

Purity and Dispersion Measurement Issues Workshop on Single Wall Carbon Nanotubes (SWCNTs)

Workshop Summary

**NIST
Gaithersburg, Maryland
May 27-29, 2003**

A workshop organized jointly by the National Aeronautics and Space Administration, Lyndon B. Johnson Space Center (JSC) and the National Institute of Standards and Technology (NIST) was held May 27-29, 2003 at NIST in Gaithersburg, MD. In attendance were 68 participants, representing 11 private corporations, 19 universities, and 9 government agencies. The primary purpose of the workshop was to bring together leading researchers in the field of single wall carbon nanotubes (SWCNTs) to discuss and prioritize measurement needs relative to nanotube purity and dispersion.

The topics of purity and dispersion were chosen because it was recognized that the ability to accurately measure and describe the purity of nanotube-containing materials and their dispersion in liquids or polymers is crucial for future development and use of SWCNTs. Currently, a variety of measurement techniques are utilized for purity and dispersion; significant differences in both methodology and interpretation exist from one laboratory to another. For this reason, comparison of different SWCNT materials is extremely difficult.

To address these challenges, the organizing committee invited 23 speakers, and developed an agenda that encouraged active participation from attendees. Breakout sessions addressing both workshop topics were held to foster open discussion and to invite consensus regarding best techniques and measurement methods. A final panel discussion led to recommendations for future work and to plans for developing documentation of existing techniques. The agenda, as well as speaker and poster session abstracts, is included in the appendices.

The following sections provide details of the issues relative to measurement of purity and dispersion.

Purity

The purity of single walled carbon nanotubes can be loosely defined as the quantity of SWCNTs relative to the metal catalysts and other carbon-like materials present (amorphous, graphitic, and C₆₀ carbons). A number of measurement techniques used for purity determination were discussed. The most extensively utilized techniques are thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and infrared spectroscopy, but others are employed as well. The comment was made that no single technique can describe the quality of a sample of nanotubes.

TGA is commonly used to determine the presence of both carbon and non-carbon impurities, e.g., metal. A draft TGA protocol was proposed by Nikolaev et. al. (JSC) that specified parameters for pre-desiccation, maximum heating rates, moisture content in the ambient atmosphere, minimum sample mass, and minimum number of samples. The authors stated that the residual mass, M_r , after burnout can be used to determine the fraction of residual metal. The maximum temperature is a measure of thermal stability. The standard deviation of both of the above parameters gives a picture of the homogeneity of the sample. Issues of detecting non-metallic impurities, e.g., metal carbide, through TGA analysis were also discussed. Various limitations to the use of TGA were identified, e.g., the presence of metal carbides or oxide, temperatures spikes at high heating rates, etc.

Both TEM and SEM are used extensively for qualitative analysis of a sample containing SWCNTs. There was general accord that **unless the TEM image demonstrates the existence of a significant quantity of SWNTs, no one will agree on the quality of the material.** A draft protocol for TEM specimen preparation and observation was proposed by Nikolaev et. al. (JSC). Discussions at the breakout sessions led to a modification of this protocol. Nikolaev et. al. also pointed out that electron dispersive spectroscopy (EDS) can be used in combination with observation in the TEM to yield information on the chemistry of impurities. There was consensus that the methodology by which TEM and SEM images are selected should always be specified.

Haddon (U. Ca., Riverside) suggested that Near Infrared Absorption (NIR) can be utilized for carbon characterization and to distinguish SWCNT from “schmutz”. At present, such analysis is limited to nanotubes produced by the arc process. Haddon also pointed out that NIR cannot identify non-SWCNT carbons. Samples must be in the solution phase or be in film form for rapid analysis. The NIR technique must be normalized with a “best available” material standard; other needs include a correction for metal, an absolute scale of purity, an extension to SWCNTs of all diameters and production methods, as well as a correction for diameter distribution.

Raman spectroscopy was discussed as an important technique--an excellent quick test for the presence of SWCNTs. Dresselhaus (MIT) pointed out that Raman is also valuable as a tool to distinguish metallic-type nanotube samples from semiconducting-type nanotube samples, which is critical for electronic applications. The interpretation of Raman spectra is complex, and not uniformly applied. The minimum detectable level of nanotubes is one percent. It was pointed out that Raman spectroscopy cannot be used to detect the presence of metallic impurities.

During the panel discussion, it was pointed out that magnetization measurements can also be used to obtain quantitative metal analysis.

Dispersion

Dispersion can be defined as the distribution of nanotube bundles, the splitting of the bundles into individual tubes, and the agglomeration of SWCNTs in solvents or polymers. A fundamental question is that of dispersability, i.e., the degree and the ease of placing the nanotubes in suspension. In macrodispersion, the focus is on eliminating agglomerates. In nanodispersion, the focus is on eliminating SWCNT ropes. The question of dispersion stability over time is also important.

The first step is to disperse the nanotube-containing sample in a solvent or surfactant. It was decided that the community should agree upon a dispersive agent--a standard solvent or surfactant to be used at the concentration 0.1 mg per ml, for the purpose of measurement characterization only. It is understood that various applications will require various solvents. Useful organic solvents include dimethyl formamide (DMF) (which, unfortunately, interacts with samples); tetrahydrofuran (THF); and tetrachloroethylene (TCE). Organic solvents for the dispersive medium are necessary for subsequent dispersion into organic polymer. It was suggested that an impartial laboratory should develop a stable suspension in an appropriate solvent or surfactant and then coordinate a round robin to characterize the sample.

All dispersion characterization methods have in common the critical need for careful sample preparation. Many researchers use sonication, although some use mechanical stirring, because it was determined that chemical reactions can occur during sonication. It was postulated that there is a power floor above which sonochemistry occurs. All agreed that sonication depends on ultrasonic frequency. Vessel specifications and displacement are also thought to be important. Sonication is broadly used yet conditions vary considerably among researchers. Workshop participants unanimously agreed there was an urgent need for sonication methods research that will study the effects of time, frequency, power, and concentration of nanotubes in dispersion.

The technique of choice to determine the degree of macrodispersion appears to be optical microscopy. However, there is lack of agreement on what constitutes good versus poor dispersion. It was suggested that Raman mapping techniques and SEM were useful as complements to optical microscopy.

In the case of nanodispersion, the best method seems to be UV/Vis Spectroscopy, for which researchers did not agree on standard sample preparation. However, there was consensus that the conditions for running the UV/Vis need to be standard and consistent and the method for quantification should be standard and needs further development. Other techniques that may be of value include light scattering, Raman, AFM, dynamic light scattering, and electrophoretic spectrophotometry.

A method for determining dispersion stability was suggested by Nikolaev (JSC). There was a general consensus that this method would be a useful starting point for developing a standard protocol. Researchers were encouraged to use centrifugation to speed the settling and then measure dispersion again. The measurements seem to be very dependent on the sample preparation. It was agreed that further studies are needed on the effects of one, two, and four hours of sonication.

SEM studies can also yield valuable information, but sample preparation is absolutely critical. The two sample preparation techniques that were suggested were freeze-drying of liquids and spin coating. Unfortunately, pullout of nanotubes often occurs during cryofracture. In spin coating, researchers can make thicker coatings and selectively etch away the matrix to expose particles, thereby enabling the examination of particle distribution. A choice must be made between selective etches: either oxygen sources, which have the disadvantage of possibly attacking nanotubes, or hydrogen sources, which can possibly attack the matrix. SEM has limitations, particularly when the dispersion is so fine that small single bundles are created.

Atomic Force Microscopy (AFM) can eliminate some of the problems with artifacts that are inherent in electron microscopy. Compared with SEM, AFM provides higher magnification and better depth of field. Protocols are needed to standardize AFM methods. Key issues are the development of methods by which to hold a single nanotube onto the surface, as well as methods to eliminate charging. One limitation is that the AFM does not give a true representation of the nanotube because the tip is so large in comparison with the nanotube. It is therefore necessary to deconvolute the AFM tip shape to give an accurate representation of the tip.

It was noted that the nanotube community may be able to adapt some measurement methods from the industries that produce carbon black and carbon fiber, where there exist very well established characterization methods. In those industries, commercial standards are available to measure the dispersion of particles of carbon down to 2 nm. There are also standards for TEM imaging and sample preparation.

Summary

This workshop focused on present-day techniques for characterizing the purity and dispersion of single wall carbon nanotubes. A number of the attendees commented that they appreciated the opportunity to openly discuss their measurement concerns with their colleagues, and to learn about different approaches to the various techniques. A questionnaire filled out by the attendees confirmed the value of this workshop.

Participants agreed to support a special issue of the Journal of Nanoscience and Nanotechnology. The issue will feature a workshop summary, multi-authored review papers on specific techniques, and articles on research findings presented during the workshop. Possible topics are TGA, TEM, SEM, EDS, optical microscopy, UV/IR, light scattering, SANS, surface energy/area/tension, surfactants/dispersants, sonication, and magnetic techniques. In some instances NIST Recommended Practice Guides will also be written in order to provide more technical detail.

On the topic of purity, the strengths, limitations, and research needs for most of the commonly used techniques, e.g., TGA, TEM, SEM, Raman, and NIR were discussed. It was agreed that TEM observations are of primary importance. While reference materials will ultimately be useful, it was noted that the nanotube community must first agree on measurement and characterization methods. There was consensus that protocols for measurement techniques would be valuable even if they were incomplete.

In the area of dispersion, the most prevalent need was for information on sonication methods, e.g., power levels, frequency, and time. There was a suggestion that a standard dispersed liquid and a standard dispersed solid be distributed to researchers willing to perform characterization so that methods can be compared. Variables could include composition, particle size, and dispersability. An agreement on a solvent for dispersion is also needed. Optical microscopy was conceded to be the primary technique for determining dispersion, but other techniques of value include SEM, UV/Vis Spectroscopy, and the AFM.

Potential future workshop topics were discussed. These include: 1) diameter, chirality, length, and types of nanotubes; 2) defects 3) surface chemistry and functionalization; 4) functional, e.g.

electronic properties; 5) applications and performance measures; and 6) health and safety issues. **There was consensus that identification of measurement procedures relative to nanotube size and chirality would be particularly welcomed. NIST and NASA/JSC agreed to plan for such a workshop.**