

Functionalization of Carbon Nanotubes by Free Radicals

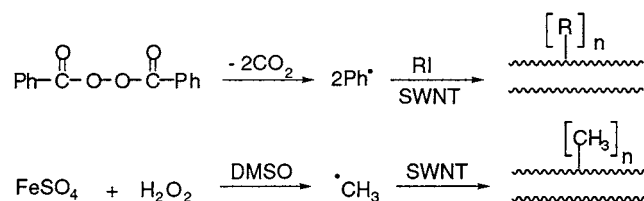
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ABSTRACT



Free radicals generated by decomposition of benzoyl peroxide in the presence of alkyl iodides have been used to derivatize small-diameter single-wall carbon nanotubes (HiPco tubes). The degree of functionalization, estimated by thermal gravimetric analysis, is as high as 1 in ~5 carbons in the nanotube framework. The derivatized nanotubes exhibits remarkably improved solubility in organic solvents. The attached groups can be removed by heating in an atmosphere of argon. Derivatization was also accomplished by treating SWNTs with various sulfoxides employing Fenton's reagent.

There is considerable interest currently in the chemical modification¹ of single-wall carbon nanotubes (SWNTs). In this way materials that are more amenable to spinning and to composite formation can be expected; improved solubility in common organic solvents can also be expected. Fluorination leads to a high degree of sidewall derivatization.² The fluorinated nanotubes have been functionalized by treatment with Grignard and alkyllithium reagents and metal alkoxides.^{3,4} Sidewall functionalization has also been achieved in a few instances using organic reagents.^{5–10} Addition of

azomethine ylides,⁵ carbenes,^{6–8} and nitrenes⁸ has been described. Addition of aryl radicals has been observed when aryl diazonium salts are reduced electrochemically using SWNTs (bucky-paper) as electrodes.⁹ Diazonium compounds generated in situ can also be used for functionalization.¹⁰ Radical addition of a perfluoroalkyl group generated by photolysis of a carbon–iodine bond has been reported.⁸ Addition of aromatic amines is achieved by refluxing the amine with SWNTs.¹¹ Other examples include electrochemical reductive and oxidative coupling by substituted phenylated derivatives¹² and electrophilic addition of chloroform followed by hydrolysis and esterification.¹³ Dissolved lithium metal in liquid ammonia (Birch reduction) is used to

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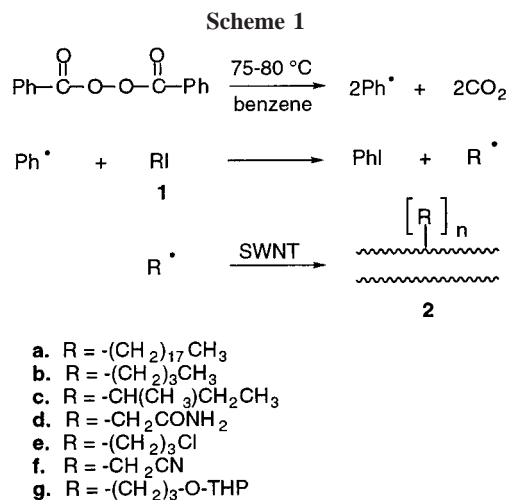
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hydrogenate SWNTs.¹⁴ Several reports describe the functionalization of the carboxylic acid groups on the ends and defect sites by using thionyl chloride and subsequent reactions of the resulting acyl chloride.^{7,15,16}

In this Letter, we report new routes to covalently functionalized nanotubes by the addition of free radicals. The method is particularly useful for large-scale syntheses and provides functional groups conducive to further elaboration.

The SWNTs used in this work were produced at Rice University by the HiPco process and purified as described previously.¹⁷ SWNTs with residual metal less than 0.1 atom % and impurity carbon less than 1 wt % were obtained after purification.

Although the availability of free radical precursors suitable for our studies is somewhat limited, we found that benzoyl peroxide is a suitable source of phenyl radicals. Benzoyl peroxide is readily available and decomposes under mild conditions of temperature (75–80 °C) with the formation of carbon dioxide and phenyl radicals. Since alkyl iodides react in a diffusion-controlled process with radicals, we have observed that a large variety of functional groups may be added to the SWNTs when benzoyl peroxide is decomposed in the presence of alkyl iodides (Scheme 1).



The reactions were carried out by sonicating purified SWNTs suspended in benzene for 30 min. The suspension was then heated to 75 °C with the peroxide and the alkyl

iodide for 24 h under argon and worked up as described.¹⁸ Representative groups that have been added to the nanotubes are shown in Scheme 1. The reaction works well on a multigram scale (3g) if the nanotubes are sonicated prior to reaction.

Direct evidence for covalent sidewall functionalization can be found by Raman spectroscopy. Pristine SWNTs exhibit a weak diameter-dependent radial breathing mode at ca. 230 cm^{-1} and a stronger tangential mode band at ca. 1590 cm^{-1} . A weak band centered at ca. 1290 cm^{-1} is attributed to sp^3 -hybridized carbon in the hexagonal framework of the nanotube walls. This disorder mode band is enhanced, as expected, as groups are attached to the sidewalls of the nanotubes. This effect is illustrated in Figure 1 where

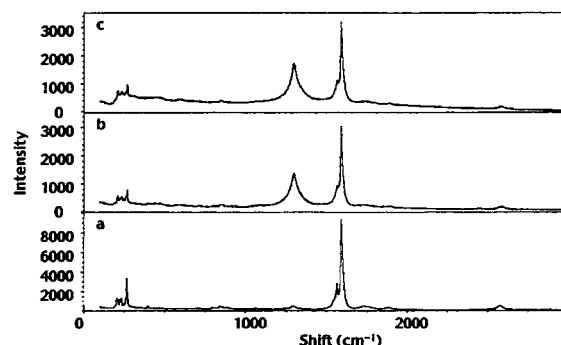


Figure 1. Raman spectra of derivatized SWNTs: (a) pristine nanotubes, (b) SWNTs functionalized by phenyl group, and (c) SWNTs functionalized by octadecyl group.

nanotubes functionalized by *n*-octadecyl groups are illustrated along with phenylated¹⁹ and pristine SWNTs. We suggest that it is prudent to include Raman spectroscopy as part of the protocol when functionalized nanotubes are subjected to analyses. We have observed instances where the disorder peak was not present even when TGA analysis revealed the expected increase in weight. Under these conditions the reagent is held to the walls of the nanotubes via van der Waals interactions.

The phenylated tubes that are formed in the absence of iodides can be chromatographed using a silica gel (230–400 mesh) column and DMSO as eluent. Although discrete bands are not formed, the fractions that elute first exhibit a higher degree of functionalization as demonstrated by the more intense disorder peak in the Raman spectrum. The phenylated nanotubes exhibit remarkably improved solubility

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(18) **General Procedure.** SWNTs (20 mg, 1.6 mmol of carbon) were suspended in benzene (30 mL) and sonicated for 30 min in a bath sonicator (Cole Parmer). The alkyl iodide (4.0 mmol) and benzoyl peroxide (403 mg, 1.6 mmol) were then added to this suspension. The contents were heated under argon at 75 °C for 24 h with stirring. The contents of the flask were diluted with 100 mL of benzene, filtered over a PTFE (0.2 μm) membrane, and washed exhaustively with benzene. The material was then suspended in benzene, sonicated for 20 min, and filtered. This procedure was repeated twice with benzene and once each with acetone and methanol. The bucky-paper was then dried in vacuo at 80 °C for 12 h.

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or dispersability in CHCl_3 , CH_2Cl_2 , DMSO, DMF, and 1,2-dichlorobenzene but are less soluble in benzene, toluene, and THF and are insoluble in *n*-hexane and ether.

The infrared spectrum (FT-IR, ATR) of nanotubes substituted by phenyl and octadecyl groups are presented in Figure 2. Weak C–H stretching vibrations in the 3000–

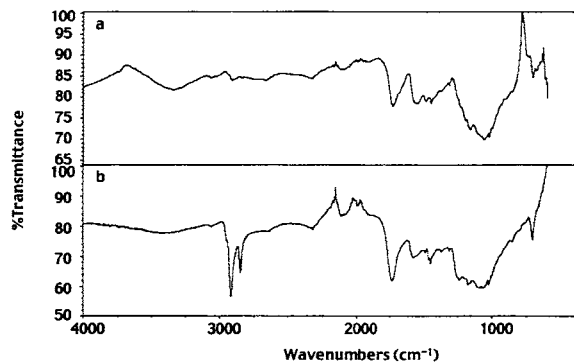


Figure 2. Infrared spectra with ATR accessory of derivatized SWNTs: (a) phenylated SWNTs and (b) SWNTs functionalized by octadecyl group.

3060 cm^{-1} region are observed for the phenylated nanotubes, whereas strong C–H stretching vibrations are observed at 2850 and 2920 cm^{-1} for the nanotube functionalized by octadecyl groups.

Weight loss data from TGA analyses are compiled in Table 1 (Figure S1, Supporting Information). Weight loss occurs

Table 1. Weight Loss and Estimated Carbon/Alkyl Group Ratio from TGA, with Heating to 800 °C in Argon

compound	weight loss (%) ^a observed	carbon/alkyl group ratio
NT-pristine	3.6	na
NT-phenyl	30.56	14.25
2a	39.97	31.29
2b	42.44	6.30
2c	46.06	5.46
2d	47.92	5.04
2e	44.28	7.91
2f	29.69	7.69
2g	41.01	16.70
3	15.00	6.83

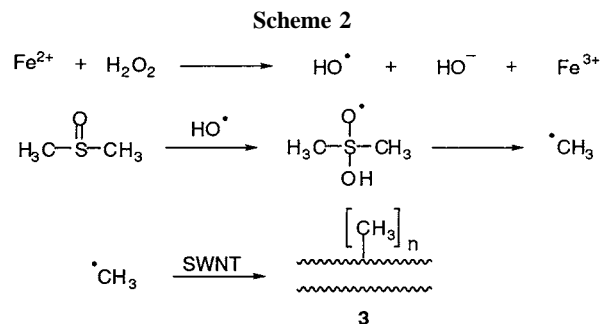
^a These values are adjusted for weight loss at low temperature due to degassing (ca. 2–3% in all cases).

primarily in the temperature range 250–500 °C. The Raman spectrum of the pristine SWNTs were restored after TGA analysis. From the data it is evident that a high degree of functionalization has been accomplished.

UV–vis–NIR spectroscopy can also be used to demonstrate covalent sidewall attachment. This may be attributed to rehybridization at carbon (sp^2 to sp^3) since the π electrons

in the highest occupied molecular orbitals that are used to form new bonds are no longer available, and the van Hove transitions, characteristic of unperturbed SWNTs vanish. The UV–vis–NIR spectra of pristine, **2a**, and **2g** SWNTs are displayed in Figure S2 (Supporting Information). Thus, the absence of electronic bands centered at 1400 and 800 nm in alkylated samples supports the assumption that sidewall functionalization has occurred.

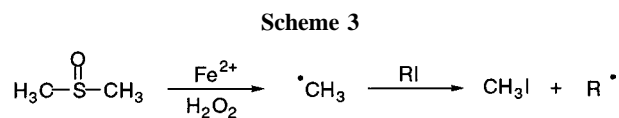
Methyl radicals generated by the method of Minisci²⁰ may also be added to the sidewalls of SWNTs. This route utilizes dimethyl sulfoxide as the source of the methyl radicals. The steps involved in this reaction are outlined in Scheme 2. We



have demonstrated that SWNTs capture the methyl radicals effectively, although the resulting methylated SWNTs exhibit low solubility in most organic solvents.

Other sulfoxides have also been investigated. These results will be reported in the full paper.

A new radical is formed when the Minisci route is used to generate methyl radicals in the presence of alkyl iodides. This process offers an alternative route to nanotubes functionalized by alkyl groups (Scheme 3). This pathway is under investigation.



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Supporting Information Available: TGA weight losses of functionalized SWNT-phenyl, **2a**, **2d**, and **2e** (Figure S1) and UV–vis–NIR spectra of functionalized SWNT **2a** and **2g** (Figure S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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