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Measurement of functionalised carbon nanotube carboxylic acid groups using a simple chemical process

Matthew W. Marshall [a], Simina Popa-Nita [b], Joseph G. Shapter [a,*]

[a] School of Chemistry, Physics and Earth Sciences, Flinders University, Sturt Road, Bedford Park, South Australia 5042, Australia
[b] Institut National des Sciences Appliquées de Rennes, Avenue des Buttes de Coesmes, Rennes, Cedex, CS 14315-35043, France

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Abstract

Chemically functionalised single-walled carbon nanotubes were formed using sonication in a mixture of concentrated sulphuric and nitric acids for varying lengths of time which resulted in carboxylic acid group functionalisation, predominantly at the ends. The carboxylic acid groups were used to form an ionic bond with dodecylamine. The weight of this complex was used to monitor the number of carboxylic acid groups present in the cut SWNT.

Keywords: Carbon nanotubes; Chemical treatment; Functional groups; Chemical structure; Atomic force microscopy

1. Introduction

Carbon nanotubes are low in weight, have high strength and a high aspect ratio (long length compared to a small diameter), and because of these properties are considered to be the ultimate in carbon fibers [1]. They also have remarkable optical properties and individual tubes vary in conductivity from semi-conducting to metallic behaviour.

There are two distinct types of carbon nanotubes. The single-walled carbon nanotube (SWNT), first reported in 1991 [2,3], resembles one layer of graphene sheet rolled into a tube while the multi-walled carbon nanotubes (MWNT) are made up of more than one layer that form concentric tubes [4]. They usually have a diameter from a few angstroms to tens of nanometers and can have lengths up to several microns [4]. SWNTs are considered to be one-dimensional molecules due to their high aspect ratio [5].

SWNTs tend to aggregate into bundles with varying lengths and diameters. Scanning electron microscopy of SWNT material resembles cooked spaghetti, hopelessly tangled and seemingly endless [2]. For SWNTs to become useful they must be separated into individual molecules or small bundles of SWNTs [6]. Previous work to solubilise and disperse SWNTs has included the use of polymer wrapping, such as Gum Arabic, reaction with amines, and the use of surfactants [6]. All of these methods have advantages and disadvantages with some of the disadvantages being difficult removal of the wrapping polymer or the tying up of functional groups so they are not available for use once the SWNTs are in solution.

SWNT functionalistion is important for dispersion and solubilisation [7] and to enable further modification for other uses. Functionalisation must ideally occur at the ends of the SWNT, as side wall functionalistion has been shown to disrupt the electronic structure [8] causing it to lose its intrinsic electronic capabilities as well as some strength [1].

In the untreated state SWNTs may be dispersed in solution using ultrasound, however they do not remain in suspension for any significant time. Chemical oxidation and functionalisation can dramatically increase the stability of the suspensions [9]. Defects can occur at the tube ends, and occasionally on the sidewalls [10] and these defects are usually the prime sites for functionalisation [8]. A

* Corresponding author. Tel.: +61 8 8201 2005; fax: +61 8 8201 2905.
E-mail address: joe.shapter@flinders.edu.au (J.G. Shapter).

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now well established and efficient method to oxidise and functionalise SWNTs is to subject them to prolonged sonication in a mixture of concentrated sulphuric and nitric acids (3:1 ratio by volume, 98% and 70%, respectively) at room temperature [1,6]. The reaction is easy to start at the end caps because of the heavy strain of the hexagon–heptagon pairs [11]. In this way the end caps are quickly removed leaving open-ended tubes, functionalised with carboxylic acid (COOH) groups.

To cut the tubes into shorter lengths, sonication in the acid mixture described above, is used because the collapse of cavitation bubbles in sonication produces microscopic domains of high temperature that attacks the surface of the SWNT, leaving an open hole in the tube side [6]. The acid mixture then oxidises the tube at this newly created defect and cleanly cuts the tube. The tubes are not only cut shorter but are also purified because the acid mixture is known to intercalate and exfoliate graphite [11]. It has been shown in Raman and temperature programmed oxidation (TPO) studies that treatment with concentrated nitric acid lead to impurities of less than 1% [12]. This method of cutting, exfoliating SWNTs from rope bundles, and functionalisation with COOH groups suggests that the abundance of –COOH groups increase with the treatment time [11]. An additional effect from chemical cutting and oxidation is a shift in chirality from the zigzag toward the armchair direction [13].

The cut, open-ended SWNTs, should now have COOH, quinone, ester and anhydride groups from which further modification can be achieved [14]. Previous work by Chen et al. [1] and Niyogi et al. [2], functionalised the COOH groups with octadecylamine ($CH_3(CH_2)_{17}NH_2$). Instead of forming an amide bond with covalent bonding they instead formed an ionic zwitterion (Fig. 1) with the cut SWNT [1]. They found that ionic functionalisation approach gave a much higher yield of SWNTs in organic solution than the covalent functionalisation approach. The presence of zwitterions can significantly improve the solubility of cut SWNTs [1] and leaves the carboxylate groups on the SWNTs available for exchange with other cations in solution [2].

The acidic groups in both multi-walled carbon nanotubes (MWNTs) and SWNTs have been determined previously [8,15,16]. One procedure is based on simple acid–base titrations that in fact are quite difficult to carry out requiring filtration and back titrations. Simpler IR-based approaches to measure the total number of defects sites where oxidation might occur showed considerable error of about 50% from sample to sample. The approach reported in this paper determines the number of the carboxylic acid groups on SWNTs through the formation of a dodecylamine zwitterion. This approach is simpler in that only a very simple reaction with a single subsequent filtration is required. After that filtration, no further chemical manipulation is required.

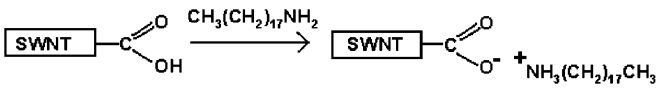

Fig. 1. Schematic representation of the formation of the SWNT-octadecylamine zwitterion.

2. Experimental

2.1. Cutting and oxidation of SWNT

Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Solutions Inc. (P2-SWNT, purified low functionality) and were used as purchased. For every 2 mg of full length SWNT, 1 ml mixture of 3:1 (V/V) concentrated H_2SO_4 and HNO_3 was added and the SWNT/acid mixture was then subject to sonication (Soniclean Pty Ltd, model 160HT, 220/240 V 50/60 Hz) for the required time. To make SWNT with different lengths, excision was carried out over 2, 4, 6, 8, 10, 12, and 14 h. The water in the sonicator was cooled using ice to maintain a temperature of approximately 20 °C. When the desired time had elapsed, the SWNT/acid mixture was diluted with a minimum of 250 ml of deionised water. The resulting diluted nanotube-acid mixture was then filtered using a 0.45 μm polytetrafluoroethylene filter (PTFE—Alltech) leaving a SWNT filter cake. The nanotubes were then rinsed with water until a pH above 5 was obtained. Final rinsing was done using ethanol and the resulting filter cake dried in a vacuum desiccator.

2.2. Atomic force microscopy

Adding approximately 1.0 mg of SWNT to 1 ml of *N*,*N*-dimethylformamide (DMF) and sonicating for approximately 4 h made solutions of the cut SWNTs. One to three microliters of the solutions were put onto freshly cleaved mica surfaces which were then placed into a vacuum desiccator and allowed to completely dry.

Atomic force microscopy (AFM) was used for the characterisation of cut SWNTs. A Digital Instruments Nanoscope IV controller with a multimode head was used and all experiments were performed in air. Tapping mode was used for all AFM measurements. Commercial Si cantilevers/tips (Ultra-Sharp, NT-MDT, Moscow, Russia) were used at their fundamental resonance frequencies, which typically varied from 150–350 kHz. Topographic (height), amplitude and phase images were obtained simultaneously. During an AFM experiment the optimal instrument condition (set point, amplitude, scan size, scan speed and feedback control) was adjusted to allow the best resolution of images. A minimum of four scans was taken for each sample, at a resolution of 5 μm × 5μm, from different areas of the samples. Lengths of SWNTs were measured using cross section analysis and approximately 150 SWNTs or SWNT bundles were counted and measured from all scans in each sample in order to get a length distribution of nanotubes.

2.3. Formation of SWNT-DDA zwitterion

A precisely known amount of approximately 35 mg of shortened SWNTs of each cutting length (2, 4, 6, 8, 10, 12, 14 h), was added to 2 g of dodecylamine (Aldrich, as purchased). The mixture was then placed in a hot water bath (70 °C) and sonicated for 6 h followed by heating in a 110 °C oven for three days. Once cooled sufficiently, 300 ml of 100% ethanol (CSR) was added and the mixture sonicated for 30 min, followed by filtration on a 0.45 μm PTFE filter (Alltech, weight of filter accurately recorded before use) and washed with ethanol (100%). The filter cakes were dried on the filter in vacuum until constant weight.

3. Results and discussion

3.1. Cutting SWNT

The cutting of the nanotubes achieved two purposes. It firstly allowed the nanotubes to be functionalised with COOH groups from which further chemistry could be achieved and secondly, due to the COOH groups, the SWNT were able to be made more soluble in various solvents and remain in solution for a longer time without precipitation.

The temperature of the water bath in which the sonication occurred was critical. An experiment to sonicate the acid/SWNT mixture at a much higher temperature (65 °C) resulted in half of the starting mass being lost during filtration. The increased temperature was likely to have enhanced the exfoliation of SWNTs allowing the acid a greater surface area of SWNT to attack, and also increase the rate of reaction between the carbon–carbon bonds and the acid.

Immediately after sonication, the acid/SWNT mixtures were put into deionised water where they formed dark brown/black solutions. This step is necessary as previous work [6] has shown that if the SWNT are left in a concentrated acidic mixture they continue to get shorter over time, by being oxidised at the ends. The solutions formed 'clouds' of nanotubes after a period of seconds to 30 min, with the longer nanotubes (shorter cutting time) forming clouds more quickly than the shorter nanotubes (longer cutting time). The solutions were then filtered and washed.

3.2. Atomic force microscopy (AFM) of SWNTs

Atomic force microscopy (AFM) was used to characterise the SWNTs, in particular the length of the bundles of the SWNTs. Tapping mode AFM was used as contact mode AFM would have moved the SWNT on the mica surface.

A lot of material, other than nanotubes, can be seen in most scans. The nature of this material could not be determined by AFM. It is unlikely to be metallic catalyst, as metallic particles should have been oxidised during the acid treatment and be removed during filtering. The material is likely to be carbonaceous material formed during the manufacturing process of the SWNTs as many of the impurities seem to be attached to the outside of the SWNTs or have SWNTs growing through them. The AFM scans are of bundles of SWNTs. Previous work [1] has shown that the SWNTs are formed in bundles of between 10 and 30 individual SWNTs. The acid and sonication treatment of the SWNT has exfoliated the SWNT into bundles containing fewer SWNTs (Fig. 2) as the width of the bundle decrease in the scans with longer cutting times. Some of the AFM scans also reveal arrangement of the shorter SWNT. The SWNTs appear to be lying in predominantly two axes at approximately 120° to each other (Fig. 2c). Previous work suggests that the SWNTs align with the underlying structure of the mica. This phenomenon is seen only with well-purified SWNTs and is an indication of a high degree of molecular cleanliness along the tube sides [6].

It can also be clearly seen that the tubes are shorter in the samples with the longer cutting times and a length distribution of SWNT bundles for each treatment time was obtained. Fig. 3 shows mean length with standard deviations plotted against the treatment time.

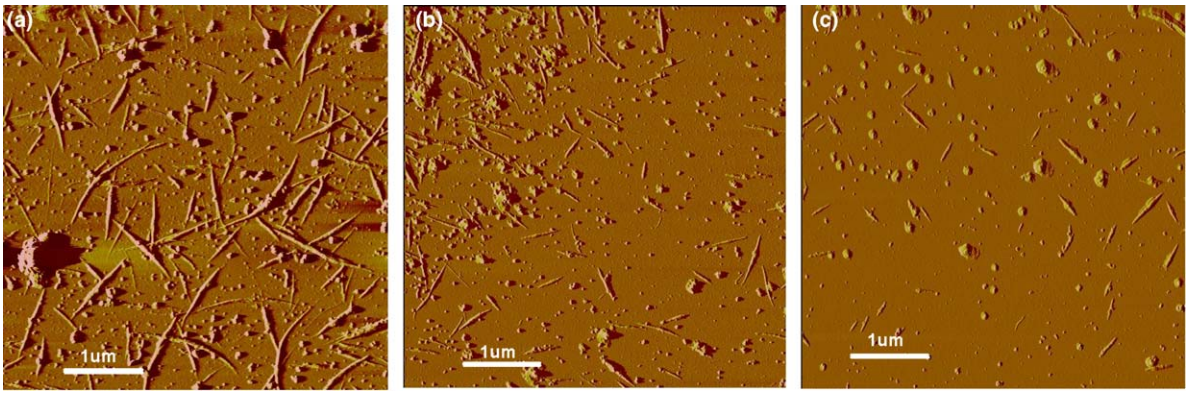

Fig. 2. Tapping mode AFM images of SWNT cut for (a) 2 h, (b) 6 h and (c) 10 h. All images are 5 μm × 5μm and taken using NT-MDT Ultra-Sharp cantilevers operating at their resonant frequency.

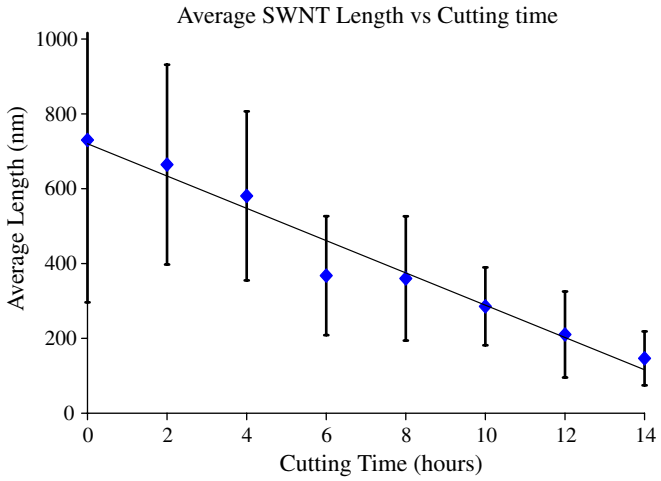

Fig. 3. Mean SWNT length as a function of cutting time. The means are averages of at least 150 SWNT lengths from AFM images.

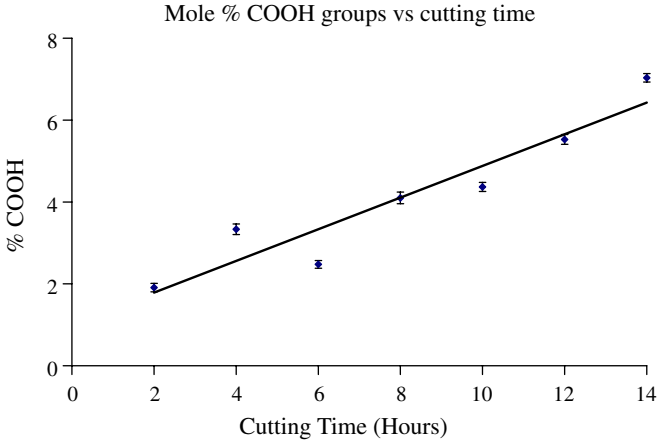

Fig. 4. Mole percent of COOH groups. The percentage is the fraction of carboxylic acid carbons to unfunctionalised or otherwise functionalised (i.e. not acid groups) carbons in the SWNT.

A question remains as to whether the SWNTs were being shortened at the ends or if the SWNT sidewalls were being randomly cut. Whilst there is no doubt some tube shortening at the ends of the SWNT, there must also a considerable amount of cutting at defect sites, introduced by sonication, along the SWNT walls to account for the large (a factor of three) reduction in average length over a short period of time. It is unlikely that shortening at the end only would lead to these changes. This is further confirmed by Fig. 4 that shows the percentage of carboxylic acid groups increasing with cutting time. This eight fold increase must arise due to cutting at defects along the sidewalls.

3.3. Functionalisation of SWNTs with dodecylamine

The cut SWNTs have COOH groups around their open ends and most likely at defect sites in their sidewalls. Previous studies [15,17] have shown that COOH groups are at the ends of oxidised SWNTs, and Hu et al. [15] determined the number of total acidic groups (OH and COOH) and COOH groups in commercial samples of SWNTs from different manufacturers. Hamon et al. [8] reported the number of COOH groups in bulk samples of SWNTs after they have been subjected to oxidative shortening and purifying. Their data, obtained by using analytical FTIR, gives a result between 3.6% and 8.0% COOH groups in their samples of SWNTs. The method they used to cut the SWNTs was the same method used in this work however they cut and oxidised the SWNTs for 24 h and collected the SWNTs that were left by filtration.

The percentage mass increase of the filtered product is an indication of the increasing functionality. The data obtained are summarised in Table 1. As the number of COOH groups increase, the sites for formation of the zwitterion also increase. The percentage mass increase was directly related to the number of COOH groups on the SWNT and increases with cutting time as expected as shown in Fig. 4. For every COOH group on the SWNT one molecule of dodecylamine is added. When a correction is made for the molecular weight of the dodecylamine there is a very good correlation to the number of COOH groups reported by Hu et al. [15] This group reported that the number of COOH groups was between 0.7% and 0.8% for the purified low functionality SWNTs. These are the same nanotubes used in this work. Extrapolating the graph in Fig. 4 to zero cutting time gives a COOH percentage of 1.0%.

Previous reports have said that the actual percentage of COOH groups in the SWNTs may be lower than that suggested by Fig. 4 as one of the major impurities in purified SWNTs is small-size carboxylated carbons with a high O/C ratio [1]. Our work suggests that this is not the case. After long periods of cutting, the vast majority of impurities will have been removed from the sample as indicated

Table 1
Summary of masses used and results for different nanotube cutting times

Cutting time (h)	Mass SWNT (mg)	Mass SWNT-DDA (mg)	Difference in mass (mg)	% Increase in mass	Mole% COOH
2	33.1	35.7	2.6	7.85	1.90
4	26.8	30.5	3.7	13.72	3.33
6	36.3	40	3.7	10.19	2.47
8	24.3	28.4	4.1	16.87	4.10
10	31.7	37.4	5.7	17.98	4.37
12	29.0	35.6	6.6	22.76	5.53
14	33.5	43.2	9.7	28.96	7.03

by the cleanliness of the sample imaged after 10 h of cutting (Fig. 2c). The AFM work shows very little contamination but the increase in the number of COOH groups for the longer cutting times is on the same line as that for shorter cutting times. At longer times, the increase in COOH groups must be due almost exclusively to reduction in the length of nanotubes and hence there is no reason to believe this is not the case at shorter cutting times even where more impurities might be present. Thus, the measured percentage of COOH groups in this work is due predominantly to SWNT and an accurate reflection of the acid group content of the nanotubes.

This approach to the determination of acid groups in cut carbon nanotubes is better than previously reported methods due to its simplicity. The titration methods reported are quite accurate but time consuming and complex. Spectroscopic based techniques suffer from several uncertainties not the least of which is the calibration required. The approach reported in this paper involves one reaction followed by a filtration and weighing. The accuracy is better than the spectroscopic methods reported which show a 50% error. The errors in this report are about 5% for the samples with low numbers of carboxylic acids and get smaller for higher concentrations. The simplicity of the method allows many replicates to be performed easily which will further reduce the errors.

4. Conclusion

The acid group content of SWNT has been measured for varying extents of functionalisations using zwitterion formation and the weight of the formed complex. As expected, the acid content increases with cutting time and the results are consistent with previous work using the uncut nanotubes. Two hours of cutting increases the acid group content by approximately 1%.

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