Available online at www.sciencedirect.com
ScienceDirect
Carbon 45 (2007) 1013–1017
CARBON
www.elsevier.com/locate/carbon

The purification of HiPco SWCNTs with liquid bromine at room temperature

Yuri Mackeyev, Sergei Bachilo, Keith B. Hartman, Lon J. Wilson *

Department of Chemistry, Richard E. Smalley Center for Nanoscale Science and Technology, Rice University, P.O. Box 1892, Houston, TX 77251-1892, United States
Center for Biological and Environmental Nanotechnology, MS-60, Rice University, P.O. Box 1892, Houston, TX 77251-1892, United States

Received 12 October 2006; accepted 18 December 2006
Available online 3 January 2007

Abstract

A new procedure to purify HiPco single-walled carbon nanotubes (SWCNTs) from iron catalyst impurity is introduced. The protocol, which uses liquid bromine at room temperature (RT) as an oxidant, improves nanotube purity from iron by a factor of approximately 10, while maintaining good nanotube integrity as demonstrated by near infrared (NIR) luminescence and absorbance measurements. When HiPco SWCNTs are dissolved in RT Br_2(l) (free of O_2 and H_2O), the metallic iron impurity is quickly oxidized to its bromide salt and easily removed by aqueous washing or by washing with dilute acid. The iron content (by ICP-AE) for the purified SWCNT material was 2.8–3.6% by weight (for three different samples) for a single purification step, but could be lowered to 1.6–1.8% with an additional purification cycle. Characterization of the resulting purified SWCNT material has been achieved by TEM imaging, XPS, ICP-AE analysis, Raman spectroscopy, electronic absorption spectroscopy, and by NIR photoluminescence measurements. Finally, the new Br_2(l) purification procedure has been compared to and contrasted with other established purification procedures for HiPco SWCNTs and found to be a highly desirable alternative.

1. Introduction

A widely used method for the catalytic production of SWCNTs is the high pressure CO (HiPco) disproportionation process, where CO gas and an iron-containing catalyst, $Fe(CO)_5$, are combusted under controlled conditions [1,2]. For many material applications of SWCNTs, the carbon-encased iron(0) impurity that results from the HiPco process must be removed with the least damage possible to the SWCNTs.

Oxidative treatment of SWCNTs, typically using O_2(g) or other reactive oxidants like HNO_3(aq), is widely recommended in literature as a good way to remove carbonaceous impurities [3–7] and metal catalyst impurities [6,8–12]. While they may effectively remove iron impurities, the main disadvantages of oxidative procedures that employ HNO_3(aq) is that the SWCNT material is also significantly damaged, shortened and/or derivatized at the ends of the nanotubes or at defect sites (i.e. with carboxylic acid groups). A non-oxidative acidic treatment (with an acid such as HCl(aq)) is an alternative purification method which does not significantly damage SWCNTs, but it is not as effective at removing other carbonaceous particles [5,9] and the iron impurity.

The new procedure, introduced here, uses Br_2(l) as the oxidant to produce SWCNTs of high purity (ca. 1–3% by weight iron) without elevated temperatures and pressures and with minimal sidewall damage, including no derivatization of ends or defect sites. The new protocol is not only a convenient laboratory procedure, but it is also commercially viable, since Br_2(l) is relatively inexpensive and can be recycled. In addition, the energy cost of the process is

* Corresponding author. Tel.: +1 713 348 3268; fax: +1 713 348 5155.
E-mail addresses: mackeyev@rice.edu (Y. Mackeyev), durango@rice.edu (L.J. Wilson).

0008-6223/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbon.2006.12.026

relatively low, and SWCNT purity and integrity have been judged to be generally as good or better than can be obtained by alternative oxidative purification methods.

2. Experimental

Raw HiPco SWCNTs were obtained from Carbon Nanotechnologies, Inc., of Houston, Texas (iron content 26.8% by weight, measured by inductively-coupled-plasma atomic emission spectrometry, ICP-AE). Liquid bromine was purchased from Acros Organics, distilled over P_2O_5 and NaBr under dry N_2(g) and stored at RT, free from O_2 and H_2O. It is important to purify the liquid bromine by distillation, since some sources of bromine also contain chlorine as a contaminate which can contribute to SWCNT degradation under the conditions of this purification procedure. It is also necessary to rigorously exclude H_2O and O_2 during the procedure for the reasons discussed below. In a typical procedure, 20 mg of raw SWCNTs were stirred with 10 ml of Br_2(l) under dry N_2(g) at RT for different periods of time. Purification generally improved with time up to 30 min, but after 30 min, the iron content of the purified sample did not decrease further, even for reaction times as long as 480 h. The SWCNT sample appeared to dissolve completely in the liquid bromine. The Br_2(l) was then removed by gradual evaporation in a stream of dry N_2(g). The resulting solid was washed at RT with dilute HCl (≈0.1 M) accompanied by low-power sonication, followed by DI water, and finally the sample was dried in the air at RT. After this treatment, the SWCNT sample contained up to 30% by weight of intercalated bromine which was removed later by heating the sample for 1 h at 400 °C under dry N_2(g). Complete bromine removal was verified by XPS; AES/XPS surface analysis showed iron content improvement (decrease) together with some decrease in oxygen content (Fig. S-1). The iron impurity for SWCNT samples treated in this manner was in the range of 2.8–3.6% by weight for SWCNTs stirred with Br_2(l) for 4 h at RT or sonicated for 30 min at RT. Elevated temperatures did not produce significant reduction in iron content, but did decrease the required treatment time. An additional second cycle of the procedure reduced the iron content to 1.6–1.8%. Once used, Br_2(l) in a closed system can be recycled for additional procedures, with only a small loss (<2%) per cycle.

Other halogen compounds, including ICl(l), IBr(l) and I_2(l), were also tested and compared to the Br_2(l) procedure. In general, the final SWCNT material, purified by the other halogen compounds but using the same procedure as for Br_2(l), contained larger amounts of iron and required higher temperatures such as ICl: 30–60 °C (6% iron); IBr: 50–80 °C (8% iron); I_2: 120–160 °C (9% iron). Solutions of bromine in CCl_4 or CS_2, and in a concentrated aqueous solution of NaBr, gave purification results in the range of 8–16% iron.

Iron analyses were performed by ICP-AE on a Perkin–Elmer Optima 4300 DV instrument. To prepare a sample for analysis, 0.2–0.5 mg (Cahn Instruments, Inc C-31 microbalance) of the SWCNT material was treated with hot chloric acid (26% by weight), prepared by a literature procedure [13], for 10 min until the sample dissolved completely. A few drops of HCl(aq) (36% by weight) were then added, and the reaction was let stand at 90 °C until the yellow color changed to a colorless solution (usually <1 min). The sample was then cooled to 20 °C, diluted with 2% HNO_3(aq) to 10 ml in a volumetric flask and used for ICP-AE analysis. NIR photoluminescence spectra were obtained using a SPEX Fluorolog 3-22 spectrofluorimeter with an InGaAs photodiode photodetector with N_2(l) cooling. Slits were set to 14.0 nm (excitation) and 4 nm (emission); the scan rate was 1.0 nm s^{-1}. All emission spectra were corrected for fluctuations in the excitation lamp intensity. For the laser-excited NIR luminescence experiments, the SWCNT sample was suspended in 1.0 wt% sodium dodecylbenzene sulfate (SDBS) solution with sonication [14] for a concentration of 1.0 mg/ml, and spectra were taken in 1 mm quartz cuvettes. Transmission electron microscopy (TEM) images were obtained using a JEOL 2010 transmission electron microscope; samples were prepared with Lacey carbon film on a 300 mesh copper grid. Raman spectra were recorded with a Renishaw Microraman.

3. Results and discussion

The Br_2(l) purification procedure as described in Section 2 (RT, 4 h), reduced the iron content of a HiPco SWCNT sample from ca. 27% to ca. 3% by weight for three different samples. A second treatment reduced the content further to ca. 1.7% iron. These values compare favorably with the best that can be accomplished using other oxidative/acidic procedures, as described in the literature and as summarized in Table 1. Our attempts to reproduce the literature procedures are also documented in Table 1. In general,

Table 1
Comparison of the oxidative/acidic purification procedures for HiPco SWCNTs

Purification procedure	Literature reference	% by weight iron remaining after purification (lit., %)	% by weight iron remaining after purification[a] (this work, %)	NIR luminescence intensity[b] (this work)
HCl (35%), 4 h at 60 °C	[10]	<1	10.2–14.4	Good
Microwave irradiation for 2 min, then HCl (35%), 4 h at 60 °C	[3]	9	10.8–12.6	Good
Microwave irradiation for 20 min, then HCl (35%), 4 h at 60 °C	[3]	7	10.5–12.5	Good
H_2SO_4 (98%) + HNO_3(70%), 4 h at 60 °C	[5]	N/A	9.7–14	Poor
H_2SO_5 (25%)[c], 10 min at 20 °C	[5]	N/A	13.9–14.8	Good
HNO_3 (10%), 4 h at 60 °C	[9]	<1	0.6–0.8	Poor
O_2 + SF_6(g) at 200–400 °C, for 3–7 days, then HCl (35%), 12 h at 60 °C	[4]	1.5	3.0	Good
Br_2(l), RT, 4 h	N/A	N/A	2.8–3.6[d]	Good
			1.6–1.8[e]	Poor

[a] Iron analysis by ICP-AE; the sample handling procedure for the present results is described in Section 2. The values reported are the range of values obtained for three different samples.

[b] Comparison with the NIR luminescence intensity of the original unpurified, raw SWCNTs (100%); an intensity greater than 25% of the original is considered as "good", below 5% – as "poor"; excitation laser at 660 nm with luminescence observed in the 900–1600 nm range.

[c] H_2SO_4 mixed with H_2O_2 (30%) at 0 °C, then diluted with water.

[d] After a first purification cycle.

[e] After a second purification cycle.