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Sample Preparation Protocols for Realization of Reproducible Characterization of Single-Wall Carbon Nanotubes

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Harmonized sample pre-treatment is an essential first step in ensuring quality of measurements as regards repeatability, inter-laboratory reproducibility and commutability. The development of standard preparation methods for single-wall carbon nanotube (SWCNT) samples is therefore essential to progress in their investigation and eventual commercialization. Here, descriptions of sample preparation and pre-treatment for the physicochemical characterization of SWCNTs are provided. Analytical methods of these protocols include: scanning electron microscopy (SEM; dry, wet), transmission electron microscopy (TEM; dry, wet), atomic force microscopy (AFM), inductively-coupled plasma mass spectrometry (ICP-MS), neutron activation analysis (NAA), Raman spectroscopy (dry, wet), UV-Vis-NIR absorption and photoluminescence spectroscopy, manometric isothermal gas adsorption and thermogravimetric analysis (TGA). Although sample preparation refers to these specific methods, application to other methods for measurement and characterization of SWCNTs can be envisioned.

Key words: AFM, carbon nanotube, CNT, single-wall carbon nanotube, SWCNT, characterization, commutability, ICP-MS, measurement, metrology, microscopy, NAA, photoluminescence, Raman, spectroscopy, SEM, SPM, toxicity, TEM, TGA, UV-Vis-NIR, manometric isothermal gas adsorption

1. Introduction

Carbon nanotubes (CNTs) are one of the first major nanoscale manufactured products to enter the market. Therefore, reliable and reproducible quantitative measurement and characterization of carbon nanotube samples are important for progress in our understanding of these materials and the development of new applications incorporating these materials. An additional value is the development of an information base for CNT toxicology. Physical properties of CNTs are known to be strongly influenced by their treatment history, i.e., method of their fabrication, sample pre-treatment and subsequent handling. These influences on the characteristics of a CNT sample can pose challenges when attempting to compare measurements performed on different batches, or measurements made on the same sample by different analysts or laboratories. A common (defined) approach to sample preparation is necessary for repeatable and reproducible measurements.

The sample preparation protocols outlined below are intended to establish a uniform basis for testing equivalence of measurements. The platform of a commonly-established starting point is imperative in order to draw conclusions from comparison experiments. Data from round-robin measurement comparisons provide the scientific evidence that measurements performed in the same way, but in different laboratories, yield the same results and validate what we believe to be our understanding of sample behaviour and the measurement method. Furthermore, data from intercomparison measurements are imperative to determine the commutability [1, 2] of CNT reference materials. These can also lead to future international standards under, for example, ISO TC229 on nanotechnologies. Comparison data are an important body of work which underpins our understanding of CNT samples, including topics such as predictive toxicology. The protocols are specifically intended for preparing single-wall carbon nanotube (SWCNT) samples for analysis, but may also be useful for the preparation of multi-wall carbon nanotube (MWCNT) samples. This sample-preparation guidance represents our best estimate of current practice and therefore could be expected to evolve with the accumulation of measurement results and comparison data.

It is recommended that trained scientific personnel handle the sample at all times. Aerosol production is to be avoided in the workplace while handling these test samples. Appropriate health and safety measures are recommended [3], such as wearing a suitable filter respirator if the work space does not provide sufficient, filtered air ventilation. Samples should be prepared in controlled chambers such as glove boxes and fume hoods equipped with suitable air filters. Objects used to handle CNTs, their containers and/or microscopy stubs and grids outside of those chambers should be thoroughly cleaned to remove SWCNT and nanoparticle contaminants.

2. Preparation of SWCNT for Imaging by Scanning Electron Microscopy

2.1 Background

Due to its ready availability, the scanning electron microscope is frequently an instrument of choice for observation of SWCNTs. Modern high-resolution field emission instruments are capable of resolving SWCNTs provided the instrument is functioning at its top performance. Performance checks on the SEM should be undertaken to ensure the ability to adequately image and measure SWCNTs. While some instruments are capable of resolving single SWCNTs, in most cases bundles of two or three SWCNTs are the minimum-sized objects that can be easily imaged. SEM imaging is typically used for the purpose of investigating bundles of SWCNTs and carbonaceous or other impurities attached to those bundles. The ability of SEM imaging to identify the type and location of the impurities present in the sample material can provide useful and relevant information. This section outlines sample preparation for reliable imaging of SWCNTs by SEM. Accurate metrology remains a challenge, requiring knowledge of electron beam interactions and the use of modeling to determine the shape and location of the edges of the structures being measured [4]. Sample preparation is thus critical to obtaining good-quality results.

SWCNT samples are subject to charging artefacts and therefore specimen observation conditions must be properly selected. Coating of the samples with conductive materials is to be avoided due to the potential for obscuring fine details. A useful approach is to work at lower accelerating voltages (landing energies) to take advantage of the extremely high resolution capabilities of modern electron energy filtered and or aberration-corrected SEMs. In SEMs, transmission scanning electron microscopy (TSEM) is a very useful technique in obtaining information in both secondary electron and transmitted electron microscope modes. This technique can be implemented with the use of special specimen holders and a varying set of detectors, as described in [5].

2.2 Sample Preparation for SEM by Dry Method

The dry method requires the SWCNT material to be attached to an aluminium SEM stub using tape or glue. These bonding materials have to be conducting in order to prevent electron beam-induced sample charging. Double-sided carbon tape and carbon- or silver-based epoxies are typically used for sample mounting. These materials have the disadvantage of having high carbon contents themselves, potentially making it difficult to find very well-dispersed bundles against the carbon background. Thicker materials, such as the as-produced mats of SWCNTs and impurities that are typical of many production processes, are easier to image on tape or glue. The method described is well-suited to direct analysis of as-produced material when determining the location and distribution of impurities is important.

1. Select the sample material and transfer it to the fume hood or glove box where the sample preparation will take place.
2. Place a sample stub in an appropriate holder or clamp.
3. Apply the carbon tape or glue to the top surface of the sample stub. Apply the tape to the sample stub in a manner that minimizes lateral tension build-up in order to lessen sample creeping, which is common even after several hours of sample mounting, and it is especially notable at high magnifications.
4. Place the sample stub inside the fume hood or glove box.
5. Attach a very small amount of SWCNT material to the surface of the stub by lightly pressing it against the tape or glue.
6. Allow time for the glue to set.
7. Remove loose sample material by gently knocking the holder to a hard surface. Briefly applied clean, gentle nitrogen jet can also be used.
8. Transfer the stub with sample directly to the SEM or to a storage facility for later imaging.

2.3 Sample Preparation for SEM by Wet Method

The wet method of sample preparation is typically used with SWCNT material that has been either purified using a liquid or has been dispersed in liquid. In this case, the liquid containing the SWCNT material is deposited on a metal SEM stub or TEM grid and allowed to desiccate. Van der Waals force then causes the SWCNT material to adhere to the surface of the stub or grid. This method has the advantage of providing high contrast between the stub and the sample material and is useful for the investigation of liquid-based processing methods. Differences in the impurity distribution between the central region of the adhered sample and its rim are an indicator that the desiccation process may

have altered the distribution of carbonaceous impurities within the SWCNT material as the liquid was removed. As a result, TEM grids may be more appropriate where SEM and TEM imaging on the same sample is desired or the intent is to examine a small amounts of SWCNTs with an emphasis on the SWCNTs themselves, rather than the distribution of impurities in the sample. Image analysis for the purpose of determining the success of purification processes may be easier to carry out with larger droplets of material on standard SEM stubs. The choice of dispersing liquid is important to avoid unintentionally affecting any impurities. Dispersion by ultrasonic treatment may remove loose material, but inappropriate choice of the dispersive medium may dissolve some forms of impurities or assist in detaching them from the SWCNT bundles, giving an inaccurate account for the purity of the material. Toluene will dissolve fullerenes and some fullerene-like impurities from the sample. In our experience, n,n-dimethylformamide (DMF) shows a stronger affinity to solubilising the impurity carbons than the SWCNT; we can exploit this in the purification process. None of these solvents should be used if the entire, unaltered composition of the sample is to be probed.

1. Select the sample material, transferring it to the fume hood or glove box where the sample preparation will take place.
2. Place a sample stub in an appropriate holder or clamp.
3. If the sample material has not already been dispersed in liquid, add the material to ~10 ml (milliliter) of isopropanol in a small vial. Place the vial in a standard laboratory sonication bath filled with water and sonicate for 5 to 30 minutes or until a uniform appearance is achieved. Sonicate in an ice water bath to minimize thermal damage to the SWCNTs.
4. Place the sample stub inside the fume hood or glove box.
5. Deposit a very small drop of the liquid containing the SWCNT material on the stub or grid.
6. Allow the sample to air dry, then place the sample into a clean vacuum oven at a temperature of approximately 75 °C for an additional 15 minutes to remove all residual liquid.
7. Remove loose sample material by gently knocking the holder to a hard surface. Briefly applied clean, gentle nitrogen jet can also be used.
8. Transfer the stub with sample directly to the SEM or to a storage facility for later imaging.

2.4 Reporting Issues Related to Sample Preparation

Report the method of sample preparation (dry or wet). If the dry method was used, report the method used to bond the sample to the SEM stub. If the wet method was used, report the solvent used, the time and the power, temperature and time of the ultrasonic treatment step.

3. Preparation of SWCNT for Transmission Electron Microscope Imaging

3.1 Background

Transmission electron microscopy (TEM) utilizes an electron beam accelerated to a high energy (80 - 400 keV typically) transmitted through a very thin specimen. High

magnification of this transmitted beam onto an array detector or phosphor screen results in an image of the specimen with atomic-scale resolution. Information about morphology, crystal structure or defects, phases and composition can be obtained via combination of high resolution imaging with other techniques such as electron diffraction, energy dispersive X-ray analysis, and electron energy loss spectroscopy. A sample for TEM analysis must be about 100 nm or thinner in the area of interest to get a clear, high-resolution image. While bulk materials require complicated thinning treatments, nanostructured materials such as SWCNTs can be imaged without such thinning. Since the discovery of CNTs, TEM has been widely used to study their structures with very high spatial resolution, and to characterize size parameters, structural details and tube chirality. The best resolution of instruments equipped with energy filtered electron source and aberration-corrected electron optical column can be a few pm (picometer). TEM has also been used *in-situ* to study growth mechanics of SWCNTs with the help of a specially designed sample holder.

3.2 Sampling Issues

SWCNT starting materials may be obtained in many different forms, including as-grown SWCNTs (dry), “bucky paper” of purified SWCNTs (dry) and SWCNT suspensions (wet). Because of the high magnifications used in TEM analysis, information is only obtained from a small number of SWCNTs in the sample, therefore a number of test samples must be prepared and analysed in order to relevantly characterize the ensemble. About 0.05 mg of SWCNTs is needed for each preparation.

3.3 Preparation of dry SWCNT samples for TEM analysis

For SWCNTs collected for TEM analysis from dry samples (e.g., as-grown products and SWCNT bucky paper), the following procedure is used:

1. Add the sample material (0.05 mg) to 10 ml of isopropanol in a small vial.
2. Place the vial in a standard laboratory sonication bath and sonicate for 5 to 30 minutes or until a uniform appearance is achieved. Sonicate in an ice water bath to minimize thermal damage to the SWCNTs.
3. In a fume hood or glove box, place a 200-mesh, lacey-carbon, copper TEM grid in an appropriate holder or on a water-absorbent, low-particulate laboratory tissue.
4. Use a micro pipette or dropper to deposit 1 ml of the SWCNT solution onto the TEM grid.
5. Allow the grid to dry in air and then transfer the grid to a clean vacuum oven at a temperature of approximately 75 °C for 15 minutes.
6. Remove loose sample material by gently knocking the holder to a hard surface. Briefly applied clean, gentle nitrogen jet can also be used.
7. Return the grid to the vacuum oven to continue to dry for a few hours before transferring to the TEM for analysis.

3.4 Preparation of wet SWCNT sample for TEM analysis

A wet SWCNT starting material may contain chemicals other than the SWCNTs that could obscure the TEM imaging of the SWCNTs, damage the lacey-carbon grid, or contaminate the TEM chamber. A wet SWCNT starting material may contain chemicals

other than the SWCNTs (e.g. surfactants, acids) and the sample must be washed of these materials before preparation for TEM analysis.

1. Add the selected sample material (0.05 mg of SWCNTs in the solution) to a centrifuge tube.
2. Fill the centrifuge tube with isopropanol and sonicate for about 1 min in a standard laboratory sonication bath filled with ice water.
3. Centrifuge the suspension and discard the supernatant.
4. Repeat steps 2 and 3 until the supernatant is clean (typically 5 cycles is sufficient).
5. Transfer the sample to a vacuum oven at low temperature (75 °C) to dry it.
6. Prepare the TEM grid as described in Section 3.3 (Preparation of dry SWCNT sample for TEM analysis) above.

3.5 Reporting Issues Related to Sample Preparation

The sonication conditions and time (or visual end-point) should be reported, as well as any pre-washing of wet SWCNT samples.

4. Preparation of SWCNT for Atomic Force Microscopy (AFM) Imaging

4.1 Background

Atomic force microscopy (AFM) is a technique that can operate in air, liquid or vacuum. A sharp tip performs a raster-scan across the sample surface providing a 3D image. Variations in AFM instrumentation can provide a wide range of additional information including chemical, friction, electrical and magnetic information. The method is well suited to provide high-resolution topographic data of SWCNTs and some instruments have the capability to resolve individual tubes. An AFM scan can provide the height of the tubes, and provide an indication of whether single tubes or bundles are present in a sample.

The resolution of an AFM image can be in the range of 1 nm to 5 nm, depending primarily on the sharpness of the probe tip. A sharp tip and low force assist in avoiding damage to the tip or sample and provide the highest resolution images. For accurate dimensional measurements the AFM should be in dimensional calibration, which is typically performed by imaging reference standard artefacts of known dimensions traceable to the International System of units (SI).

4.2 Sample preparation for AFM for the dry method

For imaging a SWCNT sample in the dry state as received, the SWCNTs are pressed into a substrate; indium foil is preferred as long as the roughness of the foil is very small. (see also the methods described in section 2.2 above). Preparation steps include:

1. Select the sample material, transferring it to the fume hood or glove box where the sample preparation will take place.
2. Cut an appropriate size (e.g., 1 cm x 1 cm) of indium foil and press it onto the top surface of an AFM sample stub.
3. Place the sample stub inside a fume hood or glove box.
4. Attach the SWCNT material to the indium foil by firmly pressing it against the foil.

5. Remove loose sample material by gently knocking the holder to a hard surface. Briefly applied clean, gentle nitrogen jet can also be used.
6. Transfer the sample to the AFM or a storage facility for later imaging.

4.3 Sample preparation for AFM for the wet method

Methods in the literature for preparation of SWCNTs typically involve dispersion in a solution with the help of acids, macromolecules or surfactants and then spin-casting or evaporation on a clean, flat substrate of mica, glass or silicon. Here we detail a method using a surfactant.

SWCNTs have been found to naturally aggregate into bundles and ropes [6]. Since the tubes are polarizable and smooth-sided, they easily form bundles with a Van der Waals energy of 500 eV per micrometer of tube-tube contact [7]. The aim of this method [7] is to produce well-dispersed individual SWCNTs, the caveat being that the aggressive methods used such as sonication and ultracentrifugation may result in modifying the properties of the original sample in terms of length of tube and amount of contamination.

1. Prepare a solution of the surfactant sodium dodecylbenzene sulfonate (SDBS) in ultra pure water at a concentration of 5 mg/ml; stir overnight
2. Add SWCNTs to the SDBS solution such that the SDBS:SWCNT mass ratio is 5:1.
3. Take 8 ml of the SDBS/SWCNT mixture and apply high-power tip sonication with ice cooling for 5 minutes followed by sonication in an ice water bath for 10 minutes; decant the supernatant.
4. Centrifuge at 5500 rpm for 90 minutes to remove micrometer sized aggregates. Functionalize a clean silicon oxide surface by soaking it in a 1 mM solution of 3-aminopropyltriethoxysilane in chloroform for 30 minutes. The samples should then be rinsed in chloroform followed by a rinse in isopropanol, and air dried.
5. Immerse the functionalized silicon substrates in the SWCNT dispersed solution for approximately 3 hours.
6. Rinse with methanol; Remove loose sample material by gently knocking the holder to a hard surface. Briefly applied clean, gentle nitrogen jet can also be used.
7. Image using AFM.

4.4 Reporting Issues Related to Sample Preparation

Sample preparation in a clean room, fume hood or glove box is recommended. A minimum of three samples should be prepared on substrates of approximately 1 cm x 1 cm. During imaging, at least 3 regions of each sample should be observed. The AFM images should include length-scale bars; details of the instrument, set-up, preparation method and substrate should be reported.

5. Preparation of SWCNT Samples for Determination of Residual Catalyst and Impurity Metals by Neutron Activation Analysis (NAA)

5.1 Background

The characterization of residual catalyst and impurity metals in carbon nanotube materials ranging from raw soot to highly defined purified material represents a broad analytical task: the metals may be present as major constituents or at trace and ultra-trace levels, they may be loosely adducted to the matrix, or firmly incorporated, or chemically bound. NAA provides reliable results over the full range of potential elemental content in a sample independent of these physical and chemical properties. Both neutrons and gamma rays penetrate sample materials well, providing a non-destructive analysis capability for determining the composition of the entire volume of a sample. In addition, neutrons react with the nucleus of the atoms independent of oxidation state, chemical form, or physical surroundings of the desired element. Moreover, NAA requires minimal sample preparation for irradiation and measurements so chemical blanks and losses or gains of the element of interest before the actual analytical step are excluded. The most precise and accurate method for quantification is through comparison of the induced radioactivity of the unknown samples with standard samples of known composition, which are irradiated and measured under exactly the same conditions. Therefore, an exact match of the standard matrices and composition with the unknown samples is not required. The sequential use of neutron capture prompt gamma activation analysis (PGAA) and instrumental neutron activation analysis (INAA) can accomplish the determination of fifty or more elements in one sample test portion. A parametric analysis (k_0 -technique) is also feasible.

5.2 Sample Preparation

NAA with PGAA and INAA provide for direct determination of constituents with minimal sample preparation. Powder samples are prepared for NAA irradiation and measurement by pelletizing, weighing, and packaging in irradiation containers. The CNT material requires the addition of a non-hydrogenous binder; graphite is recommended. A stable pellet is formed in a 1:1 mixture as follows: the aliquots are poured into a stainless steel die to form pellets under about 3.6 tonnes load. The pellets are weighed, each pellet representing about 20 mg to 40 mg of SWCNT material for INAA and 100 mg for PGAA. The samples are heat-sealed in bags made from fluorinated ethylene propylene (FEP, Teflon) film (hydrogen free) for PGAA and in bags made from high-density polyethylene film for INAA. Sub-sampling should be done at minimum in triplicate, as are procedural blanks, preferably in a clean room or a contamination-free environment. If test material is limited, the same sub-sample should be first prepared and submitted to PGAA and subsequently to INAA. A separate sub-sample is to be prepared for the purposes of determining the dry weight correction (described in section 6.5 below).

Quantitative analysis is undertaken by the comparator method with known standard samples irradiated and measured under the same conditions as the unknown sub-samples. Standard samples in the form of element solutions pipetted on filter papers or pure elements or compounds (as mixtures with graphite as required) are prepared in a similar way for the irradiations. A parametric analysis (k_0 -technique) is also feasible.

5.2 Preparations for Quality Assurance

Empty Teflon and polyethylene bags, graphite samples and titanium foil flux monitors should be prepared. These samples are irradiated under the same conditions as the CNT samples to serve as a background measurement for blank subtraction when required. Titanium foil flux monitors are irradiated at regular intervals to monitor any changes in the neutron fluence rate. Quality assurance (check) samples of suitable certified reference materials (e.g., SRM 1632c, Trace Elements in Coal, SRM 1633b Coal Fly Ash, SRM 2702 Marine Sediment) should be included in the assays, irradiating and measuring these samples the same way as the samples under investigation.

5.3 Reporting Issues Related to Sample Preparation

Details of sample preparation are to be outlined (sample mass, constituents, load) including the reference samples used for calibration and the results of quality assurance measurements and dry weight correction (see section 6.5 below).

6. Preparation of SWCNT Samples for Determination of Residual Catalyst and Impurity Metals by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

6.1 Background

Inductively coupled plasma-mass spectrometry provides a sensitive multi-elemental approach to analysis of SWCNTs for the detection of metallic impurities as well as residual catalyst at amount contents ranging from 10^{-9} to 10^{-2} . The limitation of the technique is that quantitative sample dissolution is required. Potential influences from residual carbon content and dissolved solids can be accounted for by suitable calibration techniques, including isotope dilution, matrix matched standards and the method of additions [8]. Mass spectral interferences are well documented and results traceable to the SI can be readily achieved using traceable high-purity calibration standards. The rapid sample throughput of this method is attractive for routine screening.

6.2 Sample Preparation

Semi-quantitative analysis of a test sample is initially undertaken to establish sample dilution factors and needed calibration standards, spikes and enriched spikes (for ID-MS when appropriate). An acid leach of the sample may be undertaken on a 25 mg test sample using 10 ml 50 % HNO_3 by reflux heating in a pre-cleaned Teflon beaker at near boiling for several hours until dissolution is nearly complete, followed by heating to ~ 100 °C until near dry. The resultant residue is dissolved in 0.25 ml HNO_3 and then diluted to 10 g with high-purity water. For most elements, a further 20-fold dilution of the leach solution with 0.1 M HNO_3 is undertaken prior to semi-quantitative analysis by ICP-MS. Based on these preliminary results, the dilution factors, required calibration ranges and spike additions required for quantitative evaluation of subsequent samples can be determined.

Quantitative analysis is undertaken on samples initially characterized as described above in section 6.2. Minimum 25 mg test portions are gravimetrically transferred to individual high-pressure, pre-cleaned Teflon digestion vessels. Six ml high-purity nitric acid and 0.5 ml of H_2O_2 are added along with appropriate masses of enriched spikes for

those elements determined by ID-MS techniques. Three sample blanks are prepared concurrently, with enriched spikes added at a level 10-fold lower than used for the test sample. The vessels are sealed and heated in a scientific microwave oven for digestion. A recommended digestion program consists of the following steps:

1. 10 min. at temperature 80 °C and 1000 W power,
2. 15 min. at temperature 150 °C and 1000 W power,
3. 15 min. at temperature 180 °C and 1000 W power and
4. 25 min. at temperature 210 °C and 1000 W power.

After cooling, the caps are removed and rinsed. The vessels are then placed on a hot plate in a Class-10-100 fume hood and the contents heated to ~100 °C until near dry. The resultant residues are dissolved in 0.25 ml HNO₃ and then diluted to 10 g with high-purity water. Sample solutions are transferred to and stored in pre-cleaned polyethylene screw-capped bottles. Dilution factors determined from the semi-quantitative data are applied prior to analysis.

As an alternative to the above methodology, application of microwave induced combustion of samples in closed quartz vessels pressurized to 2 MPa with oxygen, as proposed by Flores [9] could be considered; however, this approach has yet to be validated.

6.4 Quality Assurance

At the time of publication there are no specific reference materials available for validation of these measurements. By the principle of commutability, NIST SRM 1633b Coal Fly Ash or more appropriately SRM 1632c Trace Elements in Coal may be utilized as these provide similar carbonaceous matrices. Both sample digestion, to ensure quantitative dissolution of the elements of interest (and equilibration of the ID spikes) as well as resultant solution matrix, present areas of concern for accuracy.

6.5 Reporting Issues Related to Sample Preparation

The method of sample preparation should be summarized in the report. The dry weight correction (a correction factor based on the determination of the moisture content of the material) should be applied to the data such that they can be reported in terms of dry weight of sample. Use of a separate test portion of the material following procedures outlined in [10] offers a potential methodology, but this procedure may not address this issue satisfactorily. Further study is required to determine if the use of a common desiccator employing anhydrous magnesium perchlorate (caution – potential interaction with organic materials) offers a more suitable solution.

7. Preparation of SWCNT Samples for Raman Spectroscopy

7.1 Background

Raman spectroscopy as a general analysis tool has the benefit of being largely independent of sample preparation procedures; measurement of a material in different physical forms (e.g., powder, solution) typically results in the same Raman signature. For the case of SWCNTs however, there are considerations that must be made with respect to sample preparation. Raman spectra of SWCNT samples are dominated by the individual

nanotubes that have electronic transitions at or very near resonance with the excitation laser. Moreover, the precise resonance energy of a given nanotube can shift slightly depending on its environment. Changes in a sample environment can result in different nanotubes coming into and out of resonance, resulting in a noticeably different Raman signature. For comparison of the Raman spectra of different SWCNT samples, it is therefore important that the samples be in the same physical form, prepared in the same way, and measured under the same conditions. The most common physical forms of SWCNT samples for Raman analysis are dry powder and liquid dispersion. Recommended preparation methods are outlined here in Section 7 for dry SWCNT samples and below in Section 8 for wet samples.

7.2 SWCNT Sample Preparation of Dry Powder for Raman Spectroscopy

SWCNT materials are often inhomogeneous in their composition, particularly in their as-produced state. It is recommended that the material be homogenized prior to measurement, and that several (at least three) measurements be made at different locations on the sample. Dry samples can be measured as raw, as-received powder in a quartz vial, or dispersed and then dried on a substrate. The protocol for homogenization and sample preparation includes the following steps:

1. Place 0.5 mg to 1 mg of SWCNT sample into a glass vial with approximately 2 ml of isopropanol (reagent grade).
2. Sonicate in an ice water bath for 5 to 30 minutes or until a uniform appearance is achieved. High-powered ultrasonic horns and probes should be avoided as they can induce sidewall damage in the nanotubes over time.
3. Pour the resulting dispersion in its entirety directly onto a Si wafer substrate. Si is useful as a substrate due to its clear Raman signature for reference.
4. Allow the sample to air dry, then place in a clean vacuum oven at 75 °C for 15 minutes to remove remaining solvent.
5. Return the sample to the fume hood or glove box and gently remove any loose material by blowing the surface with clean nitrogen. When fully dry, the SWCNT sample will adhere to the substrate, allowing for easy transport to the Raman spectrometer; this greatly reduces any possibility of inhalation of aerosolized SWCNT particulates during the Raman measurements.

The laser power density incident on a SWCNT sample should be carefully monitored, particularly when using a microscope-based Raman spectrometer in which the laser is focused to a very small focal volume. Optical heating effects can easily raise the local temperature of the sample to several hundred degrees Celsius, resulting in shifts of the Raman spectral frequencies and possibly oxidation of sample components. Powder samples containing larger fractions of carbonaceous impurities, catalyst residues, and nanotube defects are most susceptible to laser heating effects. In practice, power densities maintained below 3 kW/cm² should avoid heating-induced effects. Excitation laser power at the sample location should be measured and reported.

8. Preparation of Liquid Dispersed SWCNT Samples for Raman Spectroscopy, UV-Vis-NIR Absorption and Photoluminescence Spectroscopy

8.1 Background

The dispersion of single-walled carbon nanotube (SWCNT) soot into a suspension of individual nanotubes, and the purification of the initial suspension via centrifugation is becoming a more developed area of SWCNT technology [11, 12]. The procedure described herein has been shown to produce dispersion of individual single-walled carbon nanotubes in aqueous surfactant solution and is applicable to Raman, UV-Vis-NIR and photoluminescence spectroscopies.

Liquid dispersed samples are typically prepared for two purposes: to generate individualized SWCNTs, and for purification by elimination of impurity materials such as amorphous carbon and catalyst particles. While the purification step alters the composition of the sample from the source soot, this type of sample preparation is suitable for many spectroscopic techniques, such as UV-Visible-Near Infrared Absorbance, Raman mapping experiments, and NIR Fluorescence. The presence, and to some degree relative quantity, of individual chiralities of the SWCNT species present in the dispersion can be measured, particularly for samples with minimal chemical functionalization.

The optical absorption of single-walled carbon nanotube (SWCNT) suspensions and dispersions is a quick and facile method for obtaining information about SWCNTs. UV-Vis-NIR allows for the measurement of the number, location and intensity of the intrinsic SWCNT optical absorption transitions. For well-dispersed liquid samples in the concentration range of 50 mg/L to 500 mg/L, absorbance can typically be measured over the wavelength range of 200 nm to 2500 nm with the exact location and intensity of peak features in the optical spectrum dependent upon the diameter distribution of the nanotubes, the surfactant used to disperse the SWCNTs, the length and concentration of the nanotubes, and the path length through the sample.

8.2 Sample Preparation

A key interlaboratory difference in the production of SWCNT samples often can be traced to the dispersion equipment. Previous literature reports contain use of bath sonicators [13] tip sonicators [14], and horn sonicators [15]. For the production of reasonable volumes of dispersed SWCNT liquids, the tip sonication method is preferred. Ultrasonic processors which are typically used for membrane disruption of biological samples are widespread and are most suitable of the available techniques. 1/8 inch (~3 mm) tips are used for samples between 3 ml and 10 ml and 1/4 inch (6.35 mm) tips are used for between 10 and 50 ml. Models providing control of the applied power are preferred. The protocol below is for a batch size of 35 ml; sodium deoxycholate is the preferred dispersing agent, as it is relatively inexpensive, has relatively low health risks, and has been shown to maintain near total individualization of SWCNTs less than 1.5 – 1.6 nm in diameter at apparent SWCNT concentrations of ≥ 0.5 mg/ml.

Centrifugation is performed to reduce the percentage of non-SWCNT carbon in the sonicated suspension. This assumes that the impurity components are less well dispersed, or have a significantly higher sedimentation rate in the surfactant solution than the nanotubes, which is not true for all impurities. Available centrifuges also vary widely

across laboratories. Typically, longer or faster centrifugation will result in increased reduction of the impurity components in the supernatant, as well as some loss of SWCNT material. A large percentage of impurities fractionates rapidly to a sediment under moderate 20000*g centrifugation in 15 min ($g = 9.81 \text{ m/s}^2$). Relatively common tabletop centrifuges will centrifuge 8 to 16 ml to 1.5 ml tubes at 20000*g. This is the minimum recommended applied acceleration; 2 h is a preferred amount of time as it balances the achieved purification with the time cost. Greater acceleration possible in high speed centrifuges yielding about 40000*g yield a purer SWCNT dispersion without the significant loss of SWCNTs to sedimentation that can occur under ultracentrifugation conditions.

1. SWCNT soot is selected and the exact mass of SWCNT soot is recorded to 0.01 g. The soot is transferred to an appropriately sized bottle into which 2 % sodium deoxycholate solution is added to make a master parent suspension of 1 mg/ml SWCNTs.
2. The bottle containing the master liquid is shaken and sonicated for 1 to 2 minutes in an ice water bath to achieve moderate homogeneity.
3. Aliquots, or the entire suspension, are introduced into a 50 ml vessel, filling the vial to the 35 ml mark.
4. Sonication of each 35 ml batch is performed using a tip sonicator with a 1/4 inch (6.35 mm) tip-probe sonicator set to produce 30 W continuous output. Prior to sonication, the tip of the probe is visually inspected for degradation from pitting; if the tip is found to be significantly pitted, the probe is replaced. The state of the probe tip should be inspected before sonication at the start of each batch. Sonication is performed for 1 hour $\pm$ 5 minutes. During sonication, the 50 ml vessel is immersed above the level of the SWCNT solution in an ice-saltwater bath, and the top of the vessel is roughly sealed to the sonicating tip by an aluminum foil cap. The position of the tip is approximately 1.5 cm from the bottom of the 50 ml vessel. Post-sonication all the liquid is collected into a holding bottle to await centrifugation.
5. Centrifugation is performed at a minimum of 20000*g for 2 hours. After 2 hours, the initial suspension is separated into a liquid supernatant, primarily containing individualized SWCNTs, and a solid residue, which contains metallic and carbonaceous impurities and a small percentage of SWCNT carbon. The supernatant is carefully removed and collected; the residue is dislodged, if desired, by the addition of a small amount of pure water and collected in a separate container.
6. The supernatant can be used for spectroscopic measurements.

Quartz cuvettes should be used for all samples because they are sufficiently transparent throughout the measurement range. Dual or double-beam spectrophotometers are recommended; with these instruments the light alternately passes through the sample and a reference path allowing for more accurate measurement than a single beam spectrophotometer.

8.3 Quality Assurance Issues Related to Sample Preparation

It has been demonstrated that some surfactants are more efficient at the solubilization of specific SWCNT diameters and/or conductivities. The process of centrifugation in the presence of surfactants can result in representation of only a subset of the original SWCNT population in the final liquid dispersion; therefore liquid-dispersed samples are not recommended if detailed analysis of the entire original SWCNT population is desired.

Care should also be employed in the use of high-power ultrasonication in the sample preparation as there is evidence in the literature that the propensity for cutting nanotubes and inducing sidewall damage increase with exposure time.

Samples should be measured immediately after preparation. If storage is necessary, care should be undertaken in a manner to avoid contamination of the sample by storing under an inert atmosphere to avoid adsorption of oxygen, water, or other gases over time.

Data Collection Notes:

1. Evenly-distributed inhomogeneities, such as large particles, tend to appear as wavelength-independent contributions to the absorbance; therefore, suspensions with large particles or unevenly distributed inhomogeneities are not suitable for accurate characterization of SWCNTs. The absorption spectrum of a SWCNT dispersion contains contributions from SWCNT optical transitions, underlying graphitic carbon background (Pi-plasmon absorption), and absorption by the surfactant and impurities.
2. Rayleigh scattering can increase the absorbance of a solution in a different way, depending on whether standard detector or an integrating detector sets are employed. A typical standard detector set collects a small percentage of scattered light within a few degrees of the central beam axis, whereas an integrating sphere set captures a larger angular range of scattered light. Comparison of absorbance spectra in both geometries leads to the conclusion that SWCNTs in deoxycholate solution are weak scatterers, and thus Rayleigh scatter should not be an important contributor to UV-Vis-NIR absorbance.
3. Similarly, fluorescence of SWCNTs can contribute to apparent transmittance. Moreover, fluorescence decreases the measured absorbance as photons emitted at lower energy are collected in the measurement together with the incident wavelength. Depending on the instrument, fluorescence can affect measured signal only in the NIR region, or throughout the entire measured spectrum. The determining factor is the sensitivity of the visible and/or NIR detectors to NIR photons during UV or visible illumination. As with Rayleigh scattering, the limited angular capture of photons in the geometry of the standard detector set-up typically limits the effects of fluorescence on the apparent transmittance, but should be considered as a source of possible deviation.

8.4 Reporting Issues Related to Sample Preparation

The form of Raman spectroscopy (solid or liquid), measurement conditions such as excitation laser wavelength(s), laser power and spot size at the sample should be reported. Centrifugation time and acceleration should be reported for liquid sample preparation methods. The surfactant in use, sonication times and powers should also be reported.

9. Preparation of SWCNT Samples for Characterization by Manometric Isothermal Gas Adsorption

9.1 Background

There are several methods for characterization of porous materials by adsorption of fluids [16]. Sample preparation methods for manometric isothermal gas adsorption are described.

As-grown SWCNT material typically consists of nanotube bundles and may also include other carbonaceous material and metallic particles (catalyst). SWCNT bundles can adsorb simple gases in external grooves, voids, the nanotube interior, and sometimes interstitial channels as well as on the external surface. Grooves, interior and external surfaces of nanotube bundles are characterized by relatively well-defined binding energy as compared to other adsorption sites in the SWCNT material, and steps may be identified on the isotherm corresponding to adsorption on these sites. Other carbonaceous materials may include nanotube debris (shells, nanotube fragments), graphitic particles, amorphous carbon, and possibly residual solid precursor material. Debris, graphitic particles, and residual solid precursor material can adsorb gases on highly polyenergetic surface adsorption sites. Metallic particles are typically covered by multi-layer-thick graphitic shells, thus they exhibit gas adsorption properties similar to those of carbonaceous material. Amorphous carbon does not have energetically well-defined adsorption sites and it can accumulate on other components of SWCNT material blocking the above-mentioned adsorption sites.

9.2 Sampling

It is recommended that the test samples be prepared in a contamination-free environment. While some laboratories may be able to perform measurements on samples as small as 50 mg, larger samples of 200 mg or more are recommended for general purpose manometric gas adsorption apparatus. If sample processing beyond the basic sample preparation described below is intended, sampling in triplicate is recommended. One unprocessed dry sample should be retained for future reference.

9.3 Sample Preparation

Manometric isothermal gas adsorption analysis is capable of yielding a range of sample characteristics, some of which can be obtained with unprocessed sample while others require irreversible sample processing. Dry powder samples are recommended. SWCNT material pellets may also be formed by compression (see section 5.1 above).

9.3.1 Drying and Degassing

Basic sample preparation is performed in order to restore the original state of the material, namely to remove solvents and weakly bound species such as H₂O and CO₂ to which the sample has been exposed during post-production handling. Removal of strongly bound species can be conducted in a separate sample processing step (see below) and may require heating the sample to temperatures as high as 1100 K. The basic sample preparation should always include drying and/or degassing the as-produced material, regardless of the intended scope of the measurements [17]. If SWCNT material is exposed to a solvent during material production or post-production handling, the sample

should be filtered and dried in flowing dry nitrogen, preferably at room temperature (~295 K) or slightly elevated temperature not exceeding 340 K. Visibly dry samples should be transferred to a vacuum system and further dried and degassed at room temperature to better than 10^{-4} Pa. Vacuum drying and degassing is typically conducted for ~48 hours, but should not be shorter than 24 hours. After first reaching the dynamic pressure of less than 10^{-2} Pa, the sample should be purged at least 3 times with nitrogen by pressurizing the sample cell to ~1 atm and subsequently evacuating it to better than 10^{-2} Pa. Elevated temperatures not exceeding 375 K can be used at late stages of the degassing process. It is recommended that sample drying and degassing, especially during development of a reference sample or optimization of a sample preparation procedure, be monitored with a coupled mass and/or molecular analyzer.

The mass of the sample should be measured following the basic sample preparation described above. Mass measurements should be corrected for buoyancy, mass of gas enclosed in a cell, and other effects dependant on the particular weighing technique and instrument used. Weighing the sample after the isotherm acquisition is recommended, and if a different sample mass is determined, the difference must be properly accounted for or the measurements repeated.

9.3.2 Removal of impurities and opening nanotubes

Subsequent sample processing may be conducted in order to remove carbonaceous impurities (amorphous carbon, debris) or strongly bound functional groups and to open close-ended nanotubes thus to free external (grooves, external surface) or internal (internal surface, interior, voids) adsorption sites for gas adsorption. Heating in dry air is recommended; if other processing options are used, such as oxygen plasma treatment, ozonation, or mechanical cutting, the method should be specified.

9.3.3 Heating in dry air

Heating of the degassed sample in dry air should be conducted at a temperature of 460–480 K for ~2 hours. Longer heating time will result in opening a larger fraction of nanotubes and more thorough removal of amorphous carbon and carbonaceous debris. Heating time can be optimized for various types of SWCNT material. The temperature may also be varied, but should not exceed 500 K. If carbon-coated metallic nanoparticles are present in the sample, long heating times greater than 5 hours should be avoided to prevent complete removal of graphitic shells. Heating in air should be followed by degassing the processed sample at 375–390 K in vacuum for 12–24 hours to better than 10^{-4} Pa. If removal of strongly bound species (functional groups) from either unprocessed or processed material is intended, the vacuum degassing of the sample should be conducted at higher temperatures up to 1100 K.

9.4 Quality Assurance Issues Related to Sample Preparation

Reference samples should be measured the same way as the unknown samples, periodically or whenever an irregularity is observed or suspected.

9.5 Reporting Issues Related to Sample Preparation

Details of the procedure (temperatures and settling times) should be provided in reporting. Tests performed on compressed pellets should be reported as such, including indication of the compression pressure.

10. Preparation for Characterization of SWCNT by Thermogravimetric Analysis

10.1 Background

Thermogravimetric analysis (TGA) is a method used to monitor the weight change of a material when it is heated. In most cases, a linear heating rate is used to heat the sample to a maximum temperature at which the sample mass is stable, indicating that all thermally-induced chemical reactions are complete. For SWCNT samples which consist of amorphous carbons, structured carbons (e.g., SWCNT, MWCNT), and metal catalyst particles, the TGA method can be used to monitor the composition of the constituents of the sample by their thermal stability.

Results obtained from TGA analysis are: the residual mass at a given temperature (M_{res}) which in turn provides the ash content of the material, and the oxidation temperature (T_o) (the temperature of maximum rate of mass loss (dm/dT_{max})) which is a measure of the thermal stability of the nanotubes in an oxidative environment. M_{res} provides a measure of the metallic content of a SWCNT sample. T_o can be influenced by a number of factors, including defects, length, and metal impurities and it is thought that a higher T_o is an indicator of a SWCNT sample that is relatively pure and contains defect-free nanotubes [18]. Both M_{res} and T_o are influenced by the rate the sample is heated. For TGA to be comparable from one laboratory to the next, sample heating rate must be kept constant.

10.2 Sample Preparation by Dry Method

Samples should be stored in a dry environment (desiccator) at room temperature. All sampling of SWCNT material should be performed in ceramic TGA pans. To combat static electricity when working with SWCNT powders, a piezoelectric static gun can be used.

1. SWCNT and ceramic TGA pans should be placed in a glove box or fume hood when dealing with loose powders.
2. For a 100 μL pan, 1 mg - 5 mg of SWCNT powder should be placed into the pan with a spatula, taking care to remove any material that is spilled on the exterior of the sample pan.
3. Pans with SWCNTs should be placed into the sampling tray for the TGA.
4. The sample run should consist of an equilibration step at 40 $^{\circ}\text{C}$, followed by heating at 10 $^{\circ}\text{C}/\text{min}$ to 800 $^{\circ}\text{C}$. The air flow should be set to 25 ml/min and the nitrogen should be set to 10 ml/min.

An average of at least three measurements on the SWCNT sample is recommended for statistical significance.

10.3 Sample Preparation by Wet Method

Thermogravimetric analysis of wet samples is more complicated than for dry powders. For all samples, a small silicon chip is introduced onto the sample pan prior to taring and SWCNTs are dried onto this chip from suspensions.

1. Tare ceramic sample pan with silicon chip.
2. Remove chip from pan and place on a warm (30 °C) hot plate. Heating is used to help dry excess liquid from the sample.
3. Pipette on SWCNT solutions until chip has approximately 1-2 mg of SWCNTs on the chip surface. Care should be taken to make sure the SWCNTs remain on the top of the chip, without running off to the side/bottom of the chip.
4. Excess liquid should be allowed to dry by leaving the chip on the hot plate for 30 minutes.
5. Silicon chip should be placed, SWCNT side up, into the ceramic sample pan.
6. The sample run should consist of an equilibration step at 40 °C, followed by heating at 10 °C/min to 800 °C. The air flow should be set to 25 ml/min and the nitrogen should be set to 10 ml/min.

When an aqueous solvent that remains on the silicon chip after drying (e.g., surfactants) is used to hydrate the SWCNT samples, the surfactant will remain associated with the SWCNT sample through the TGA run. In these cases, it is recommended that the solvent be run following the above method without the SWCNT material to allow for deconvolution of the peaks after the sample run is complete.

10.4 Quality Assurance Issues Related to Sample Preparation

Thermogravimetric analysis is usually a reproducible technique; although all TGA instruments have a lower limit for sample size at which sampling becomes unreliable. This limit should be investigated for the instrument and a sample size above this threshold should be used to reduce inaccuracies. Samples above 1 mg are typically sufficiently large for TGA sampling.

Common organic solvents (e.g., chloroform, ethanol) and ultrapure water do not usually interfere with the sampling of SWCNTs from a liquid suspension by TGA. Other aqueous solvents, such as surfactants, in which the solvent is dried along with the SWCNTs, can change the thermal profile of the SWCNT. This change could result in either blocking the signal with additional peaks due to the solvent material, or potentially influencing the extent of thermal decomposition.

10.5 Reporting Issues Related to Sample Preparation

The sample preparation method used (wet or dry) should be reported. TGA conditions such as sampling conditions, heating rate, sample pan type and gas flow rates should also be part of the reported sampling conditions. Based on our investigations of a SWCNT sample, uncertainty in M_{res} and T_o are lowest when the sample is heated at 10 °C/min and can be twice as high for SWCNT samples heated at rates of 5 °C/min and 20 °C/min.

The oxidation temperature (T_o) and residual mass (M_{res}) should be reported along with the data analysis for the SWCNT samples. A M_{res} at 635 °C typically provides a measure of the ash content and is sufficiently high enough that the sample has reached

thermal equilibrium. Additional parameters, such as the onset temperature and oxidation temperature of other side peaks, can provide additional information on the samples.

11. Conclusion

This paper outlines sample pre-treatment protocols in order to establish a common starting point whereby measurements of SWCNT samples can be reliably compared, this is essential for round-robin measurement comparisons. Confidence in the commonality of the starting material is important for validation of measurements performed in the same way in different labs or by different operators and is a necessary first step towards understanding behaviours of SWCNT materials and commutability of SWCNT reference materials.

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