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Attachment of Nitrogen and Oxygen Centered Radicals to Single-Walled Carbon Nanotube Salts

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Carbon nanotube salts, prepared by treating single-walled carbon nanotubes (SWNTs) with lithium in liquid ammonia, react with *N*-halosuccinimide by electron transfer to generate transient radical anions that yield succinimidyl radicals and halide anions. Similarly, alkyl peroxides, when treated with SWNT salts, give rise to alkoxy radicals and alkoxides. The free radicals add to the sidewalls of nanotube salts to form succinimidyl and alkoxy derivatized SWNTs. The functionalized SWNTs can then be converted to amino and hydroxyl SWNTs by hydrolysis with hydrazine or with fuming sulfuric acid, respectively. Hydrolysis of alkoxy derivatized SWNTs with D_2O/D_2SO_4 led to the deuterated analogue of hydroxy SWNT, as shown by Fourier transform infrared (FTIR) spectroscopy. These reactions constitute a two-step synthesis of aminated and hydroxylated SWNTs. Covalent sidewall functionalization was confirmed by thermal gravimetric analysis (TGA), Raman spectroscopy, FTIR spectroscopy, and high-resolution transmission electron microscopy (HRTEM). Aminated and hydroxylated SWNTs were characterized by FTIR and X-ray photoelectron spectroscopy (XPS).

Introduction

Covalent sidewall functionalization[1−5] of single-walled carbon nanotubes (SWNTs)[6,7] has been an important area of research since the discovery of SWNTs. Functionalized nanotubes show great promise in nanocomposite[8−10] formation as well as in biomedical applications.[11,12] Functionalization of SWNTs by free radicals[13−17] provides an efficient and flexible route to derivatized carbon nanotubes. Reductive alkylation[18] of SWNTs using lithium and organic halides in liquid ammonia yields nanotubes functionalized by alkyl or aryl[19] carbon-centered radicals with preferential attack on metallic and small diameter SWNTs.[20] A recent report[21] on single electron transfer (SET) from SWNT salts to sulfides and disulfides supports the free radical mechanism. In this manuscript we demonstrate that SWNT salts react with *N*-halosuccinimide to yield transient radical anions that dissociate into nitrogen-centered free radicals and halides. These nitrogen-centered radicals add readily to the sidewalls of the debundled carbon nanotubes. In a similar fashion, alkoxy functionalized SWNTs are formed when alkyl peroxides are added to the carbon nanotube salts. The succinimidyl and alkoxy-derivatized SWNTs are then hydrolyzed to form aminated and hydroxylated SWNTs. These simple functionalized SWNTs are promising for attaching various other functional groups, amino acids, and DNA to the SWNTs for chemical and biological applications.[22−24]

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Experimental Section

Materials. SWNTs were prepared by the HiPco process using carbon monoxide as the feedstock and iron pentacarbonyl as the catalyst. The crude SWNTs were purified using the method of Xu et al.[25] Lithium (granules, 99%), *N*-bromosuccinimide (NBS), *N*-chlorosuccinimide (NCS), *N*-iodosuccinimide (NIS), *N*-bromophthalimide, dicumyl peroxide, hydrazine monohydrate (≥98%), fuming H_2SO_4 (20% free SO_3), and D_2SO_4 (98 wt % solution in D_2O) were purchased from Aldrich.

General Procedure for Functionalization of SWNTs.[18] In a typical experiment, SWNTs (1.6 mmol) were added under argon to a dry 100 mL three neck round-bottomed flask fitted with a dry ice condenser. Ammonia (60 mL) was condensed into the flask followed by the addition of lithium metal (16.6 mmol). The selected reagent (6.4 mol) was added, and the mixture was stirred overnight at −33 °C with slow evaporation of ammonia. The flask was cooled in an ice bath, and the reaction mixture was quenched by the slow addition of ethanol (15 mL) followed by water (20 mL). The reaction mixture was acidified with 10% HCl and the nanotubes were extracted into hexane and washed several times with water. The hexane layer was filtered through a 0.2 μm PTFE membrane and the residue washed successively with ethanol and chloroform. The functionalized SWNTs were dried overnight in vacuo at 80 °C.

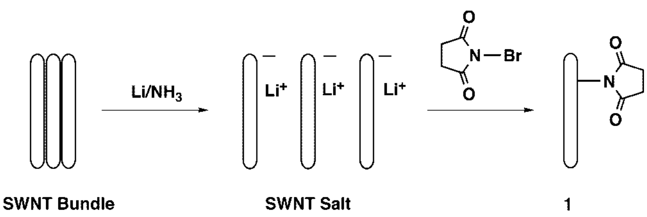
Synthesis of Aminated SWNTs. Twenty milligrams of the succinimide or phthalimide derivatized SWNTs were treated with 5 mL of hydrazine monohydrate (≥98%) in 10 mL of methanol. The reaction mixture was stirred under an argon atmosphere for one day. The resulting product was filtered through a 0.2 μm PTFE membrane and washed several times with methanol. The functionalized SWNTs were dried overnight in vacuo at 80 °C.

Synthesis of Hydroxylated SWNTs. Twenty milligrams of the cumyloxy derivatized SWNTs were dispersed in oleum (20 mL, H_2SO_4, 20% free SO_3) and heated under argon at 80 °C for 4 h to yield hydroxylated SWNTs. The suspension was diluted with water, filtered through a PTFE membrane (0.2 μm), washed with water, and dried overnight in vacuo at 80 °C.

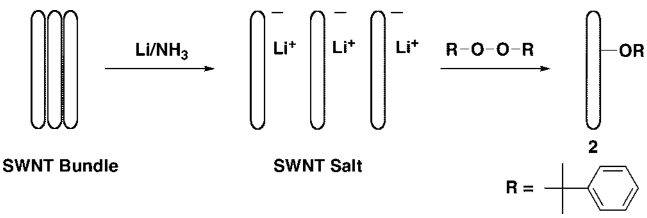
Synthesis of the Deuterated Analogue of Hydroxylated SWNTs. Twenty milligrams of the *t*-butyloxy or cumyloxy functionalized SWNTs were dispersed in D_2SO_4 (98 wt % solution in D_2O) and heated under argon at 80 °C for 4 h. The suspension of SWNT-OD was then diluted with water, filtered through a PTFE membrane (0.2 μm), and dried overnight in vacuo at 120 °C.

Characterization. The functionalized SWNTs were characterized by Raman spectroscopy, thermal gravimetric analysis (TGA), FTIR-ATR spectroscopy, X-ray photoelectron spectroscopy (XPS), and high-resolution transmission electron microscopy (HRTEM). FTIR spectra were obtained using a Nicolet spectrometer with an ATR accessory. Raman spectra were collected from samples using a Renishaw 1000 micro-Raman system with a 785 nm laser source. Multiple spectra (3−5) were obtained, normalized to the G band, and averaged to present a comprehensive overview of the material. TGA data were obtained using a model SDT 2960 TA instrument in an argon atmosphere. Samples were degassed at 80 °C and then heated at 10 °C/min to 700 °C and held there for 20 min. XPS data were obtained using a physical electronics (PHI QUANTERA) XPS/ESCA system, with a base pressure of 5 × 10^{-9} Torr. A monochromatic Al X-ray source at 100 W was used with a 26 eV pass energy, a 45° takeoff angle, and a 100.0 μm beam diameter. Low-resolution survey scans and higher resolution scans of C, O, and N were taken. At least two separate locations were analyzed for each sample. HRTEM images were taken using a high-resolution transmission electron microscope (JEM-2010F) operated at an accelerating voltage of 200 kV.

Scheme 1. Functionalization of SWNTs by *N*-Bromosuccinimide



Scheme 2. Functionalization of SWNTs by Dicumyl Peroxide



Results and Discussion

Single-walled carbon nanotube salts,[26] prepared by the reduction of purified HiPco SWNTs using lithium in liquid ammonia, react with *N*-bromosuccinimide (NBS) to yield nanotubes functionalized by nitrogen-centered free radicals (Scheme 1). Addition of NBS to a suspension of the SWNT salts leads to NBS radical anions that eventually produce succinimidyl radicals.[27] A similar reaction was observed when dicumyl peroxide (98%) was reacted with single-walled carbon nanotube salts (Scheme 2).[28]

Although succinimidyl[29] and alkoxy radicals[17] can attack neutral SWNTs, the dominance of SWNT radical ions in our system leads us to suggest that these radical ions recombine with succimidyl and alkoxy radicals. When similar reactions were performed with *N*-chlorosuccinimide, *N*-iodosuccinimide, and *tert*-butyl peroxide, all of them were found to react with the SWNT salts, as verified by TGA and Raman spectroscopy. The presence of succinimide as a major byproduct is revealed by a peak at *m/z* 99 $\{C_4H_5NO_2{}^{+}\}$ upon GC-MS analyses of the filtrate from the preparation of **1**. This byproduct presumably arises by protonation of succinimide anion during workup.

Raman spectra of the SWNTs before and after functionalization by *N*-iodosuccinimide are presented in Figure 1a,b, respectively. Unfunctionalized material shows bands corresponding to the disorder mode (D band) at 1290 cm^{-1} and

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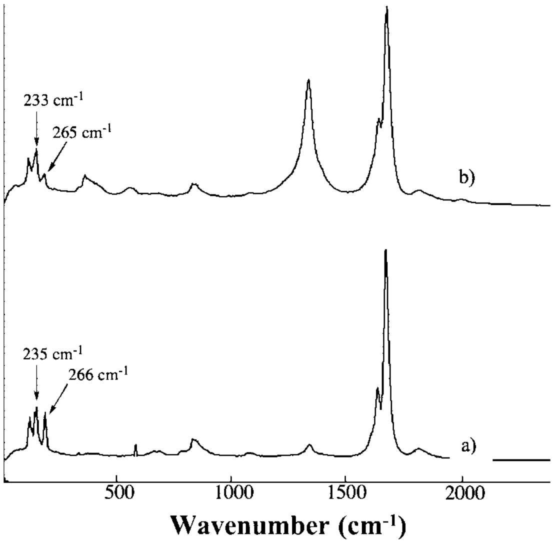


Figure 1. Raman spectra of (a) purified SWNTs; (b) succinimide functionalized SWNTs.

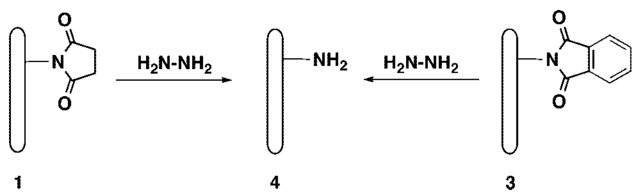
Table 1. Weight Loss of SWNT Derivatives Determined by TGA in Argon from 80 to 800 °C

derivatizing reagent	observed weight loss (%)	carbon/functional group ratio
N-bromosuccinimide	19	34:1
N-iodosuccinimide	25	21:1
N-chlorosuccinimide	10	68:1
dicumyl peroxide	16	48:1
tert-butyl peroxide	14	27:1

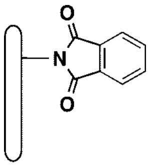
the tangential mode (the graphitic "G" band) at 1590 cm^{-1}. The greatly enhanced D band observed upon functionalization (Figure 1b) results from the chemical disruption of the sp^2 hybridized carbon atoms in the hexagonal framework of the nanotube walls. The strong radial breathing mode (RBM) feature observed at 266 cm^{-1} (Figure 1a) is attributed to bundling of the pristine SWNTs. This band is less intense (Figure 1b) in the functionalized material, demonstrating that debundling has occurred[26,30] by intercalation of lithium ions. The Raman spectrum of **2** displays a D/G ratio (by height) of 0.45 that supports the covalent attachment of oxygen radicals onto the sidewalls of SWNTs (SI-1, Supporting Information).

TGA of degassed (800 °C) functionalized SWNTs was used to estimate the extent of functionalization. Functionalized SWNTs **1** and **2** exhibit substantial weight loss at 120−500 °C due to detachment of succinimidyl and cumyloxy radicals, respectively. The weight losses, 19% for **1** and 16% for **2**, are consistent with the large D/G ratio observed in the Raman spectrum of **1** and **2**. Weight loss data indicate that one functional group is present for every 34 and 48 nanotube carbon atoms of **1** and **2**, respectively. The carbon/functional group ratios determined by TGA on the basis of the weight loss of degassed samples are presented in Table 1.[31] In a control experiment, we observed no significant weight loss (<2%) after exposure of the starting material to lithium in liquid ammonia (without adding any reagents, i.e., NBS, NIS, NCS, dicumyl peroxide, and *tert*-butyl peroxide).

Scheme 3. Hydrazinolysis of Succimidyl and Phthalimidyl Functionalized SWNTs



Phthalimide functionalized SWNTs (**3**) were formed when *N*-bromophthalimide was reacted with a suspension of the nanotube salt in liquid ammonia. Sidewall attachment is evident from a substantial enhancement of the Raman D band. TGA of the functionalized SWNTs indicates a weight loss of 16%, corresponding to a carbon/functional group ratio of 45.



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When succinimidyl and phthalimidyl functionalized SWNTs (**1** and **3**) are treated with hydrazine, aminated SWNTs (**4**) are formed as shown in Scheme 3.

The aminated SWNTs were characterized by XPS and FTIR spectroscopy. Peak areas for the C 1s, O 1s, and N 1s of the unfunctionalized and functionalized SWNTs were determined by XPS. The atomic percentages are based on the averaged peak areas of two different spots in the same sample and calculated using sensitivity factors 1.0, 2.33, and 1.59 for carbon, oxygen, and nitrogen, respectively. The high-resolution C 1s XPS spectrum of **1** (Figure 2a) shows the nanotube carbon C 1s peak at 284.6 eV. A shoulder on the main C 1s peak at 287.9 eV is assigned to the amide (−N−C=O) group.[21,23] SWNT-NH2 (**4**) shows a small hump at ~285.7 eV that is 2.2 eV less than the amide peak, attributed to the C−N bond (Figure 2c). The high-resolution N 1s XPS spectrum of **1** (Figure 2b) clearly exhibits a characteristic amide peak for nitrogen 1s (3.1%) at 399.7 eV (NIST XPS database), confirming the presence of an amide bond[21,23] (N 1s binding energies for amides and amines are expected to lie between 399.5 and 400.5 eV).[32,33] In the case of **4**, the N 1s peak (2.9%) at 400.5 eV confirms (NIST XPS database) the presence of an amino group (Figure 2d). As expected, N 1s peaks are not observed neither in the starting SWNTs nor in the materials obtained after exposing them to lithium in liquid ammonia alone.

The FTIR-ATR spectrum of pristine SWNTs (Figure 3a) shows very weak peaks and a small hump at 1600 cm^{-1}

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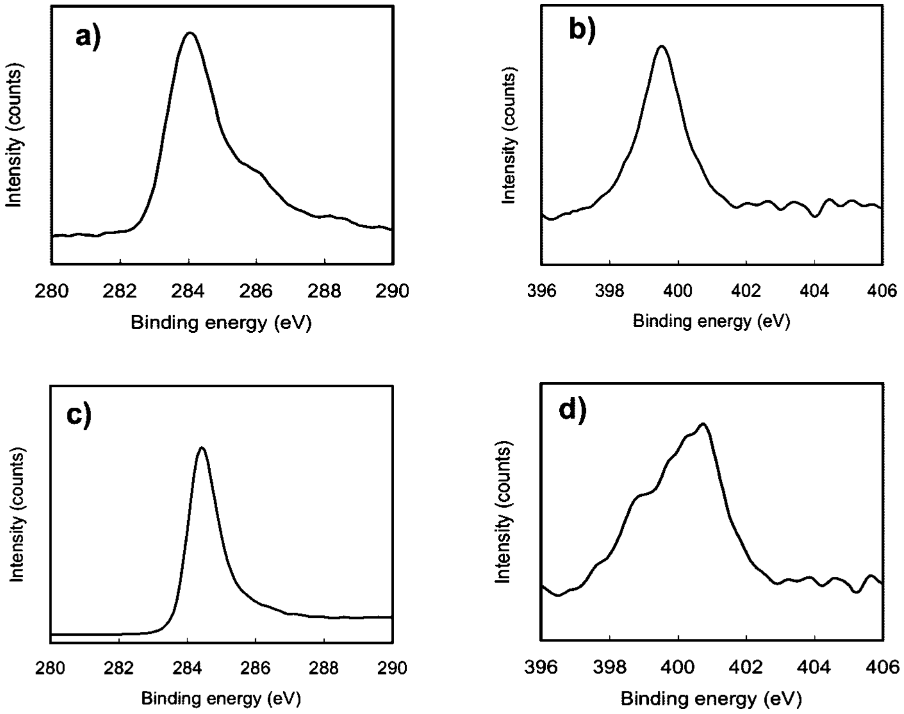


Figure 2. XPS analysis of functionalized SWNTs. For compound **1**: (a) the carbon 1s region, 81.5%; (b) the nitrogen 1s region, 3.1%. For compound **4**: (c) the carbon 1s region, 89.6%; (d) the nitrogen 1s region, 2.9% (atomic percentage).

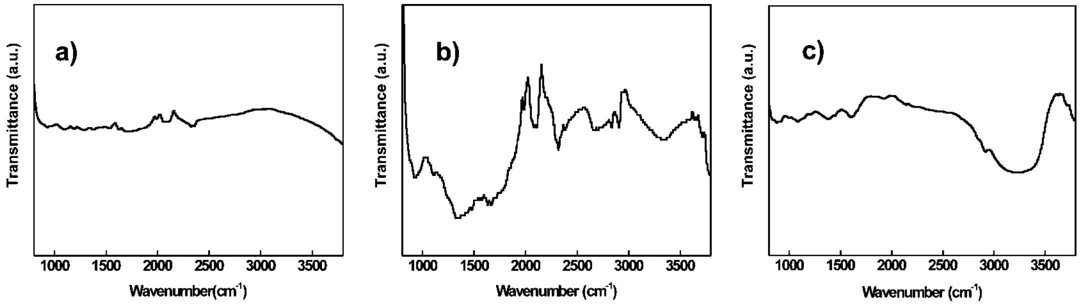
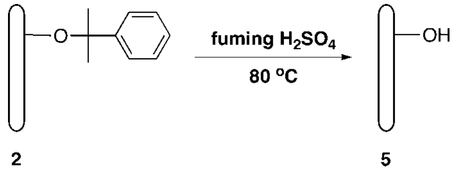


Figure 3. FT-IR analysis of (a) pristine SWNTs, (b) *N*-succinimidyl functionalized SWNTs (**1**), and (c) aminated SWNTs (**4**).

corresponding to the aromatic stretching (C=C) of SWNTs.[34] In the FTIR spectrum of *N*-succinimidyl-functionalized SWNTs (Figure 3b), the peaks at 1655 cm^{-1} and 1370 cm^{-1} are attributed to the imide carbonyl (C=O) stretch and C—N bond of the succinimidyl moiety, respectively.[21] Sharp peaks at 2840 and 2910 cm^{-1} correspond to the aliphatic C—H stretching frequencies associated with the succinimidyl-functionalized SWNTs. The FTIR-ATR spectrum of **4** (Figure 3c) shows the NH_2 stretching band at 3400 cm^{-1} and a broad in-plane bending mode of the primary $-NH_2$ group at 1620 cm^{-1}.[21] The absence of carbonyl peaks of the succinimidyl precursor **1** shows disappearance of the succinimidyl moiety while the appearance of a much broader peak at 1620 cm^{-1} suggests the presence of an amino group in the functionalized SWNTs **4**. The broad peak at 1090 cm^{-1} is attributed to C—N bond stretching vibrations for saturated amines.[21] Also, the disappearance of the aliphatic C—H stretching peaks at 2840 and 2910 cm^{-1} confirms the removal of the succinimide group to produce the amine. Similar IR results have been reported previously on diamine functionalized SWNTs.[35,36]

Scheme 4. Hydrolysis of Cumyloxy Functionalized SWNTs by Fuming H_2SO_4



Hydrolysis of cumyloxy-derivatized SWNTs (**2**) was carried out using fuming H_2SO_4 (20% free SO_3) under argon at 80 °C for 4 h to give hydroxylated SWNTs (**5**), as shown in Scheme 4. A control hydrolysis experiment using H_2SO_4 was carried out on unfunctionalized SWNTs. The absence of a O—H peak in the FT-IR spectrum shows that hydroxy functionalized SWNTs are derived from cumyloxy functionalized SWNTs and not from the SWNTs themselves.

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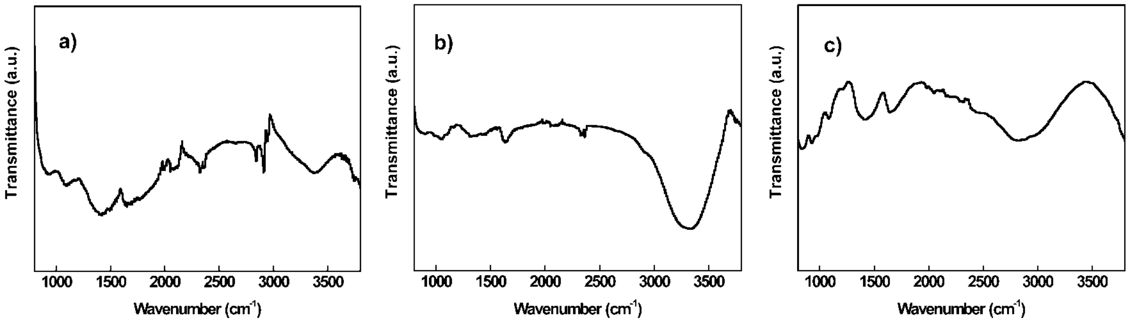

Figure 4. FT-IR analysis of (a) cumyloxy functionalized SWNTs (**2**), (b) hydroxylated SWNTs (**5**), and (c) deuterated analogue of hydroxylated SWNTs (**6**).

XPS data of cumyloxy functionalized SWNTs (**2**) (Supporting Information SI-1) show the main C—C peak at 284.6 eV and a shoulder at 286.1 eV corresponding to —C—O— contributions.[21,36]

As expected, the XPS data for hydroxylated SWNTs (**5**) show two main peaks in the carbon region. The C 1s peak at 284.6 eV is due to the nanotube carbon, and the small hump at 286.1 eV corresponds to —C—O— contributions. The lower carbon content and higher surface oxygen content for the hydroxylated SWNTs, in comparison to that of the cumyloxy functionalized SWNTs, is evidence for hydrolysis of the covalently attached cumyloxy group to give hydroxylated SWNTs.

The IR spectrum of cumyloxy functionalized SWNTs (Figure 4a) shows peaks at 2840 and 2910 cm^{-1} corresponding to aliphatic C—H stretching. The strong, broad hump between 1300−1600 cm^{-1} can be attributed to phenyl ring stretches[37] whereas the broad peak at 1110 cm^{-1} is due to the C—O stretch.[36] Figure 4b shows the IR spectrum of SWNTs attached to a hydroxyl group. The huge, broad peak at 3330 cm^{-1} corresponds to the O—H stretching frequency. The disappearance of aliphatic C—H and phenyl ring stretches confirms the hydrolysis of the side chain. As expected, the C—O stretching peak shifts to 1060 cm^{-1} from 1110 cm^{-1} after hydrolysis.[38] To further confirm the hydrolysis reaction, cumyloxy functionalized SWNT (**2**) was hydrolyzed in D_2SO_4 (96—98 wt % solution in D_2O, 99.5 atom % D) to form the deuterated analogue **6**. The FT-IR spectrum of **6** (Figure 4c) shows the expected O—D stretching peak at 2750 cm^{-1}.[39]

A HRTEM image of the cumyloxy functionalized nanotubes (Figure 5) shows “bumpy” sidewalls that can be attributed to the cumyloxy groups.[18]

Interestingly, upon treatment of **3** (phthalimide functionalized SWNTs) with oleum (20% SO_3), a small broadening of the XPS peaks at 400.9, 401.3, and 402.3 eV indicates the presence of various N—O species (N 1s: 3.2% atomic percentage) in the functionalized material. However, failure to detect sulfur rules out the possibility of sulfonation of the phenyl ring under the reaction conditions. Similarly, the absence of sulfur in the XPS data of hydroxylated SWNTs (**5**) shows that sulfonation of the phenyl ring does not occur; instead, an energetically more feasible hydrolysis reaction takes place via an S_N1 mechanism.

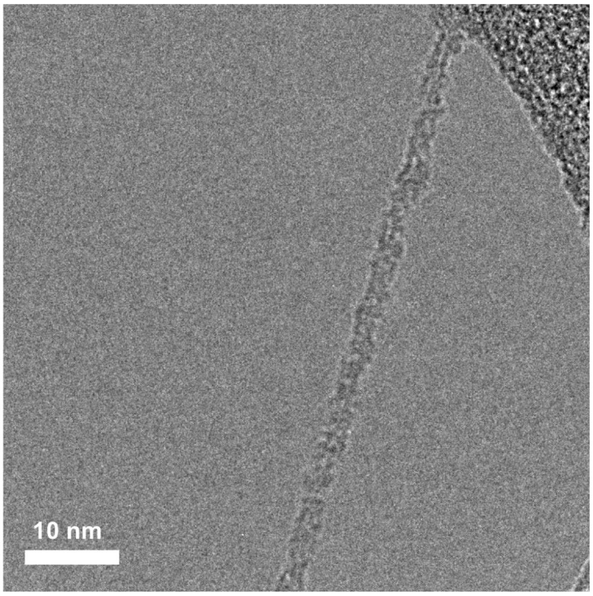

Figure 5. HRTEM image of cumyloxy functionalized SWNT.

Conclusions

We have presented an efficient method to functionalize carbon nanotubes by nitrogen and oxygen-centered free radicals using SWNT salts as an intermediate. Hydrolysis of succinimidyl-functionalized SWNTs with hydrazine leads to aminated SWNTs. We have also shown that hydroxy functionalized SWNTs can be prepared using SWNT salts. These aminated and hydroxy functionalized SWNTs are potential points of departure for the introduction of other functional groups.

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Supporting Information Available: (SI-1) Raman data for cumyloxy functionalized SWNTs and (SI-2) XPS data for cumyloxy and hydroxy functionalized SWNTs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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