Covalent sidewall functionalization of single-walled carbon nanotubes: a photoreduction approach

This article has been downloaded from IOPscience. Please scroll down to see the full text article.
2007 Nanotechnology 18 495703
(http://iopscience.iop.org/0957-4484/18/49/495703)

The Table of Contents and more related content is available

Download details:
IP Address: 202.120.54.134
The article was downloaded on 10/04/2010 at 12:27

Please note that terms and conditions apply.
Covalent sidewall functionalization of single-walled carbon nanotubes: a photoreduction approach

Liangming Wei and Yafei Zhang

National Key Laboratory of Nano/Micro Fabrication Technology, Key Laboratory for Thin Film and Microfabrication of Ministry of Education, Institute of Micro and Nano Science and Technology, Shanghai Jiao Tong University, Shanghai 200030, People’s Republic of China

E-mail: lmwei@sjtu.edu.cn

Received 25 July 2007, in final form 4 October 2007
Published 2 November 2007
Online at stacks.iop.org/Nano/18/495703

Abstract

Covalent sidewall functionalization of single-walled carbon nanotubes (SWNTs) via photoreduction of aromatic ketones by alcohols is reported for the first time. Irradiation of benzophenone, benzhydrol and SWNTs in benzene resulted in covalent attachment of benzhydrol to the sidewalls of the SWNTs. A variety of tools were used to characterize the functionalized SWNTs. Raman scattering, UV–visible and near-IR spectroscopy confirm the covalent nature of the sidewall functionalization. Attenuated total reflection (ATR) FTIR and NMR provided evidence for attachment of benzhydrol onto the sidewalls of nanotubes. Thermogravimetric analysis (TGA) showed that the degree of functionalization was about one benzhydrol in 52 sidewall carbons. A long-chain hydrocarbon marker (n-C_{18}H_{35}) was also grafted onto the functional groups by esterification reaction for high-resolution TEM (HRTEM) visualization.

1. Introduction

The chemical sidewall functionalization of single-walled carbon nanotubes (SWNTs) has received much attention [1], as it can improve solubility and processability and allows the unique properties of SWNTs to be coupled with those of other types of materials [2]. Several methods for sidewall functionalization have been developed, using fluorine [3], carbenes [4], azomethine ylides [5] or organic radicals [6]. The photochemical approach for functionalization of solid substrates is particularly interesting due to its significant advantages [7, 8]: mild reaction conditions, low cost of operation, selectivity to absorb UV light without destroying the bulk structure and convenience to asymmetrical modification [9]. Recently, photochemical sidewall functionalization of SWNTs via photolysis of some materials such as heptadecafluoro-octyl iodide [10], azide reagents [11] or organosilanes [12] has been reported. Argon plasma-assisted UV grafting of vinylimidazole has also been developed for functionalization of carbon nanotubes [13]. However, the samples of photochemical sidewall functionalization of SWNTs are still limited, in contrast to a large variety of wet-chemical functionalization of SWNTs [1]. In this paper, we report a photoreduction method for covalent sidewall functionalization of SWNTs via photoreduction of aromatic ketones by alcohols (scheme 1). The photoreduction mechanism could be explained by a benzophenone (BP) in the excited triplet state abstracting a hydrogen atom from the carbinol carbon within a benzhydrol (BZ) [14], leading to the formation of BZ radicals which add readily to nanotubes. The BP/BZ system was chosen in this study because the bimolecular reaction gave only one type of radical (BZ radical) [14], leading to the formation of BZ radicals which add readily to nanotubes. The BP/BZ system was chosen in this study because the bimolecular reaction gave only one type of radical (BZ radical) [14], leading to the formation of BZ radicals which add readily to nanotubes. The BP/BZ system was chosen in this study because the bimolecular reaction gave only one type of radical (BZ radical) [14], leading to the formation of BZ radicals which add readily to nanotubes. The BP/BZ system was chosen in this study because the bimolecular reaction gave only one type of radical (BZ radical) [14], leading to the formation of BZ radicals which add readily to nanotubes. The BP/BZ system was chosen in this study because the bimolecular reaction gave only one type of radical (BZ radical) [14], leading to the formation of BZ radicals which add readily to nanotubes. The BP/BZ system was chosen in this study because the bimolecular reaction gave only one type of radical (BZ radical) [14], leading to the formation of BZ radicals which add readily to nanotubes.

Most reports on addition of radicals onto SWNTs thus far are based on decomposition of unique molecules, such as organic peroxides [6], 4-methoxyphenylhydrazine [15], heptadecafluoro-octyl iodides [10] or diazonium salts [16]. In our case, the radicals were formed via hydrogen abstraction from C–H bonds by excited BP triplets. Since the excited BP triplet is reactive to many types of C–H bonds such as alcohols [17], amines [18], ethers [19], hydrocarbons [20] or aliphatic sulfides [21], a wide variety of radicals can be generated using this photochemical method. In principle,
these radicals are also feasible for functionalization of SWNTs, which could lead to a large variety of functional systems. Particularly, a molecule with chemical inertness, such as polypropylene, is easy to change to a highly reactive radical species via hydrogen abstraction by the excited BP triplet [7], which makes it possible to covalently graft the molecule onto the sidewalls of carbon nanotubes. Additional advantages of BP systems are thermal stability, chemical inertness in the absence of light [22], and the reactants are easily accessible.

A big challenge in the field of nanotube chemistry is the characterization of the functionalized SWNTs [23]. Many traditional tools of organic chemistry are of limited use or cannot be applied [24]. Here, we provided a detailed characterization of functionalized SWNTs using a variety of tools. A long-chain hydrocarbon marker \( n\)-C\(_{18}\)H\(_{35}\) was also grafted onto the functional groups by esterification reaction for high-resolution TEM (HRTEM) visualization.

2. Experimental section

2.1. Materials

The purified SWNTs (purity \( \geq 90\% \)), stearoyl chloride, benzhydrol and benzophenone were purchased from Aldrich. Benzene and pyridine were purchased from Shanghai Reagents Co. The 200 W mercury lamp was purchased from Advanced Radiation Corporation.

2.2. Preparation of benzhydrol-functionalized carbon nanotubes (BZ-SWNTs) via a photoreduction approach

The photochemical functionalization was carried out as follows: 2.25 g of BP and 2.25 g of BZ were dissolved in 20 ml of benzene. The solution was transferred into a quartz vessel, and then 5 mg of purified SWNTs was added. The solution was degassed by introducing nitrogen, and then sonicated for 10 min. The mixture was irradiated under a 200 W mercury lamp for 4 h. During the irradiation, if the solvent was evaporated, an additional 20 ml of benzene was added to the quartz vessel. Following the irradiation, the mixture was further stirred for 12 h and then filtered. The solid was flushed with tetrahydrofuran, and dried in vacuum at 60 °C.

2.3. Grafting of long-chain hydrocarbon onto the sidewalls of BZ-SWNTs

In a typical experiment, BZ-SWNTs (5 mg), stearoyl chloride (5 ml) and 10 ml of pyridine were added to a dried flask and stirred for five days at 100 °C. After the reaction was completed, the mixture was centrifuged, washed with plenty of tetrahydrofuran and dried in vacuum at 60 °C.

2.4. Characterization and sample preparation

The Raman spectra of pristine and functionalized SWNTs were collected with a Dilor Labram-1B Raman spectrometer with He–Ne laser at 632.8 nm (1.96 eV). UV–visible spectra were recorded on a Unicam UV-300 spectrometer. The powder samples were sonicated in DMF for 1 h and then centrifuged. The supernatant was taken for characterization. Solution-phase near-IR spectra were obtained on a Bruker MPA spectrometer equipped with a CaF\(_2\) beam splitter and InGaAs detector. The powder samples were dispersed in DMF, and then sonicated for 1 h. FTIR spectra were recorded on a Nicolet Nexus 479 FTIR system with a ZnSe attenuated total reflectance (ATR) accessory. The samples were dispersed in chloroform and then dripped on a ZnSe crystal. Hydrogen nuclear magnetic resonance (\( ^1\)H NMR) spectra were measured with a Varian Mercury Plus 400 MHz spectrometer. The samples were dissolved in CDC\(_3\) by sonication. The high-resolution TEM images were obtained from a JEOL 2100 operating at 200 kV. The samples were sonicated in chloroform for 10 min and then centrifuged. The supernatant was dripped onto a Cu grid coated with a lacy carbon film. TGA was conducted on a PE TGA-7 instrument at a heating rate of 10 °C min\(^{-1}\) from 50 to 800 °C under nitrogen flow.

3. Results and discussion

The covalent nature of the sidewall functionalization was confirmed by Raman, UV–visible and near-IR spectroscopy. The Raman spectrum shows that the purified SWNTs exhibit a tangential mode (G band) at 1560 cm\(^{-1}\), a weak disorder mode (D band) at 1313 cm\(^{-1}\) and diameter-dependent radial breathing modes (RBM) at 140–253 cm\(^{-1}\) (figure 1). The
The weak D band is attributed to the presence of disorder or sp\(^3\) hybridized carbon atoms in the benzenoid framework of the carbon nanotube walls [4]. Compared with the purified SWNTs, the Raman spectrum of BZ-SWNTs shows a greatly enhanced D band (figure 1(b)). This increase is due to the covalent binding of the addends leading to sp\(^3\) defects in the sidewalls [23].

According to the Kataura plot [25, 26], the RBM features at 140 and 253 cm\(^{-1}\), corresponding to diameters of 1.77 and 0.93 nm, respectively, arise from semiconducting nanotubes which are in resonance with the laser energy (1.96 eV), and the features located between 170 and 230 cm\(^{-1}\) are assigned to metallic nanotubes. For the purified SWNTs, the semiconducting nanotube RBM features are pronounced, and the metallic nanotubes show indistinct features (figure 1(a)). The semiconducting nanotubes features decreased significantly upon functionalization, whereas the features located at 175, 195 and 221 cm\(^{-1}\), ascribed to metallic nanotubes with diameters of 1.39, 1.24 and 1.08 nm, respectively, show the opposite trend (figure 1(b)). It is well known that the addition of the functional groups to the sidewall of nanotube disrupts the radial breathing oscillation of the nanotubes, which causes the mode to decay accordingly as the particular nanotube reacts [27]. Our results suggest that BZ radicals are more reactive toward semiconducting nanotubes than metallic nanotubes. The same behavior was observed in chemical functionalization using pyrene-linked azomethine ylides [28]. The reason for the preferential reactivity for semiconducting nanotubes remains unclear. However, we speculate that the phenyl groups within BZ could π-stack preferentially with more aromatic semiconducting nanotubes [28, 29].

The van Hove singularities typical for purified SWNTs [30] are absent (figure 2). The loss of the van Hove singularities is indicative of covalent sidewall functionalization [31], which destroys the electronic structure of the nanotubes. It should be mentioned that, for purified SWNTs, the UV–visible spectra of dispersion of SWNTs are known to be sensitive to aggregation state [32]. As the number of suspended individual nanotubes increases, the absorption band becomes sharper and more intense [33]. In our case, the UV–visible spectra were measured in dimethylformamide (DMF). As compared to the surfactants such as sodium dodecylbenzenesulfonate (SDDBS), DMF is less effective to exfoliate the SWNTs bundles [34]. As a result, even for the purified SWNTs, the absorption bands are very weak. Indeed, the weak absorbance bands were also observed by other research groups when DMF was used as solvent [28].

The solution-phase NIR analysis (figure 3) shows that the intensity of the S\(_{11}\) transition of the semiconducting SWNTs [4] decreased significantly after functionalization, which further confirmed the changes in the electronic structure of the nanotubes. In brief, Raman, UV–visible and near-IR spectroscopy provided unambiguous proof of the covalent sidewall functionalization of the SWNTs.

The ATR-FTIR spectrum of BZ-SWNTs. The weak C–H stretching vibrations in the 3000–3100 cm\(^{-1}\) range are characteristic of the phenyl groups within BZ. The band at 3328 cm\(^{-1}\) was ascribed to the O–H stretches of the grafted BZ, and several absorptions in the 1400–1600 cm\(^{-1}\) range are characteristic of the benzene ring. The weak bands at 3100 and 1465 cm\(^{-1}\) are characteristic of the C–H and C=C stretching vibrations, respectively.
range were assigned to phenyl ring stretches [35]. The band at 1155 cm$^{-1}$ was ascribed to the C–O stretching vibration, and the band at 1212 cm$^{-1}$ was assigned to C–O stretches or the O–H deformations of the C–OH groups [36, 37]. It should be mentioned that the peaks at 2923 cm$^{-1}$ and 2856 cm$^{-1}$, which were assigned to aliphatic C–H stretching vibrations, were observed in BZ-SWNTs. We also observed these peaks in the purified SWNTs. These peaks could not be removed even if we performed a high-temperature vacuum anneal on the purified SWNTs (1200 °C, 10$^{-6}$ Torr, 2 h). These peaks could be associated with hydrocarbon contamination in the spectrometer and/or with C–H groups introduced by atomic hydrogen generated in cold plasma [36, 38].

To further confirm the successful graft of BZ onto the sidewalls of nanotubes, a long-chain hydrocarbon marker ($n$-C$_{18}$H$_{35}$) was grafted onto the BZ by esterification reaction for HRTEM visualization, as outlined in scheme 1. FTIR (figure 4(b)) shows that after BZ-SWNTs reacted with stearoyl chloride the peak at 3328 cm$^{-1}$, assigned to O–H stretches in BZ-SWNTs, disappeared, aliphatic C–H stretching vibrations (3000–2800 cm$^{-1}$) were greatly enhanced, and a new peak at 1465 cm$^{-1}$, attributed to a long-chain hydrocarbon C–H deformation mode [35], was observed. The resulting C$_{18}$–BZ-SWNTs exhibit high solubility (0.8 mg ml$^{-1}$) in chloroform, whereas the BZ-SWNTs show poor solubility (<0.2 mg ml$^{-1}$).

The solubility of BZ-SWNTs was not high enough to allow solution state NMR spectra to be obtained. Fortunately, C$_{18}$–BZ-SWNTs show high solubility in CDCl$_3$, and the corresponding $^1$H NMR spectrum is shown in figure 6. A pronounced resonance signal at 7.26 ppm was observed for the C$_{18}$–BZ-SWNT sample. A resonance signal assigned to a few protons of CHCl$_3$ in CDCl$_3$ was observed at this position, but its intensity is low. The considerable increase in the intensity of the resonance signal after C$_{18}$–BZ-SWNTs were dissolved in CDCl$_3$ was due to the presence of the protons of phenyl groups. Several new signals in the 1.0–1.4 ppm range are ascribed to the protons of the long-chain hydrocarbon in C$_{18}$–BZ-SWNTs.

The degree of functionalization was measured by TGA (figure 7). For purified SWNTs, the weight loss of 6% is attributed to the removal of the oxidized carbon groups in the purified SWNTs [15]. The overall weight loss is 28.7% for BZ-SWNTs. The increased weight loss (22.7%) is attributed to the presence of BZ on the sidewalls. Based on the weight loss ($W\%$), the molecular weight of the addends ($M_{add}$) and
the atomic weight of carbon ($M_c$), the degree of coverage ($X$) can be calculated from

$$X = \frac{[M_{ads}(1 - W\%)]/(M_c \times W\%)}{100\%}.$$ 

Here, the degree of functionalization is about one BZ in 52 carbon atoms.

In summary, we successfully developed a photoreduction route based on the BP/BZ system for covalent sidewall functionalization of SWNTs, as confirmed by Raman scattering, UV–visible and near-IR spectroscopy, ATR-FTIR, HRTEM, NMR and TGA. Application of other BP/hydrogen donor systems for photochemical functionalization of SWNTs is currently under investigation.

Acknowledgments

We thank the National Natural Science Foundation of China No 20504021, 60576064, Shanghai Science and Technology grant 0452 nm056 and the National Basic Research Program of China No 2006CB300406 for the financial support. We also thank the Instrumental Analysis Center of SJTU for characterization of the samples.

References

[26] Lutz T and Donovan K J 2005 Carbon 43 2508
[31] Dyke C A and Tour J M 2003 Nano Lett. 3 1215
[34] Buffa F, Hu H and Resasco D E 2005 Macromolecules 38 8258