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Assessing the Quality of Carbon Nanotubes

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Abstract

We have assessed the quality of a commercial source of bulk multi-walled carbon nanotubes with respect to purity and degree of acid functionality. In addition, we have evaluated the applicability of several methods commonly used by suppliers to ascertain the purity of carbon nanotubes (SEM, TEM, and TGA).

ICP-MS data indicate that residual metal catalyst is present, and is comprised primarily of nickel (1.2 weight %). It was also determined that most of the metal (> 99.5%) is encapsulated by carbon (likely amorphous carbon). Most of the catalyst was removed by acid oxidation, preceded by thermal treatment (400 – 500 ℃ in air) which liberated the metal from the encapsulating carbon. Based on mass loss during thermal oxidation, the amorphous carbon content was estimated to be approximately 45%.

Titration analysis data of the as-received material indicate that the degree of acid functionality is 3.07 ± 0.27 mequiv/gram. This value decreases appreciably upon thermal treatment (2.56 ± 0.03 mequiv/gram at 500 ℃, and 1.50 ± 0.05 mequiv/gram at 600 ℃), which likely drives off the functional groups.

Résumé

Nous avons évalué la qualité des nanotubes de carbone à parois multiples en vrac vendus par une source commerciale, sur les plans de la pureté et du degré de fonctionnalisation par traitement acide. De plus, nous avons évalué l'applicabilité de plusieurs méthodes couramment utilisées par les fournisseurs pour déterminer la pureté des nanotubes de carbone (microscopie électronique à balayage, microscopie électronique à transmission et analyse thermogravimétrique).

Les données obtenues par spectrométrie de masse à source de plasma inductif (ICP-MS) indiquent la présence de résidus de catalyseur métallique — essentiellement du nickel (1,2 % de la masse). Nous avons également déterminé que la plus grande partie du métal (plus de 99,5 %) est enrobée de carbone (probablement du carbone amorphe). La majeure partie du catalyseur a été éliminée par un traitement thermique (400 – 500 ℃ dans l'air), suivi d'une oxydation acide, ce qui a libéré le métal du carbone qui l'enrobait. D'après la perte de masse au cours de l'oxydation thermique, nous estimons que la teneur en carbone amorphe se situait autour de 45 %.

Les données de titrage des matériaux, analysés tels qu'ils ont été reçus, indiquent que le degré de fonctionnalisation par traitement acide est de $3,07 \pm 0,27$ $mol_{éq}/g$. Cette valeur diminue grandement sous traitement thermique ($2,56 \pm 0,03$ $mol_{éq}/g$ à 500 ℃, et $1,50 \pm 0,05$ $mol_{éq}/g$ à 600 ℃), lequel a probablement pour effet d'expulser les groupes fonctionnels.

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Executive summary

Introduction

As-prepared carbon nanotubes contain impurities that consist of residual metal catalyst particles, as well as non-nanotube carbon species, such as amorphous and graphitic carbon. The quality of bulk nanotubes (presence of impurities), as well as the quality of individual nanotubes (presence of defects), can dramatically affect the properties of interest. Commercial suppliers generally report the purity of carbon nanotubes in terms of % carbon. The % carbon nanotube content may be substantially less than this reported value, as the % carbon value encompasses all types of carbon present (nanotube and non-nanotube). Furthermore, the techniques by which the % carbon value is often determined are not necessarily a reliable source of quantitative data. Hence, it is highly recommended that all carbon nanotube batches are assessed for the presence of impurities.

We have applied several techniques to assess the quality of a commercial source of multi-walled carbon nanotubes (MWNT). The techniques, which are commonly employed by suppliers, include transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA). The results of these techniques, and their efficacy in evaluating the quality of carbon nanotubes, are discussed in this technical memorandum.

Results

Residual metal catalyst content may be accurately determined using inductively coupled plasma mass spectrometry (ICP-MS). Evaluation of amorphous carbon content is more difficult, although a rough assessment may be determined based on mass loss (during thermal oxidation), and supported by precision of titration analysis data. The reduction of amorphous carbon content may be confirmed using the techniques described previously. The estimation of amorphous carbon is based on mass loss, and thus care must be taken to ensure that much of the catalyst has been removed prior to thermal oxidation (to avoid significant catalytic oxidation of nanotubes).

The commercial sample is reported to contain > 95 % carbon, which is a reasonable evaluation based on our results. Nickel was found to be the major source of metallic impurity, and its content was determined to be 1.2%. Thus, the non-carbon assessment of <5% is reasonable. An evaluation of the nanotube content is not provided, however, our results suggest that the sample contains less than 50 weight %.

Future plans

For effective removal (or at least significant reduction) of most impurities, more than one step is required, and an iterative process may be necessary. Experiments are

underway to elucidate an effective purification methodology that maintains (and perhaps improves) the integrity of the nanotubes.

Kopac, M.C., Huber, T.A.. 2007. Assessing the Quality of Carbon Nanotubes. DRDC Atlantic TM 2007-136. Defence R&D Canada – Atlantic.

Sommaire

Introduction

L'analyse des nanotubes de carbone tels que reçus indique la présence d'impuretés : particules résiduelles de catalyseur métallique et formes du carbone autres que les nanotubes, le carbone amorphe et le graphite par exemple. La qualité des nanotubes en vrac (présence d'impuretés), ainsi que la qualité des nanotubes individuels (présence de défauts), peuvent grandement affecter les propriétés qui nous intéressent. Les fournisseurs commerciaux indiquent généralement la pureté des nanotubes en carbone en terme de teneur (%) en carbone. La teneur en carbone des nanotubes peut être passablement inférieure à la valeur indiquée, car elle englobe toutes les formes de carbone présentes (dans les nanotubes et autres). De plus, on estime que les techniques souvent utilisées pour établir la teneur en carbone ne sont pas suffisamment fiables pour l'obtention de données quantitatives. Par conséquent, il est grandement recommandé d'évaluer tous les lots de nanotubes de carbone pour découvrir la présence d'impuretés.

Nous avons utilisé plusieurs techniques pour évaluer la qualité des nanotubes à parois multiples offerts par une fournisseur commercial. Ces techniques — couramment employées par les fournisseurs — comprennent la microscopie électronique à transmission (TEM), la microscopie électronique à balayage (SEM) et l'analyse thermogravimétrique (TGA). Ce mémoire technique présente les résultats de ces techniques et leur efficacité sur le plan de l'évaluation de la qualité des nanotubes de carbone.

Résultats

La teneur en catalyseur métallique résiduel peut être déterminé précisément par spectrométrie de masse à source à plasma inductif (ICP-MS). Toutefois, il est plus difficile d'évaluer la teneur en carbone amorphe, bien que l'on puisse en faire une évaluation approximative d'après la perte de masse (pendant l'oxydation thermique), et les confirmer à l'aide des données de titrage précises. La réduction de la teneur en carbone amorphe peut être confirmée à l'aide des techniques décrites ci-dessus. L'estimation de la teneur en carbone amorphe est basée sur la perte de masse, et il faut donc s'assurer que la majeure partie du catalyseur a été retirée avant l'oxydation thermique (pour éviter une oxydation catalytique importante des nanotubes).

Selon le fabricant, l'échantillon commercial analysé contient > 95 % de carbone, ce qui semble raisonnable d'après nos propres résultats. La principale impureté métallique constatée est le nickel, dont nous avons établi la teneur à 1,2 %. Par conséquent, l'évaluation des matières autres que le carbone en concentration < 5 % est raisonnable. Une évaluation de la teneur en carbone des nanotubes n'est pas présentée; toutefois, nos résultats semblent indiquer que l'échantillon en contient moins de 50 % en masse.

Recherches futures

Pour éliminer effectivement la plupart des impuretés (ou de baisser leur concentration à une valeur acceptable), on doit recourir à plusieurs étapes, voire à un processus itératif. Des expériences en cours permettront d'établir un protocole de purification efficace qui préservera, voire améliorera, l'intégrité des nanotubes.

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1. Introduction

Carbon nanotubes are extremely small tubes of carbon which may be envisioned as rolled up graphene sheets. Each carbon in the graphene hexagonal lattice is considered to be sp^2 hybridized with an unpaired electron in the unhybridized valence p orbital taking part in the π system which extends over the entire lattice. The exceptional electrical and mechanical properties exhibited by carbon nanotubes are derived from this extended π system. The nanotubes may be formed as single tubes, known as single-walled nanotubes (SWNT), or in sets of concentric tubes, known as multi-walled nanotubes (MWNT). In addition to variation in the number of concentric tubes, each tube possesses a specific helicity or chirality, which describes the twist of the tube, and dictates the electronic properties of the tube. Statistically, approximately ⅓ of the tubes are metallic, and ⅔ are semi-conducting in nature.

There are two important aspects to assessing the quality of a sample of carbon nanotubes: impurities and defects. The presence of both impurities and defects is a function of the synthetic technique and reaction conditions, and will dramatically affect the properties. Although optimization of synthetic processes is the focus of many scientists, and research is ongoing, the preparation of nanotubes free of defects and impurities is not yet realized. Given the current state of the art, it is essential to assess the state of as-received product, and treat as necessary to optimize the properties of interest.

1.1 Carbon Nanotube Purity

The quality of a bulk sample of nanotubes is a function of the presence and quantity of impurities. Impurities commonly present in carbon nanotube samples are residual metal catalyst particles and non-nanotube carbon species, such as amorphous carbon, graphitic carbon, and carbon nanoparticles (including fullerenes).

Most commercial suppliers assign a numerical assessment of purity to bulk nanotube samples; the purity assessment corresponds to the % *carbon* in the sample. There are two problems associated with this; firstly this value corresponds to all types of carbon, hence amorphous carbon, graphitic carbon, and carbon nanoparticles are included in this value. Secondly, this value is based on a visual evaluation of electron microscopy (EM) images, which are unlikely to be representative of the whole sample, and certainly cannot quantify the purity. Furthermore, some suppliers present only scanning electron microscope (SEM) images, which are much less informative than transmission electron microscope (TEM) images. Inaccurate purity assessment can result in the reporting of a grossly overestimated degree of purity; the actual nanotube content in commercially available products can be significantly lower than the reported carbon content.[1]

1.1.1 Purification Methods

Purification of carbon nanotubes is not straightforward, as various impurities exhibit differing properties, and hence respond to purification treatment differently. Thus, purification methods are generally designed for the removal of specific impurities. Residual metal catalyst is commonly removed by an acid oxidation treatment of the bulk sample, resulting in the metal particles being oxidized and dissolved in the acid. The oxidation conditions range from room temperature reactions in highly concentrated acid or acid mixtures to refluxing in a range of concentrations.[2, 3] Acid oxidation is highly effective for the removal of accessible metal particles, however, metal particles encapsulated in carbon may be unaffected by this method. The greatest disadvantage of acid oxidation purification is that the carbon nanotubes are also oxidized, resulting in the introduction of acid functionality on the carbon surface (see section 1.3), as well as shortening of the tubes under severe conditions (*vide infra*). Indeed, extreme effects on the tubes have been observed, such as the transformation of SWNT into MWNT under extended acid oxidation conditions.[3]

A less common method for the removal of metallic species, involves the high temperature (> 2000 ℃) treatment of the nanotubes under inert atmosphere, or vacuum.[4-6] Results indicate that this purification method is much less destructive to the nanotubes.

Non-nanotube carbon is comprised of amorphous carbon, graphitic carbon, and carbon nanoparticles. Methods designed to remove amorphous carbon and carbon nanoparticles generally exploit their higher reactivity relative to most nanotubes. The most common method employed for the removal of more reactive carbon is thermal oxidation, in which the more reactive carbon undergoes oxidation at a lower temperature than most nanotubes.[3, 7] However, loss of small diameter nanotubes may occur prior to complete removal of more reactive carbon, thus extended oxidation should be avoided to minimize nanotube loss. Moreover, the thermal degradation of the carbon nanotubes is catalyzed by the presence of metal particles, thus it may be important to reduce the metal content prior to any thermal oxidation treatment. Fullerenes may easily be removed by dissolution in toluene.[8] Graphitic carbon is extremely difficult to remove, as it is highly stable to oxidative conditions.

Several purification methods have been developed in which the nanotubes are physically separated from the impurities, based on the varying size of some impurities relative to the nanotubes. These methods are attractive as nanotube degradation is minimized. The removal of amorphous carbon and carbon-coated metal particles from SWNT has been accomplished by ultrasonic-assisted filtration, although some large impurity particles are still present.[8] Some success with graphite removal by physical separation utilizing a surfactant solution has also been demonstrated.[9]

Due to the varying nature of the impurities, the requirement for a multiple step purification protocol, where each step targets a specific impurity, is obvious. A multi-step approach is generally the most effective, and depending on the nature of the impurities, some gains may be realized by the use of an iterative approach. A number of elaborate multiple step methods have been published,[10, 11] however, one must bear

in mind that these methods may not be effective for all bulk nanotube samples. For example, some purification methods designed for MWNT are believed to be inapplicable to SWNT, which are purportedly more reactive to some conditions due to higher curvature.[2] In addition, nanotubes possessing a high defect density (see section 1.2) and/or narrow diameter will degrade substantially under aggressive oxidative conditions.[12] Hence, the nature of the bulk nanotube sample should dictate the purification protocol.

1.1.2 Assessment of Purity

Various complementary techniques are employed to evaluate carbon nanotube purity, and provide qualitative and quantitative data. Most commercially available products contain a large quantity of impurities, and these impurities are unlikely to be homogeneously dispersed throughout the sample. The random distribution of the impurities necessitates multiple sampling and measurement, in order to provide a reasonably accurate evaluation of nanotube purity.

The presence of residual metal catalyst may be detected by thermogravimetric analysis (TGA), although accurate quantification requires an analytical technique, such as inductively coupled plasma mass spectrometry (ICP-MS). Metallic particles are also observed by transmission electron microscopy (TEM), although EM methods provide only a qualitative assessment of the bulk sample, and the sample size is too small to be representative of the bulk sample.

Raman spectroscopy is useful for assessing the presence of amorphous carbon. The D band ($\sim$1350 cm^{-1}) gives a measure of sample disorder, hence presence of amorphous carbon (sp^3 and sp^2 hybridization), and the G band ($\sim$ 1580 cm^{-1}) gives a measure of crystallinity, thus the extent of graphitization (sp^2 hybridization). Often the ratio of the intensity of the D band to the G band, I_D/I_G, is reported as a rough assessment of disordered carbon content. However, this method is not truly quantitative with respect to purity, and any graphitic carbon present will skew the results. This method is most useful when comparing samples before and after treatment, as a means of assessing treatment efficacy. Again, due to sample inhomogeneity, spectroscopic investigation of several samples is recommended.

Near-infrared (NIR) spectroscopy has also been explored as a means of evaluating SWNT purity,[1] although is limited to SWNT with a fairly narrow diameter range.

1.2 Carbon Nanotube Defects

The quality of individual nanotubes is a function of the presence and quantity of defects.[13] There are three main defect types: topological defects (where non-hexagon rings exist in the sidewalls – such defects, in the form of pentagons, exist at the end caps and are mandatory to provide the curvature necessary to close up the ends), rehybridization defects (where some carbon atoms exhibit sp^3 (not sp^2) hybridization), and incomplete bonding defects (atomic vacancies or dislocations).

As mentioned previously, the exceptional nanotube properties are a direct result of the extended π system, and naturally, any disruption in the π system serves to degrade the electrical and mechanical properties. Defects disrupt the continuity of the π system, thus affect the electrical and mechanical properties of the individual tube. High defect density is highly deleterious to the favourable properties of nanotubes.

Defect density may be reduced dramatically by thermal annealing (heating) in an inert atmosphere or under vacuum, which can aid in repairing defects, rendering a highly graphitized surface.[4, 6, 13]

1.3   Carbon Nanotube Surface Functionality

Carbon nanotubes that have been subjected to any post-synthesis treatment may possess surface functionality – atoms or groups of atoms may be chemically bonded to carbon atoms in the nanotube framework. Although not listed as a defect, this functionality has the same disruptive effect on the extended π system. Surface functionality is prevalent if the nanotubes have undergone acid oxidation (for the purpose of purification). The degree and type of functionality is dependent on the concentration and oxidation strength of the acid. The nature of the functionality can vary from highly acidic carboxylic acid groups, to less acidic groups such as lactones, and phenolic hydroxy groups.[14, 15]

Low oxidizing strength acids effect functionalization at existing defect sites, and react with carbons at the highly strained end caps. More strongly oxidizing acids can introduce defects, and if strong enough, can cause shortening (cutting) of the tubes. Furthermore, strongly oxidizing acids can completely react with smaller diameter tubes, resulting in their unintentional removal.

Titration analysis is a method commonly used to assess the extent of acid functionality on the surface of carbon. The method involves the neutralization of acid groups on the surface of the carbon sample with excess base solution. A portion of the base reacts with the acid functionality, and the remaining base is quantified by titration with acid (back-titration). Employing base of varying strength enables the quantification of the different types of acid functionality present on the carbon surface.[14, 15]

In this technical memorandum, we report on the bulk quality assessment of commercially available multi-walled carbon nanotubes, and provide preliminary data on our purification methodology.

2.   Experimental

2.1   Materials

Multi-walled carbon nanotubes were purchased from Sigma-Aldrich (95+ % C, 30 –
50 nm in diameter and 0.5 – 200 μm in length). Nitric acid was purchased from J.T.
Baker, sulphuric acid from Sigma-Aldrich, and hydrochloric acid from Anachemia.
All acids were used without purification. Sodium hydroxide and sodium hydroxide
solution were obtained from BDH and Fisher, respectively, and used as received.

2.2   Instrumentation/Analytical Techniques

Scanning electron microscope (SEM) images were acquired using a JEOL LEO
1455VP instrument. SEM samples were prepared by sonicating a small amount of
material in ethanol and depositing drops of resulting dispersion on carbon or aluminum
stubs, followed by gold coating. Transmission electron microscope (TEM) images
were acquired on a Hitachi H-7000 instrument; TEM samples were prepared by
depositing a drop of dispersion (prepared as above) on a holey carbon coated copper
TEM grid. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was performed
with a Varian Ultramass 700 for the quantitative determination of residual metal
catalyst. The ICP-MS samples were prepared by digestion of the material in 8M
HNO_3; any remaining solid was filtered off, and the resulting solutions were analyzed.
Thermogravimetric analysis (TGA) data were acquired on a TA50 in ambient
atmosphere and a temperature ramp of 10 ºC /min.

Titration Analysis

Typically, a small sample of material (10 – 30 mg) is sonicated in 10.00 mL of 0.100
M NaOH solution for 2 hours, and then allowed to sit for 3 days. The suspension is
then filtered through a 0.2 μm polycarbonate membrane (Millipore), and the solid
washed thoroughly with distilled water (washings added to filtrate). The filtrate and
washings are then back-titrated against standardized HCl (aq) to assess the amount of
unreacted base. The amount of reacted base corresponds to the amount of base
required for neutralization of acid functional groups. Data are expressed in
milliequivalents of acid (functional groups) per gram of material (mequiv/g).

2.3   Thermal Experiments

Water Reflux

A sample of as-received MWNT (211 mg) was suspended in 150 mL distilled water,
followed by refluxing for 22h. Initial and final sample mass, as well as pH of solution
was measured.

Thermal Oxidation

Thermal oxidation was carried out in air (at temperatures ranging from 300 – 600 ℃) to effect the oxidation of amorphous carbon. The sample was placed in a ceramic crucible and heated in a furnace. The mass of the sample was measured before and after heating.

2.4 Acid Oxidation Experiments

Acid oxidation experiments involved refluxing the material in acid (usually 6M HNO_3) for a period of time (typically 24h). The material was collected on a sintered glass frit (medium porosity), and washed with distilled water until the pH of the filtrate indicated the washing was complete (same pH as distilled water). The material was then dried *in vacuo* overnight. The dried product was analyzed by TGA, ICP-MS, and titration analysis.

3. Results and Discussion

3.1 Assessment of As-Received Material

The state of the as-received nanotubes was evaluated by electron microscopy (scanning, SEM, and transmission, TEM), TGA, ICP-MS, and titration analysis. Transmission electron microscopy (TEM) provides a qualitative assessment of the presence of the various types of impurities (metals and non-nanotube carbon). A TEM image of as-received MWNT is presented in Figure 1. The sample is riddled with impurities, as is immediately evident by the prevalence of dark areas (A), which are likely residual metal catalyst and non-nanotube carbon. Also obvious is the wide range of nanotube diameters present in the sample.

Scanning electron microscopy (SEM) is less informative than TEM, although a qualitative assessment is possible as non-nanotube components are readily observed. An SEM image of as-received MWNT is presented in Figure 2. Large quantities of amorphous carbon (A) and carbon nanoparticles (B) are evident. The smaller particles may also be comprised of residual catalyst.

Thermogravimetric analysis (TGA) was performed and weight – temperature data are presented in Figure 3. The TGA trace represents the mass of the sample as a function of temperature. Highly pure MWNT samples exhibit a relatively high onset of oxidation (> 500 ºC). The presence of residual metal catalyst can often cause an increase in mass as the temperature increases, due to the formation of metal oxides, however this was not observed with the as-received Aldrich MWNT. The absence of this initial mass increase is likely a result of the purification step performed by the supplier, where a large portion of readily accessible residual catalyst was removed. Carbon-encapsulated catalyst particles may not be available under these conditions to undergo oxidation.

Titration analysis of the as-received MWNT indicates that the degree of acid functionality is 3.07 ± 0.27 mequiv/gram (based on three analyses), roughly corresponding to 1 in 27 carbon atoms being functionalized. As the MWNT possess a higher surface area/volume ratio than amorphous carbon, one would expect the former to exhibit a higher degree of acid functionality. Thus, it is reasonable to assume that the acid functionality of the MWNT is greater than the data indicate, due to the presence of amorphous carbon which will skew the data to lower acid functionality density values.

Figure 1. *TEM Image of As-Received MWNT*
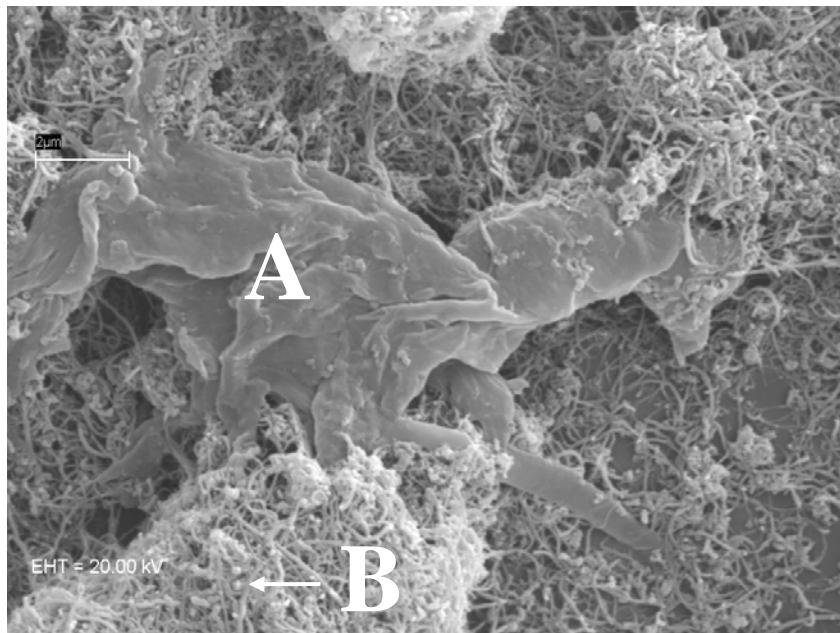
Figure 2. *SEM Image of As-Received MWNT*
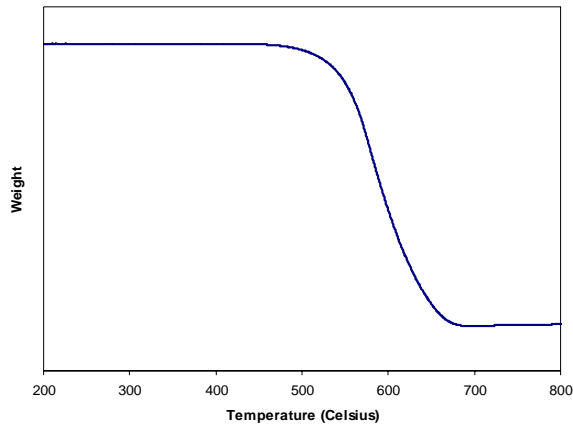
Figure 3. *TGA Trace of As-Received MWNT*

ICP-MS analysis of the as-received MWNT indicates that the major metal species present is nickel (Ni), with smaller amounts of lanthanum (La) and iron (Fe). Initial ICP-MS analysis was performed on a sample of bulk MWNT that were digested in 8M HNO_3; the carbon was not fully oxidized by the acid, hence the unreacted carbon was removed and the remaining solution was subjected to ICP-MS analysis. The ICP-MS data for this experiment (see experiment 1 in Table 1) led to the conclusion that the metal content was quite low (< 10 ppm). Subsequent experiments, however, revealed much higher metal content than reflected in the initial analysis, which suggested that much of the metal was unavailable under these conditions of ICP-MS sample preparation (8M HNO_3 digestion). It was concluded that the majority of the metallic species are encapsulated with carbon during nanotube production, and that much of this carbon coating remains intact during ICP-MS sample digestion. In an effort to assess the total metal content, a sample of as-received MWNT was heated above 600 ºC in air (ashing) to completely oxidize all carbon material. At the temperatures employed, evaporation of metals (or metal oxides) does not occur. The ashed sample completely dissolved in 8M HNO_3, and the solution was analyzed by ICP-MS (see experiment 2 in Table 1). The data indicate that the MWNT contain significantly more residual metal catalyst than that found by experiment 1. The very large value of nickel in the ashed sample (1.2 % relative to bulk MWNT) indicates that almost all of the nickel particles are encapsulated (or otherwise unavailable for oxidation). Clearly, removal of the metal impurities must be preceded by their liberation.

Table 1. *ICP-MS Data for As-Received and Ashed MWNT*

Experiment	Sample	Ni (ppm)
1	As-received MWNT	6.1
2	Ashed MWNT	11800

3.2 Thermal Experiments

Several experiments of a thermal nature were performed on as-received MWNT in order to determine the effect (if any) on the nanotubes. The majority of the experiments involved heating the solid sample under varying conditions, including refluxing the nanotubes in water. The effect of each thermal treatment was assessed by determining the mass loss (as a result of the treatment) and in some cases, the degree of acid functionality, as determined by titration analysis (see Table 2).

Samples were heated at several temperatures under vacuum as well as ambient pressure, and did not exhibit any significant loss in mass, even when maintained at 70 ºC under vacuum for 3 days (see experiments T1 – T3 in Table 2). Previously water-refluxed and ball-milled MWNT were heated at 300 ºC for 2 hours in air, and did not experience any mass loss (experiment T4). From these experiments, it may be concluded that the nanotubes have very low moisture content.

Also in experiment T4, the thermally treated nanotubes were ball-milled prior to titration analysis in an effort to improve sample homogeneity. Two separate titration analyses were performed, and the results indicate that the degree of acid functionality is 2.6 ± 0.7 mequiv/g. From the large degree of uncertainty (27%), it may be concluded that ball-milling did not improve sample homogeneity.

Samples heated in air at higher temperatures ($\geq$ 500 ºC) even for very short time periods ($\leq$ 1h) suffered significant mass losses (see experiments T5 – T7). Clearly, these losses do not correspond to loss of water, but likely to carbon oxidation. The carbon species undergoing oxidation would most likely be amorphous carbon, although loss of some smaller diameter nanotubes may also occur. Furthermore, the degree of carbon oxidation may well be greater than the mass data indicate, due to the concurrent mass gain as the residual catalyst particles become oxidized. The low degree of acid functionality exhibited by material heated at high temperatures, relative to as-received MWNT data, provides further evidence for the removal of amorphous carbon. Data for samples heated at 500 ºC, and 600 ºC (2.56 ± 0.03 and 1.50 ± 0.05, mequiv/g respectively) are lower than that of as-received MWNT (3.07 ± 0.27 mequiv/g), indicative of decreased functionalization upon heating. The significant mass losses (50% and 82%, for 500 and 600 ºC, respectively) indicate that a significant amount of the carbon has been oxidized, and presumably a large portion of that would be amorphous carbon. The presence of amorphous carbon in the sample would be expected to skew the titration analysis results to lower values. Thus, in the absence of change in the degree of functionality, the removal of amorphous carbon should result in higher titration analysis values. The actual reduction in the values, in conjunction with the significant mass loss, indicates that the nanotubes truly possess a lower degree of acid functionality.

Table 2. *Summary of Thermal Oxidation Experiments*

Expt	Sample	Atmosphere	Temperature (ºC)	Time	Mass Loss (%)	Acid Functionality (mequiv/g)[≠]
T1	As-received MWNT	Air	100	24h	~ 0	—
T2	As-received MWNT	Vacuum	70	3 days	~ 0	—
T3	As-received MWNT	Vacuum	180	16h	~ 0	—
T4	Water-refluxed, ball-milled	Air	300	2h	~ 0	2.6 ± 0.7 (2)
T5	As-received MWNT	Air	500	1h	42	—
T6	As-received MWNT	Air	500	45 min	50	2.56 ± 0.03 (3)
T7	As-received MWNT	Air	600	1h	82	1.50 ± 0.05 (2)
T8	Water-refluxed MWNT	Aqueous	100	—	~ 0	2.42 ± 0.49 (2)

≠ Number of samples analyzed in parenthesis.

Samples subjected to reflux in distilled water (see experiment T8) did not suffer any loss in mass, although the pH of the water did become slightly more acidic. This may be due to dissolution of residual acid introduced by supplier purification, or possibly the loss of some acid group functionality from the nanotube surface. Titration analysis of two samples yielded slightly lower acid group functionality (2.42 ± 0.49 mequiv/g) relative to as-received samples (3.07 ± 0.27 mequiv/g) although the data spread indicates that there is no significant statistical difference. In the literature, refluxing a sample of SWNT for several hours resulted in the water becoming yellowish; this was attributed to the dissolution of aromatic carboxylic acids.[16] In our experiment, although the pH of the water was slightly lower (more acidic) after reflux, no colour change was observed.

3.3   Acid Oxidation Experiments

Acid oxidation was employed to reduce the quantity of metallic impurities (by oxidation and dissolution) and highly reactive amorphous carbon, thereby exposing more metal particles for oxidation.

A series of experiments were performed in which the MWNT were refluxed in acid solution. The MWNT were isolated by filtration, followed by digestion in 8M HNO_3 for ICP-MS analysis. After digestion, the MWNT were filtered off and the digestion

solution was analyzed (data denoted as Ni in solid, in Table 3). The original acid reflux solution was directly analyzed by ICP-MS (data denoted as Ni in solution, in Table 3).

In the first experiment, a sample of MWNT was refluxed for 24h in 6M HNO_3 (experiment A1, Table 3); both the MWNT and the resulting solution were analyzed by ICP-MS. The concentration of nickel in the solid was determined to be 36 ppm, which is larger than data corresponding to as-received MWNT (6.1 ppm). The apparent increase in the concentration was attributed to the liberation of metallic species under the rigorous reflux conditions. Even more compelling evidence for the liberation of the metal is given by the ICP-MS data for nickel in the reflux solution (10400 ppm). Comparison of the solution data with the ashed MWNT data (11800 ppm) indicates that a significant quantity of nickel is not accounted for, and is assumed to remain encapsulated by carbon under these conditions.

In the second experiment, the MWNT underwent a multi-step pre-treatment (water reflux, ball-milling, and thermal oxidation at 300 ºC in air for 2 h) prior to reflux in 6M HNO_3 for 24 h (experiment A2). After reflux, ICP-MS analysis indicated that 39 ppm nickel remained in the solid and 11600 ppm nickel was found in the reflux solution. The higher concentration of nickel in solution compared to that in experiment A1 (10400 ppm, no pre-treatment) may be attributed to the higher degree of nickel liberation as a result of the pre-treatment.

In the third experiment, MWNT were subjected to a 24 h reflux in 6 M HCl (experiment A3). The concentration of nickel in the resulting solid and solution were determined by ICP-MS to be 505 and 4400 ppm, respectively. These values account for less than half of the actual nickel content (11800 ppm), which may indicate that the majority of the nickel remains encapsulated under these reaction conditions. It would appear that the amorphous carbon is more robust in the presence of hydrochloric acid, relative to nitric acid. The relatively high value of nickel found in the solid, is likely due to its liberation during ICP-MS sample preparation (in 8M HNO_3); it is unlikely that the nickel was exposed during reflux in hydrochloric acid but not oxidized.[17]

Table 3. Summary of ICP-MS Data for Acid Oxidation Experiments

Expt	Sample	Treatment	Ni in solid (ppm)	Ni in solution (ppm)
A1	Acid oxidized MWNT	6M HNO_3, Δ, 24h	36	10400
A2	Acid oxidized MWNT$^{\neq}$	6M HNO_3, Δ, 24h	39	11600
A3	Acid oxidized MWNT$^{\neq}$	6M HCl, Δ, 24h	505	4400

≠ The MWNT were subjected to water reflux, ball-milling, and thermal oxidation at 300 ºC for 2h, prior to acid oxidation.

4.   Conclusions

Given the standard format used by commercial suppliers for reporting carbon nanotube purity (% by weight carbon), at least a cursory examination of the supplied material is highly recommended.   Furthermore, if the presence of metallic impurities may adversely affect the properties of interest, it is essential to accurately assess the metallic content, and proceed with an appropriate purification process.   Accurate quantification of non-nanotube carbon impurities is difficult, but a rough assessment is possible (mass loss upon thermal oxidation), especially if the graphitic carbon content is relatively low.   Removal of a significant quantity of amorphous carbon may be achieved by pseudo-selective thermal oxidation. As mentioned previously, removal of all amorphous carbon without concurrent oxidation of some nanotubes is unlikely, but perhaps the presence of a small amount of amorphous carbon may not be detrimental to the performance of the nanotubes. The presence (and quantity) of graphitic carbon is even more difficult to assess, as separation from nanotubes is extremely challenging due to its high thermal stability; physical separation based on size, or dispersion techniques may provide some degree of nanotube enrichment.

Accurate analysis of residual catalyst particles is possible with ICP-MS, although it must be ensured that all metal is not encapsulated in carbon. Liberation of the metals may be achieved through chemical treatment or complete oxidation of carbon. For the MWNT data presented in this technical memorandum, the supplier claims that the % carbon in the sample is in excess of 95%. Although we have provided quantitative data only for nickel (1.2%), which is the major metallic component, it is reasonable to assume the remaining metal content is much less than the nickel. Thus, the supplier has provided a reasonable assessment of total carbon content. The question remains, however, how much of the carbon is comprised of nanotubes?

A number of assessment techniques provide a limited amount of qualitative information, and should not be relied upon to provide an accurate indication of bulk purity (with respect to nanotubes). These techniques include, but are not limited to, SEM, TEM, and TGA.   In order to rely on the information provided by these techniques, replicate samples are recommended, due to the inhomogeneity of as-received materials. Electron microscopy (both TEM and SEM) is inadequate for quantitative analysis, and care must be exercised when interpreting images in even a qualitative sense, as the images are not likely to be representative of the sample as a whole. TEM provides somewhat more information than SEM, as the nature of non-nanotube content, metallic versus non-nanotube carbon, may be gleaned from the images. Although TGA data can indicate the presence of catalyst, amorphous carbon, and even significant surface functionality, the data do not enable quantification of impurities and defects. TGA seems to be most useful for assessing thermal stability relative to another sample, so the effect of a purification process may be determined using TGA.   Titration analysis is useful for assessing the degree of acid functionality on the surface of carbon nanotubes; however, the data are only reliable when the material is relatively free of impurities, as these will skew the values. The precision of

replicate samples seems to provide a reasonable measure of homogeneity, with respect to non-nanotube carbon content. The data indicate that as the amorphous carbon content decreases (as with high temperature treatment), the uncertainty in the data decreases substantially.

Given the limitations of these techniques (in terms of quantification), it seems that a trial and error approach of thermal oxidation at varying temperature (with the mass loss being noted), followed by characterization of the heat treated product may be the most accurate means of assessing amorphous carbon content. Quantifying any graphitic carbon present is much more problematic due to its thermal stability. Based on the mass loss data (and the precision of the titration analysis data) presented in Table 3, one may conclude that the amorphous carbon content may be as high as 45%. Thus, the nanotube content is less than 50% of the supplied material.

With respect to purification of carbon nanotubes, it seems that the only viable option is to remove as much of the metal as possible, without destroying the tubes, and then thermally oxidize as much of the non-nanotube carbon as possible (without oxidizing the majority of the tubes). With respect to individual tube quality, improvement in the degree of graphitization (with respect to defects), may be realized with thermal annealing under inert atmosphere.

We are in the process of developing a methodology for carbon nanotube purification, utilizing our in-house capabilities. The techniques outlined in this technical memorandum are employed to assess the efficacy of each step. Once the purity of the nanotubes have reached the desired level, the nanotubes will be subjected to an inert atmosphere annealing process, which will enhance the individual tube quality (reduce defects).

5.   References

1.   Itkis, M. E.; Perea, D. E.; Jung, R.; Niyogi, S.; Haddon, R. C., Comparison of Analytical Techniques for Purity Evaluation of Single-Walled Carbon Nanotubes. *J. Am. Chem. Soc.* **2005,** 127, 3439-3448.

2.   Dujardin, E.; Ebbeson, T. W.; Krishnan, A.; Treacy, M. M. J., Purification of Single-Shell Nanotubes. *Adv. Mater.* **1998,** 10, 611-613.

3.   An, K. H.; Jeon, K. K.; Moon, J.-M.; Eum, S. J.; Yang, C. W.; Park, G.-S.; Park, C. Y.; Lee, Y. H., Transformation of singlewalled carbon nanotubes to multiwalled carbon nanotubes and onion-like structures by nitric acid treatment. *Synth. Met.* **2004,** 140, 1-8.

4.   Huang, W.; Wang, Y.; Luo, G.; Wei, F., 99.9% purity multi-walled carbon nanotubes by vacuum high-temperature annealing. *Carbon* **2003,** 41, 2585-2590.

5.   Zhang, H.; Sun, C. H.; Li, F.; Li, H. X.; Cheng, H. M., Purification of Multiwalled Carbon Nanotubes by Annealing and Extraction Based on the Difference in van der Waals Potential. *J. Phys. Chem. B* **2006,** 110, 9477-9481.

6.   Kim, Y. A.; Hayashi, T.; Osawa, K.; Dresselhaus, M. S.; Endo, M., Annealing effect on disordered multi-wall carbon nanotubes. *Chem. Phys. Lett.* **2003,** 380, 319-324.

7.   Sen, R.; Rickard, S. M.; Itkis, M. E.; Haddon, R. C., Controlled Purification of Single-Walled Carbon Nanotube Films by Use of Selective Oxidation and Near-IR Spectroscopy. *Chem. Mater.* **2003,** 15, 4273-4279.

8.   Shelimov, K. B.; Esenaliev, R. O.; Rinzler, A. G.; Huffman, C. B.; Smalley, R. E., Purification of single-wall carbon nanotubes by ultrasonically assisted filtration. *Chem. Phys. Lett.* **1998,** 282, 429-434.

9.   Fang, H.-T.; Liu, C.-G.; Liu, C.; Li, F.; Liu, M.; Cheng, H.-M., Purification of Single-Wall Carbon Nanotubes by Electrochemical Oxidation. *Chem. Mater.* **2004,** 16, 5744-5750.

10.   Montoro, L. A.; Rosolen, J. M., A multi-step treatment to effective purification of single-walled carbon nanotubes. *Carbon* **2006,** 44, 3293-3301.

11.   Hou, P. X.; Bai, S.; Yang, Q. H.; Liu, C.; Cheng, H. M., Multi-step purification of carbon nanotubes. *Carbon* **2002,** 40, 81-85.

12.   Park, T.-J.; Banerjee, S.; Henraj-Benny, T.; Wong, S. S., Purification strategies and purity visualization techniques for single-walled carbon nanotubes. *J. Mater. Chem.* **2005,** 16, 141-154.

13.   Ebbesen, T. W.; Takada, T., Topological and sp^3 Defect Structures in Nanotubes. *Carbon* **1995,** 33, 973-978.

14.   Boehm, H. P.; Diehl, E.; Heck, W.; Sappok, R., Surface Oxides of Carbon. *Angew. Chem. Int. Ed.* **1964,** 3, 669-677.

15.   Shaffer, M. S. P.; Fan, X.; Windle, A. H., Dispersion and Packing of Carbon Nanotubes. *Carbon* **1998,** 36, 1603-1612.

16.   Chiang, I. W.; Brinson, B. E.; Smalley, R. E.; Margrave, J. L.; Hauge, R. H., Purification and Characterization of Single-Wall Carbon Nanotubes. *J. Phys. Chem. B* **2001,** 105, 1157 - 1161.

17.   Huber, T. A.; Kopac, M. C., *unpublished results*.

List of symbols/abbreviations/acronyms/initialisms

℃	Celsius
EM	Electron microscopy
h	hour
HCl (aq)	hydrochloric acid
HNO_3 (aq)	nitric acid
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
M	moles per litre, concentration unit
mequiv/g	milliequivalents per gram, unit expressing degree of acid functionality
mg	milligram
mL	millilitre
μm	micron (micrometer)
MWNT	multi-walled carbon nanotube
NaOH	sodium hydroxide
nm	nanometer
ppm	parts per million, concentration unit
RT	room temperature
SEM	scanning electron microscopy
SWNT	single-walled carbon nanotube
TEM	transmission electron microscopy
TGA	thermogravimetric analysis

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We have assessed the quality of a commercial source of bulk multi-walled carbon nanotubes with respect to purity and degree of acid functionality. In addition, we have evaluated the applicability of several methods commonly used by suppliers to ascertain the purity of carbon nanotubes (SEM, TEM, and TGA).

ICP-MS data indicate that residual metal catalyst is present, and is comprised primarily of nickel (1.18 weight %). It was also determined that most of the metal (> 99.5%) is encapsulated by carbon (likely amorphous carbon). Most of the catalyst was removed by acid oxidation, preceded by thermal treatment (400 – 500 ºC in air) which liberated the metal from the encapsulating carbon. Based on mass loss during thermal oxidation, the amorphous carbon content was estimated to be approximately 45%.

Titration analysis data of the as-received material indicate that the degree of acid functionality is 3.07 ± 0.27 mequiv/gram. This value decreases appreciably upon thermal treatment (2.56 ± 0.03 mequiv/gram at 500 ºC, and 1.50 ± 0.05 mequiv/gram at 600 ºC), which likely drives off the functional groups.

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15. carbon nanotubes, purification, electrical conductivity, characterization

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