

LETTERS

Concise Route to Functionalized Carbon Nanotubes

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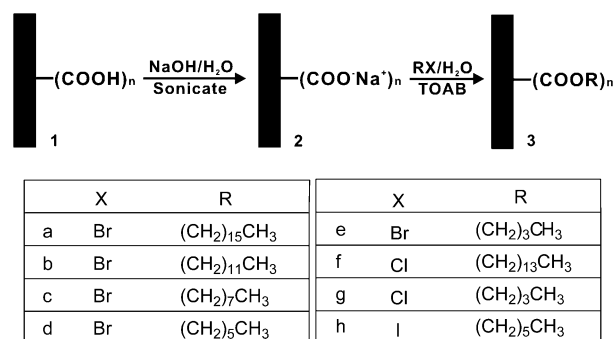
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Received: August 22, 2003; In Final Form: October 4, 2003

A concise route was developed to functionalize carbon nanotubes via the esterification reaction of the carboxylate salt of carbon nanotubes and alkyl halides in the presence of a phase-transfer reagent in water. The series of functionalized CNTs obtained were characterized and analyzed by FT-IR, ¹H NMR, TEM, and TGA techniques.

The chemical functionalization of carbon nanotubes (CNTs), which may not only bring these fascinating carbon structures into the fold of (macro)molecular chemistry but also afford the carbon nanotubes ultimate new characteristics, has attracted considerable attention.¹ The functionalization has been demonstrated at the ends and/or walls of CNTs covalently or noncovalently, while one of the dominant methods was through the reaction of carboxylic acid groups which were introduced onto the surface of CNTs by acid treatment.² In this context, amide^{3–6} and ester linkages⁷ as well as acid–base chemistry^{5,8} have been utilized to attach certain groups to CNTs to alter their properties such as solubility. For example, Haddon et al.^{4a} first synthesized solubilized CNTs by amidation reaction of a long chain amine with acid chlorides converted from the nanotube-bound carboxylic acid groups. This amidation reaction could also be accomplished via diimide-activated coupling reaction,³ which was significantly improved by sonication in water.⁶ However, most of these methods were time-consuming and tedious. To make amide or ester modified CNTs, the carboxylic acid groups usually need to be converted into acid chlorides in order to increase the reactivity of CNTs, which required inert gases, anhydrous solvents, and long reaction times

SCHEME 1



(e.g. several days). Although the separation process was greatly improved very recently,⁹ it would still be necessary to devise a more efficient and concise method to modify CNTs.

We report here a new approach to modify CNTs through the ester linkage with the surface carboxylate groups of CNTs. The underlying concept is captured graphically in Scheme 1, which is directed to our focusing target of linear alkyl chain modified multiwalled carbon nanotubes (MWNTs) (3). However, as is suggested by the reaction similarities of carboxylic acid groups of single-walled carbon nanotubes (SWNTs) and MWNTs as well as the variety of alkyl halides, this method is quite general and can be used to modify SWNTs and obtain various functionalized CNT materials. Our new strategy is based on

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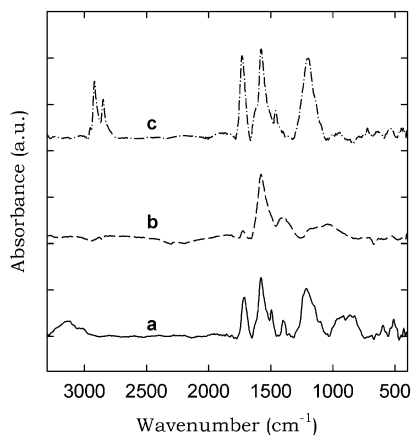


Figure 1. FT-IR spectra of **1** (a), **2** (b), and **3a** (c).

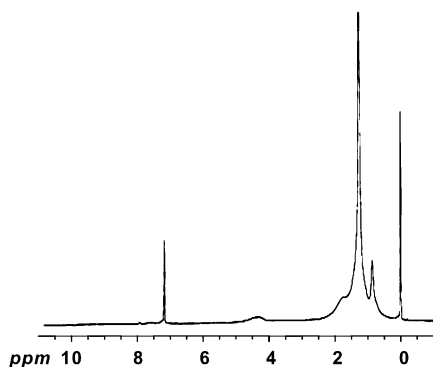


Figure 2. ^1H NMR spectrum of **3a** (CDCl_3 , TMS).

the phase-transfer reaction of carboxylate salts with alkyl halides.¹⁰ The surface carboxylic acid groups of MWNTs are first converted into carboxylate salts and then reacted with alkyl halides in the presence of a phase-transfer reagent to result in alkyl-modified MWNTs through ester linkages. The whole reaction is carried out in water and only needs several hours, which is more simple and efficient than other methods described before. As alkyl-modified MWNTs are insoluble in water, the products can be simply separated by filtering and centrifuging.

Commercially available MWNTs (CVD method, Shenzhen Nanotech Port Co., Ltd, China) were purified and converted into the acid form (**1**) via sonication in 1:3 concentrated nitric acid–sulfuric acid at $\sim 50^\circ\text{C}$. The resultant solid was washed thoroughly with deionized water until the pH value was ~ 6 . **1** was sonicated in aqueous NaOH (5 mM) for 2 min and converted into the sodium salt form (**2**). To this black homogeneous suspension were added tetra-*n*-octylammonium bromide (TOAB) and alkyl halide (RX), and the mixture was refluxed under vigorous stirring. After 1–8 h (depending on the reactivity of RX), the suspension became clear and colorless, and black precipitation was observed. The precipitation was collected and dissolved in CHCl_3 . After filtration to get rid of any unreacted MWNTs, the solution was washed with a 15% NaCl aqueous solution and dried with anhydrous CaSO_4 . The resulting CHCl_3 solution was concentrated and then precipitated into ethanol. The black solid (**3**) was collected and dried in a vacuum at 50°C .

Eight alkyl halides including chloro-, bromo-, and iodo-substituted alkyls with various alkyl chains from C4 to C16 were used to functionalize MWNTs in this communication (Scheme 1). The reaction is likely depending upon the reactivity of the halide, following the degressive order iodo, bromo, and chloro, in agreement with the sequence of reactivity of these

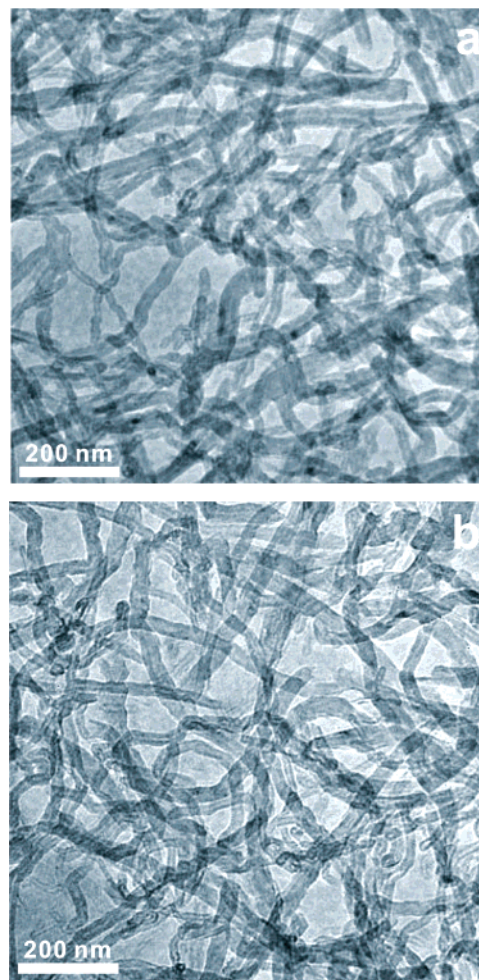


Figure 3. TEM images of **2** (a) and **3a** (b).

leaving groups in typical nucleophilic substitution reactions. Most of the products are readily soluble in common organic solvents such as CHCl_3 , CH_2Cl_2 , THF, toluene, chlorobenzene, and so forth. The solubility depends on the length of the attached linear alkyl chains. The attachment of longer alkyl chains gives better solubility. In the case of butyl-modified MWNTs (**3e** and **3g**), the samples are almost insoluble.

The whole reaction process was monitored by an FT-IR spectroscopic method. As shown in Figure 1a, **1** shows a peak at 1720 cm^{-1} , indicating the existence of the carboxylic acid groups.^{11,12} The peaks centered at 1580 and 1210 cm^{-1} could be assigned to the $\text{C}=\text{C}$ stretch of carbon nanotube backbones and the $\text{C}-\text{O}$ stretch of the acid, respectively.¹² The peak of carboxylic acid groups disappears after the addition of NaOH. The peaks centered at 1577 and 1385 cm^{-1} suggest the formation of **2** (Figure 1b),⁵ although these characteristic peaks of carboxylate salt may be overlapped with the $\text{C}=\text{C}$ stretch of the nanotube backbones. The formation of carboxylate ester (**3a** for example, Figure 1c) is confirmed by the new peaks at 2918 and 2847 cm^{-1} , which belong to the $\text{C}-\text{H}$ stretch of the alkyl chains. The $\text{C}=\text{O}$ stretch of the ester appears at 1732 cm^{-1} . Other peaks centered at 1580 and 1201 cm^{-1} correspond to the $\text{C}=\text{C}$ stretch of carbon nanotube backbones and the $\text{C}-\text{O}$ stretch of the ester, respectively.

The existence of alkyl chains bound on the surface of MWNTs was further proved via an ^1H NMR spectroscopic method. Figure 2 gives the ^1H NMR spectrum of **3a** in CDCl_3 . The signals are broadening, which results from the statistical distribution of the addends on the tube surface.^{7a,13} While the

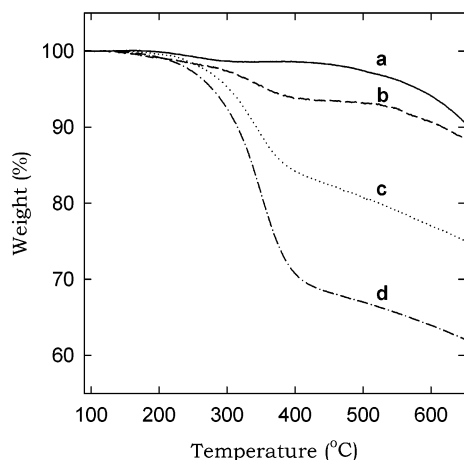


Figure 4. TGA curves of **1** (a), **3e** (b), **3c** (c), and **3a** (d), respectively.

signals at $\delta = 0.9$ – 1.7 are assigned to the protons of the long aliphatic chains at the ends of the MWNTs, the signal at $\delta = 4.4$ corresponds to the CH_2 groups directly attached to the carboxylic group. The intensity ratio of these two signals is about 15:1, which proves the attachment of the hexadecyl chains to the nanotubes.

The TEM images give direct evidence of the existence of the nanotubes in the alkyl-modified samples. Typical TEM images of **2** and **3a** are shown in Figure 3. In both of the samples, the nanotubes have an average length of $\sim 2 \mu\text{m}$ with an average diameter of $\sim 30 \text{ nm}$; the tube structures of the alkyl-modified samples are well kept.

Thermogravimetric analysis (TGA) experiments were performed to analyze the alkyl-modified MWNTs in the nitrogen atmosphere with a heating rate of $10^\circ\text{C}/\text{min}$. As shown in Figure 4, there is one inflection at $\sim 470^\circ\text{C}$ in the TGA curve of **1**, which indicates that the tubes begin to decompose at this temperature.^{9,14} However, the TGA curves of the modified MWNTs show obvious weight loss at $\sim 280^\circ\text{C}$, which should be attributed to the loss of alkyl chains.¹⁵ For different alkyl-modified MWNT samples, the weight loss increases with the increase of the length of the attached alkyl chains. The weight loss between ~ 280 and $\sim 470^\circ\text{C}$ can be used to estimate the weight percentage of alkyl chains attached to the tubes, although at $\sim 470^\circ\text{C}$ the alkyl chains may not be completely removed. From Figure 4, the weight percentage of attached alkyl chains in the samples of **3a**, **3c**, and **3e** is determined to be $\sim 33\%$, $\sim 18\%$, and $\sim 6\%$, corresponding to the tube weight percentages $\sim 67\%$, $\sim 82\%$, and $\sim 94\%$, respectively. Clearly, the nanotube content of the hexadecyl-modified MWNTs is $\sim 67\%$, which is comparable to the $\sim 70\%$ content of octadecylamine-modified MWNTs obtained from Haddon's method,⁹ indicating that the

nanotube contents in the solubilized samples from the two methods are similar.

In summary, a new concise method has been developed to functionalize CNTs via the esterification reaction of the carboxylate salt of CNTs and alkyl halides in water. Considering the abundance and diversity of halides, this method may provide an easy way to functionalize CNTs with various functional groups, which will provide the possibility to assemble CNTs in nanocomposites as well as in nanoscale devices such as biosensors and molecular electronics.

Acknowledgment. We thank the Chinese Academy of Sciences and the National Natural Science Foundation of China (Grant No. 50203015) for financial support.

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