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Defunctionalization of Functionalized Carbon Nanotubes[§]

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ABSTRACT

Soluble samples of single-wall and multiple-wall carbon nanotubes that are functionalized by lipophilic and hydrophilic dendra can be defunctionalized in homogeneous solutions under base- and acid-catalyzed hydrolysis reaction conditions. The results provide strong evidence for the ester linkages in the functionalization of carbon nanotubes.

There have been significant recent interests in the functionalization and solubilization of single-wall (SWNT) and multiple-wall (MWNT) carbon nanotubes.[1−14] Most of the reported functionalizations of SWNTs and MWNTs have been based on the use of nanotube surface-bound carboxylic acid groups.[1,2,5−9,12−14] For example, Haddon and co-workers solubilized shortened carbon nanotubes by introducing long alkyl chains to the nanotube surface, where the carboxylic acids were first converted to acyl chlorides, followed by their amidation reaction with octadecylamine or 4-tetradecylaniline.[1] Similar acyl chloride-mediated amidation and esterification reactions have been used in the preparation of other soluble functionalized carbon nanotubes.[5−9,12−14] However, despite the selectivity of these carboxylic acid derivatization reactions and the hint from FT-IR results,[1,8,9,13] more evidence for the proposed amide and ester linkages in the functionalization of carbon nanotubes is still needed. Here we report the recovery of carbon nanotubes from homogeneous solutions of the soluble nanotube samples via defunctionalization under base- and acid-catalyzed hydrolysis reaction conditions. The results provide strong evidence for the conclusion that the soluble samples indeed contain functionalized carbon nanotubes and that ester linkages are responsible for the functionalization.

SWNT and MWNT samples produced by the arc discharge method were purified using procedures similar to those reported in the literature (see Supporting Information for details).[15−18] Before functionalization reactions, the nanotube surface-bound carboxylic acid groups were fully recovered by treating the nanotube samples in concentrated HCl solution. The acids were then converted to acyl chlorides by refluxing the samples in thionyl chloride for 24 h, followed by a complete removal of residual thionyl chloride on a rotary evaporator with a vacuum pump. The carbon nanotubes with surface-bound acyl chloride moieties thus obtained were used in the esterification reactions with the dendra **I** and $\mathbf{I}_{\mathrm{PEG}}$ (Scheme 1) (see Supporting Information for details on their synthetic preparations).

The functionalization reaction procedures and conditions were similar to those already reported in the literature.[1,2,5−9,12−14] In a typical experiment for **I**-SWNT, a thionyl chloride-treated SWNT sample (30 mg) was well mixed with carefully dried **I** (250 mg) in a flask, heated to 75 °C, and vigorously stirred for 48 h under nitrogen protection. The reaction mixture was extracted with chloroform several times to obtain a dark-colored solution. The chloroform solution was repeatedly precipitated into ethanol, yielding **I**-SWNT. ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 0.88$ (t, $J = 6.5$ Hz), 1.1−1.5 (broad), 1.6−1.8 (broad), 3.5−3.9 (broad), 4.0−4.2 (broad), 6.0−6.5 (broad) ppm. The **I**-MWNT and $\mathbf{I}_{\mathbf{PEG}}$-SWNT samples were prepared in a similar fashion, except that the solubility of $\mathbf{I}_{\mathbf{PEG}}$-SWNT in water allowed further purification via dialysis against deionized water (dialysis tubing cutoff molecular weight 100 000) for several days.

The soluble functionalized SWNTs and MWNTs were characterized using several instrumental techniques, among which the transmission electron microscopy (TEM) images provided the most direct evidence for the presence of nanotubes in the soluble samples. However, a more visual indication for the functionalized carbon nanotubes in homogeneous solutions was the dark solution color, because in the absence of carbon nanotubes the dendra **I** and $\mathbf{I}_{\mathbf{PEG}}$

[§] This paper is dedicated to Professor Christopher S. Foote on the occasion of his 65th birthday.

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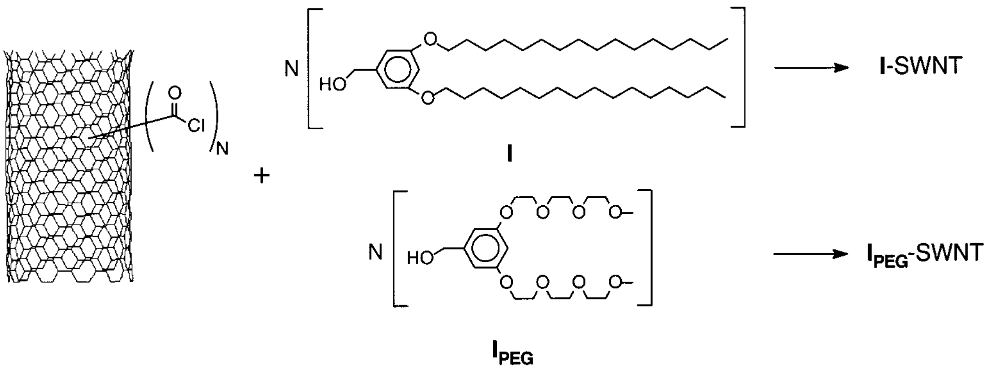
Scheme 1



remained colorless after being subject to the same functionalization reaction conditions. The UV/vis absorption spectrum of the **I**$_{\mathbf{PEG}}$-SWNT sample in chloroform solution is shown in Figure 1. The observed absorbances are linearly dependent on solution concentrations (Beer's law), indicating no effects that are associated with any aggregation or absorption of any bi- and multimolecular species.

The functionalization reaction conditions were obviously designed for the formation of ester linkages in the attachment of the dendra to SWNTs and MWNTs. FT-IR results of the functionalized nanotube samples show weak signals around 1700 cm^{-1}, consistent with the presence of carboxylates. However, the ^{13}C NMR detection of the nanotube-bound carbonyl groups in chloroform solution has been unsuccessful, even with the use of ^{13}C-enriched (up to 20 times the natural abundance) nanotube samples. To obtain more convincing evidence for the ester linkages in the functionalization of carbon nanotubes, defunctionalization experiments were performed. The results show that the functionalized carbon nanotubes can be defunctionalized under base- and acid-catalyzed hydrolysis reaction conditions.

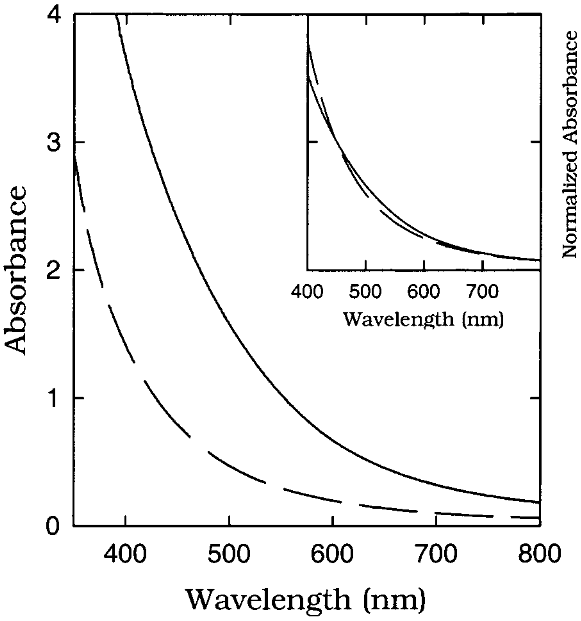


Figure 1. UV/vis absorption spectra of **I**$_{\mathbf{PEG}}$-SWNT before (—) and after (— — —) the defunctionalization. Shown in the inset are the normalized spectra.

In a typical experiment for base-catalyzed hydrolysis,[19] a purified sample of **I**-SWNT (49 mg) was dissolved in THF (5 mL) to form a brown-colored homogeneous solution. After NaH (30 mg) was added, the solution was refluxed under nitrogen protection for 2 h, resulting in the formation of dark-colored precipitates. The reaction was quenched by the addition of water; and the reaction mixture was centrifuged at a high speed (7000 rpm). The nearly black solids thus obtained were washed repeatedly with chloroform, water, and acetone, and then carefully dried for characterizations. The defunctionalization of the other soluble samples (**I**-MWNT and **I**$_{\mathbf{PEG}}$-SWNT) via hydrolysis in homogeneous THF solutions with NaH also resulted in the formation of dark-colored precipitates. For **I**$_{\mathbf{PEG}}$-SWNT, the decrease in UV/vis absorption due to the removal of nanotubes from the solution in the defunctionalization is shown in Figure 1. Separately, the hydrolysis of these soluble dendra-functionalized carbon nanotubes under strongly acidic conditions (concentrated trifluoroacetic acid (TFA) solution or neat TFA) again yielded dark-colored precipitates.

The solid precipitates from the defunctionalization reactions of the soluble SWNTs and MWNTs were analyzed by scanning electron microscopy (SEM). At both low and high resolutions, SEM images of the samples clearly show high concentrations of carbon nanotubes (Figure 2). It should be pointed out that despite repeated efforts, the SEM analysis of the soluble carbon nanotube samples before defunctionalization reactions was unsuccessful due to the presence of a large quantity of functional groups (relative to the amount of nanotubes). The recovery of defunctionalized SWNTs and MWNTs via the hydrolysis reactions apparently made possible the successful SEM imaging.

The defunctionalization of functionalized carbon nanotubes under the specific base- and acid-catalyzed hydrolysis reaction conditions provides strong evidence for the ester linkages between the nanotubes and the functionalities (dendra). The results validate the approach of using the nanotube-surface bound carboxylic acid groups for the derivatization and solubilization of SWNTs and MWNTs.[1,2,5–9,12–14]

The decrease in UV/vis absorption as a result of the defunctionalization also allowed an estimate of average absorptivities of the functionalized carbon nanotubes in solution. For the estimate, the precipitates corresponding to

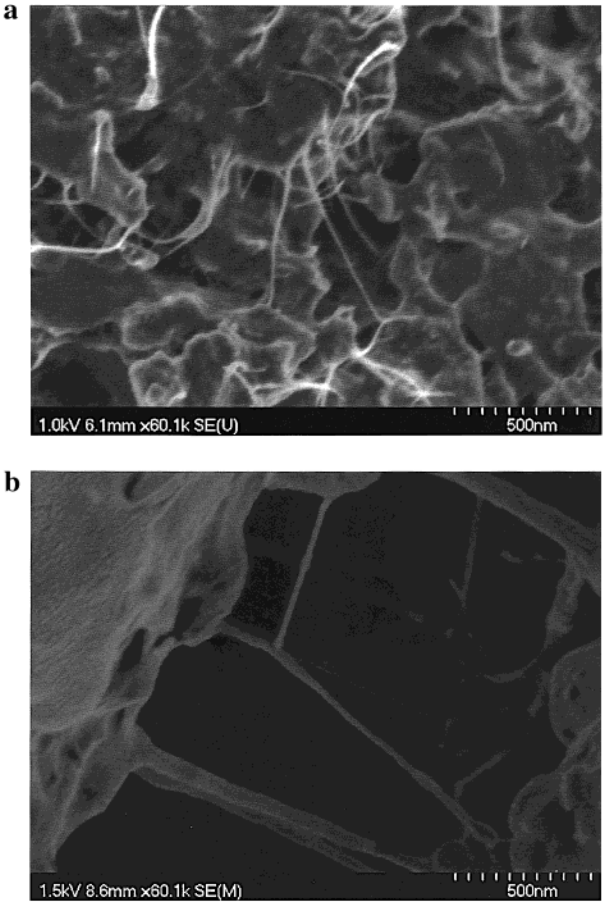


Figure 2. SEM images for the dark-colored precipitates obtained from the defunctionalization of soluble (a) **I**-SWNT and (b) **I**-MWNT samples. (The latter was coated with Pt/Au to avoid surface charging in the measurement.)

the decrease in UV/vis absorption were carefully weighed. The weight value was corrected for the contribution of residual functional groups in the precipitates (∼10%) in terms of thermal gravity analysis (TGA) to 350 °C. On the basis of the results from multiple experiments, the estimated average absorptivity for SWNTs at 500 nm is 97 ± 31 (mg/mL)$^{-1}$ cm^{-1}, which is close to 2 orders of magnitude higher than that of fullerene C_{60} on a per unit weight basis.[21]

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Supporting Information Available: Details on the synthetic preparation of dendra **I** and $\mathbf{I}_{PEG}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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