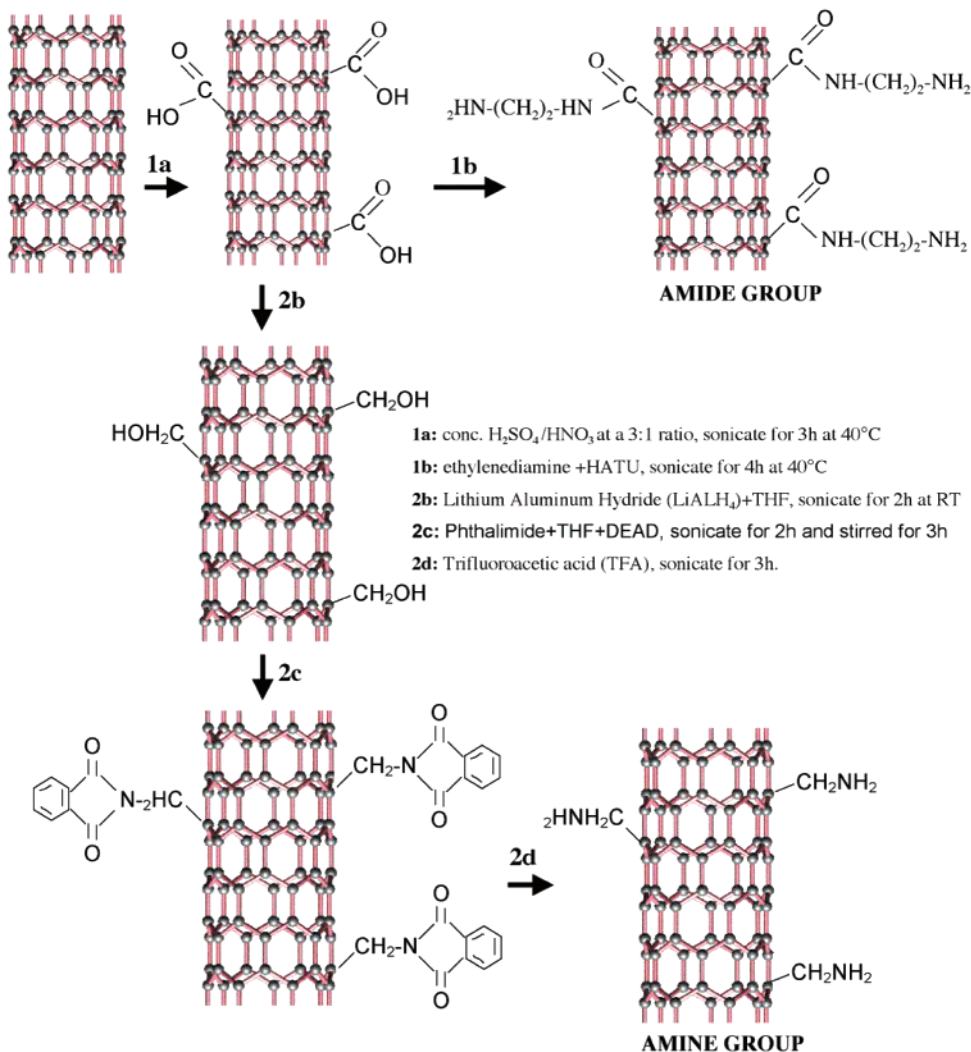


Figure 1. Schematic of the reaction scheme to form SWCNT with amino functionalization: 1a and 1b shows the direct amide functionalization while 1a–2d shows the amine functionalization of the SWCNT.

chemical versatility of the amino group will allow controlled covalent bonding to polymers or biological molecules. The reaction schemes are highlighted in Figure 1.

Experimental Section

Materials. Single-walled carbon nanotubes were purchased from Carbon Nanotechnologies, Inc. in the form of BuckyPearls. All other chemicals were purchased from Fisher Scientific and used as received without further purification. Bath sonication (Branson 3510) and filtration using polycarbonate membrane filters (Millipore, Cat. No. TCTP04700) were employed as indicated below. The progress of the reaction was characterized using Fourier transform infrared spectroscopy, FTIR (Bio-Rad FTS-60, Bio-Rad Laboratories Inc., Cambridge, MA, Resolution 4), and X-ray photoelectron spectroscopy, XPS (Al $K\alpha$ source, Omicron ESCA Probe, Taunusstein, Germany)

Oxidation of Carbon Nanotubes. Following a reported procedure, the as-received purified HiPCO SWCNTs were first treated with a 3:1 mixture of concentrated sulfuric and nitric acid (40 mL). This mixture was then sonicated for 3 h at 40°C in an ultrasonic bath to introduce carboxylic acid groups on the SWCNT surface.²⁷

[While hydrogenation²² and fluorination²³ functionalization methods have also been presented in the literature, carboxylation²⁴ is well-suited for the present work because it can be covalently bonded to form ester²⁵ or amide²⁶ linkages.] Upon completion, the mixture was added dropwise to 200 mL of cold distilled water and then filtered through a $10\text{-}\mu\text{m}$ pore size polycarbonate filter paper; the filtrant was then washed with distilled water until no residual acid was present. The sample was then dried in a vacuum oven at 80°C for 4 h.

Functionalization of Carbon Nanotubes with Ethylenediamine: Twenty milligrams of the oxidized nanotubes was dispersed by sonication in 10 mL of ethylenediamine. One milligram of the

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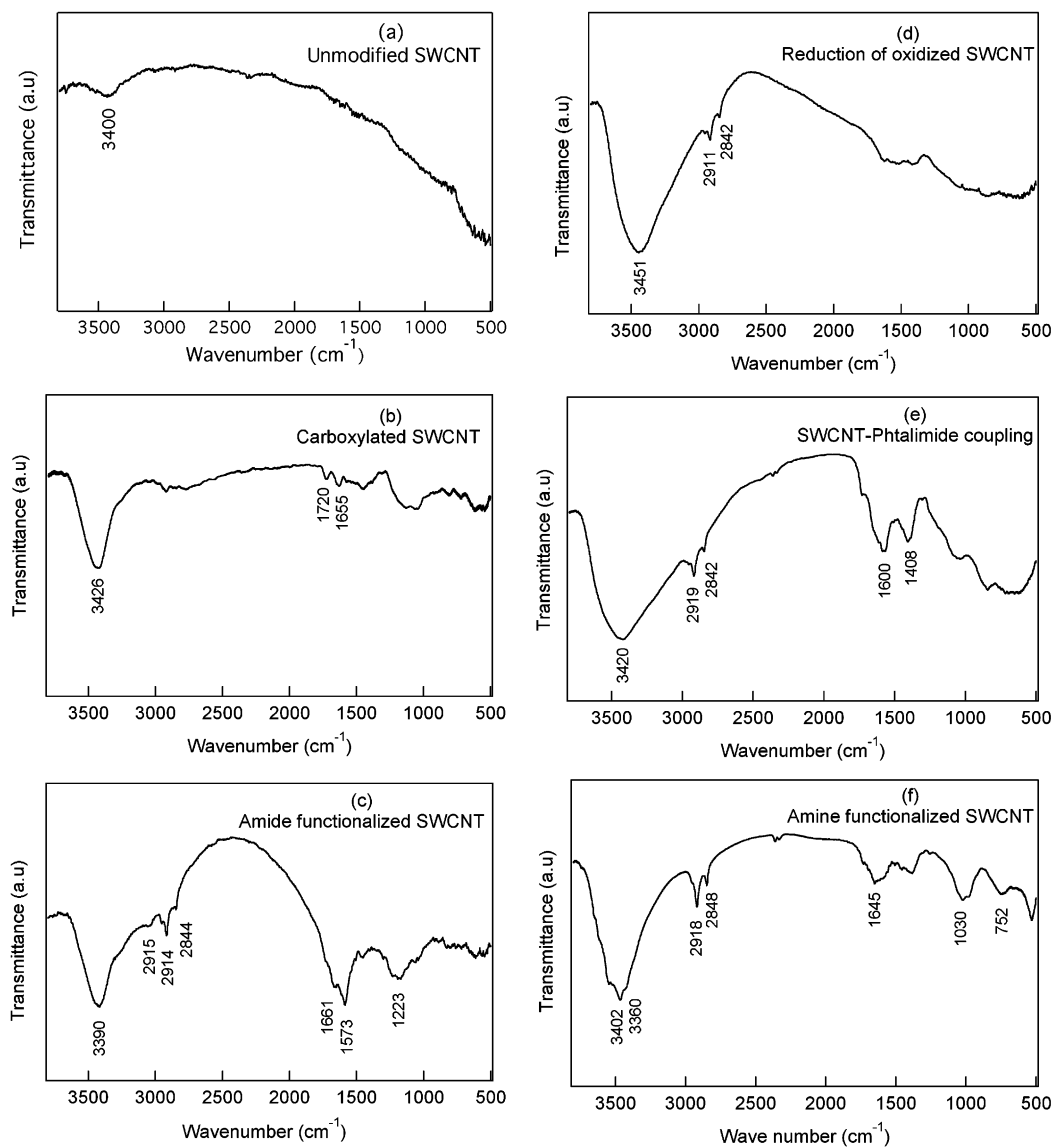


Figure 2. FTIR spectra of SWCNT samples. (a) As-received, (b) carboxylated, (c) amide-functionalized, (d) reduction of oxidized SWCNTs, (e) phthalimide coupling, and (f) amine-functionalized.

coupling agent *N*-[(dimethylamino)-1*H*-1,2,3-triazolo[4,5,6]pyridin-1-ylmethylene]-*N*-methylmethanaminium hexafluorophosphate *N*-oxide (HATU) (Scheme 1b in Figure 1)²⁸ was then added and sonication continued for 4 h. The product was then diluted with 200 mL of methanol and filtered using 10- μ m pore size polycarbonate filter paper, after which the filtrant was washed extensively with excess methanol. The functionalized SWCNTs were then dried in a vacuum oven at 80 °C for 4 h.

Reduction of Oxidized SWCNT. Twenty milligrams of carboxylated SWCNT was dispersed in anhydrous tetrahydrofuran (THF) by sonication for 30 min. After sonication, 2 mg of lithium aluminum hydride (LiAlH₄) was added to the dispersion and treated by sonication for 1 h. The reaction mixture was then slowly added to 200 mL of methanol and filtered through polycarbonate filter paper. The product was dried in a vacuum oven at 80 °C for 3 h.

Phthalimide Coupling and Hydrolysis. Reduced SWCNT material was dispersed in THF via sonication for 30 min and then 10 mg of phthalimide was added followed by 2 mg of diethylazodicarboxylate (DEAD) coupling agent. The solution was sonicated for 2 h followed by stirring for 3 h.^{29,30} The mixture was

then diluted with 200 mL of methanol and filtered. The sample was dried at 80 °C under vacuum for 4 h. The product (phthalimide-functionalized nanotubes) was treated with 10 mL of trifluoroacetic acid (TFA) for 3 h under sonication and then filtered.³¹ The resulting product, with aminomethyl groups attached to the SWCNT (Scheme 2 b–d, Figure 1), was then dried at 80 °C under vacuum for 3 h.

Analytical Procedures. FTIR and XPS were used to verify each step of the SWNT chemical functionalization process as discussed below. The chemically modified nanotubes were heated in a vacuum oven (25 in. Hg) at 80 °C overnight prior to both FTIR and XPS characterization. For FTIR, SWNTs were ground thoroughly with potassium bromide (KBr) at approximately 1–3 wt % and the resulting powder was pressed into a transparent pellet using a hydraulic press. XPS samples are prepared by placing the SWCNT sample on carbon conductive tape on the sample holder.

Result and Discussion

Infrared Spectroscopy. Figure 2a shows FTIR results for the as-received HiPCO SWCNTs. The appearance of a weak

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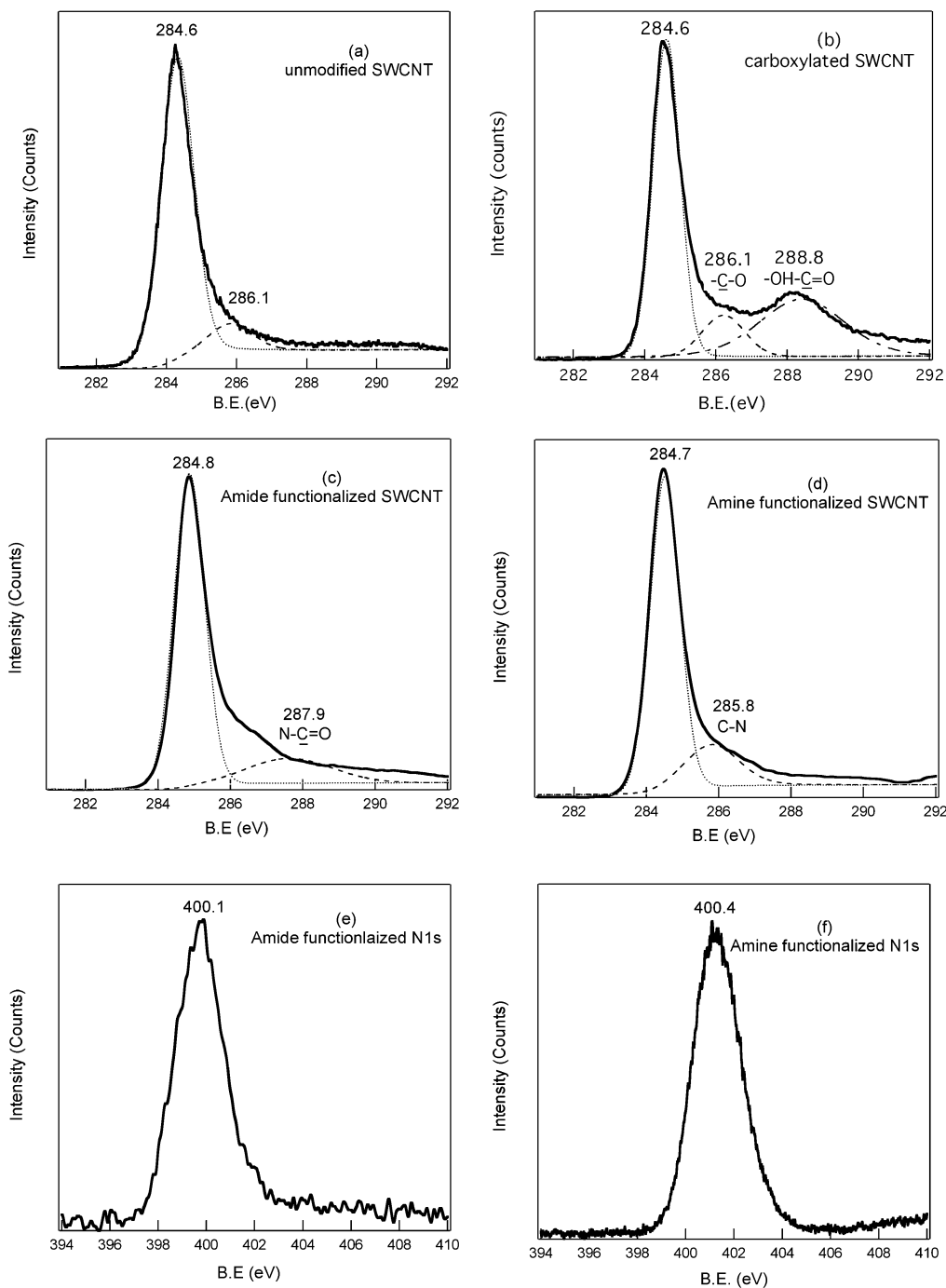


Figure 3. XPS spectra of SWCNT samples (a) as-received C1s spectra, (b) carboxylated C1s spectra, (c) amide-functionalized C1s spectra, (d) amine-functionalized C1s spectra, (e) amide-functionalized N1s spectra, and (f) amine-functionalized N1s spectra. Dashed lines represent the theoretical XPS spectra for different bonds.

and broad band at $\sim 3400\text{ cm}^{-1}$ is attributed to the presence of O–H groups on the surface of the as-received SWCNTs and is believed to result from either ambient atmospheric moisture tightly bound to the SWCNTs or oxidation during purification of the raw material. In the FTIR spectrum of the oxidized SWCNT (Figure 2b), the peak at $\sim 1720\text{ cm}^{-1}$ is attributed to the C=O stretch of the carboxylic (COOH) group.²⁵ The IR spectrum of the amide-functionalized SWCNT samples, SWCNT–CO–NH(CH₂)₂NH₂ (Figure 2c), shows the disappearance of the band at 1720 cm^{-1} and

a corresponding appearance of a band with lower frequency (1661 cm^{-1}) assigned to the amide carbonyl (C=O) stretch. In addition, the presence of new bands at 1573 and 1223 cm^{-1} , corresponding to N–H in-plane and C–N bond stretching, respectively, further confirms the presence of the amide functional group. Similar results for diamine-functionalized SWCNTs have been previously reported in the literature.^{32,33}

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Table 1. Atomic Concentrations Calculated from XPS Experimental Data

| sample | concentration of oxygen (atomic %) | concentration of nitrogen (atomic %) |
|-----------------------------|------------------------------------|--------------------------------------|
| raw HiPCO SWCNTs | 3.4 ± 0.4 | NA |
| COOH-functionalized SWCNTs | 8.75 ± 0.2 | NA |
| amide-functionalized SWCNTs | 7.14 ± 0.8 | 13.4 ± 0.5 |
| amine-functionalized SWCNTs | NA | 20.6 ± 0.6 |

The infrared spectrum of the material treated with lithium aluminum hydride (Figure 2d) shows the reduction of the carboxyl groups (SWCNT-COOH) to hydroxymethyl (SWCNT-CH₂OH) (Scheme 2b) as indicated by the disappearance of the C=O bands (at 1720 cm⁻¹) and the appearance of bands at 2911 and 2842 cm⁻¹ corresponding to the C-H stretch vibrations of the methylene group. Figure 2e shows the IR spectrum of the phthalimide derivative, where the new bands at 1600 and 1408 cm⁻¹ are assigned to the C=O and C-N bonds of the phthalimido moiety, respectively. Finally, Figure 2f shows the IR spectrum of the SWCNTs with attached aminomethyl groups (Scheme 2d). The NH₂ stretch band appears at 3402 cm⁻¹. The small 3360 cm⁻¹ peak may be due to the NH₂ symmetric stretch of the amine group. The scissoring in-plane bending mode of the primary amine NH₂ group at 1645 cm⁻¹ is broader than other peaks in this region, such as the carbonyl stretch and aromatic ring modes. A broad band at 752 cm⁻¹ is due to the out-of-plane NH₂ bending mode. Bands at 2918 and 2848 cm⁻¹ represent the stretching of the CH₂ group, while C-N bond stretch vibrations appear at 1030 cm⁻¹. The presence and location of the NH₂ and C-N bands confirm the presence of the saturated primary amine.

X-ray Photoelectron Spectroscopy. High-resolution XPS spectra for unmodified, carboxylated, and amide- and amine-functionalized SWCNTs are shown in Figure 3. Samples were degassed overnight within the XPS chamber (10⁻³ mbar) prior to analysis of the sample. The raw XPS data for each sample were analyzed to determine peak locations and areas in relation to specific binding energies which best fit the experimental data. Aside from the main C-C peak at 284.6 eV, additional photoemission present at higher binding energies for the unmodified and functionalized SWCNTs indicates the presence of carbon atoms bonded to other functional groups. The binding energy peak at 286.1 eV for the as-received SWCNT is attributed to atmospheric oxidation or residual oxides resulting from the SWCNT purification process, consistent with the FTIR results discussed above.

For the carboxylic-functionalized SWCNT sample, the additional higher binding energies at 286.1 and 288.8 eV shown in Figure 3b represent the -C-O and O-C=O (carboxylic acid) contributions, respectively.^{33,34} For the amide (-N-C=O-) functionalized SWCNTs shown in Figure 3c, the XPS results show a slight broadening of the main C1s peak at 284.8 eV as well as an additional binding energy peak at 287.9 eV, which is 3.1 eV higher than the main C1s peak and is assigned to an amide group.²¹ In addition, the absence of a peak around 288.8 eV (see Figure 3b) confirms the reduction of the carboxylic acid group as

it is converted to an amide. The peak for the amide (-N-C=O-) linkage is about 1 eV less than the carbonyl peak (C=O) in carboxylic (-O-C=O) acid group, because of an electron donation from the adjacent nitrogen atom. Figure 3d shows the C1s of the amine-functionalized SWCNTs, in which the main C-C is at 284.7 eV and the second peak at 285.8 shows the C-N bond in the amine (CH₂-NH₂), which is about 2.2 eV less than the amide (-N-C=O-) group.

The nitrogen in the amide contains nonbonding electrons that are in a P-type orbital; oxygen in the carbonyl group has electrons in the same orbital. These P-type electrons can conjugate, allowing the electrons to "smear out" along the C-N bond. The chemical effect of conjugation is a stiffer C-N bond than in the amine group, where an electron donation from the adjacent nitrogen atom may decrease the C-N binding energy. This stiffer bonding in the amide results in a higher C-N binding energy. The amide and amine functionalization are further confirmed in the N1s spectrum (see Figure 3e-f), where the binding energy peak at 399-401 eV is attributed to the formation of an amide and amine linkage on the SWCNTs. [N1s binding energies for amides and amines are expected between 399.5 and 400.5 eV.]^{12,35} As expected, no N1s peaks were observed in the pure and carboxylated SWCNT samples. These XPS results are consistent with other SWCNT studies presented in the literature.²¹

On the basis of these XPS results, the C1s, O1s, and N1s peak areas for unmodified, carboxylic, amide-, and amine-functionalized SWCNTs were determined. The peak areas and use of atomic sensitivity factors provide the atomic concentration of each element, providing a quantitative measure of the extent of functionalization.³⁵ The concentration values given in Table 1 were based on the averaged peak areas of three different spots in the same sample and calculated using sensitivity factors 1.0, 2.85, and 1.77 for carbon, oxygen, and nitrogen, respectively.³⁵ The oxygen concentration for unmodified, carboxylic-functionalized, and amide-functionalized SWCNTs calculated in this manner are given in Table 1. The higher surface oxygen content for the carboxylic acid functionalized SWCNTs, in comparison to that of the as-received materials, is evidence of COOH groups on the SWCNT surface. For the amide-functionalized SWCNTs, the slight decrease in surface oxygen content indicates the conversion of the COOH groups to CONH- groups and is again consistent with the FTIR results. No surface oxygen was found in the amine-functionalized SWCNT samples. In addition, nitrogen concentrations of 13.4 atomic % and 20.6 atomic %, respectively, were measured for the amide- and amine-functionalized SWCNTs (see Table 1). Consistent with the FTIR results, these XPS results

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confirm the conversion of the carboxylic acid to the desired amide and amine functionalization of SWCNT.

Summary

Two approaches for amino functionalization of SWCNTs were presented. Initial oxidation reaction of the HiPCO SWCNTs in the 3:1 H₂SO₄:HNO₃ acid solution results in carbonyl (C=O) groups on the SWCNT surface. In the first approach, these carboxylated SWCNTs were treated with ethylenediamine in a controlled reaction to link the free amine group to the SWCNTs to form an amide functionalization. The second approach involved the reduction of the carboxyl group to hydroxymethyl, followed by transformation into aminomethyl group. In both approaches, SWCNT contains amine groups (-NH₂) covalently tethered to the nanotube surface. FTIR and XPS results on samples at different stages of the functionalization process confirm these reactions. The amine termination of the SWCNTs thus provides a convenient link for covalent bonding between the SWCNTs and polymer or biological systems via amide and amine linkages.

The methods for achieving amide and amine functionalization described here have several potential applications. Biological systems (e.g., DNA, carbohydrates) can be attached to the amine-terminated end, allowing the SWCNT to be used for biotechnological applications. In the field of polymer composites, the proposed method provides the polymer chemist with a flexible and efficient route to

covalently link SWCNTs to the polymer matrix, which is expected to enhance the interface in these materials and result in improved mechanical performance. Common polymer matrixes such as PMMA and PAA are ideally suited to interact with SWCNTs with amino functionalization. Significant improvements in dispersion, mechanical, electrical, and thermal properties of polymer (PMMA) composites based on these functionalized SWCNTs are reported elsewhere.³⁶

Additional issues that should be explored for this and other functionalizations include quantifying the amount, distribution, and locations of functionalities on the nanotube surfaces. Recent work has illustrated that selectively attached gold or selenium nanoparticles can be used to identify the location of defects in single and multiwall nanotubes.^{37,38}

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