Carbon Nanomaterials Standards Efforts at NIST

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Development of carbon nanomaterials for applications has been hindered to date by a lack of standard protocols, i.e. documentary standards and physical standards such as reference materials, which enable the common inter-comparison between laboratories, consumers and producers during property measurements and commerce. The National Institute of Standards and Technology (NIST) will soon be releasing several carbon nanomaterial standards, specifically for several forms of single-wall carbon nanotubes (SWCNTs), to promote commerce of these materials and to ease carbon nanomaterial development. The identification of the measurement need, development of the materials and specific areas of application are addressed.

A Need for Standards

Carbon nanomaterials are expected to play an important role in future technological developments of transistors (1), photovoltaics (2), transparent thin film conductors (3-4), sensors, and fuel cell electrodes (6) among many potential applications. However, the potential of these materials has been hindered by a lack of both standard protocols (i.e. documentary standards) for determining the quality and properties of a sample material, and physical standards, which allow for common inter-comparison of measurements and a baseline from which developments can be made.

There are two key problems from which many of the common hindrances to the development of carbon nanomaterials derive; one is the large degree of polydispersisty in morphology in many materials, and the second is the historic difficulty in consistent production of homogenous and pure materials. Polydispersity of morphology is well illustrated by the example of multi-wall carbon nanotubes (MWCNTs). A sample labeled “multi-wall nanotubes” could contain materials having anywhere from three to hundreds of cylindrical walls, be open or closed cylinders with a large/small inner diameter or segmented in a “bamboo” structure, be branched or not branched, and with an aspect ratio that could vary from below 10 into the hundreds. Comparing the results of property measurements (or environmental, health and safety assessments) made with MWCNTs by different processes, at different times, or with different processing is thus intrinsically difficult, without the further complication of amorphous and graphitic carbon contamination or residual catalyst content that likely varies batch to batch.

The polydispersity and quality problems are more important for single-wall carbon nanotubes (SWCNTs) due to their exemplary projected properties, larger variation in those properties between different diameter tubes, and more demanding future applications. For many applications such as sensing or nanoelectronics, it is desirable and often necessary to select for only certain nanotubes possessing a given band gap or electronic behavior. Historically, however, SWCNT soots have been notorious for their variable and often low quality, with typical samples composed of a multitude of subtypes that differ in their distribution of lengths, diameters, and chiralities across manufacturers and synthesis processes. Other issues include variations in residual catalyst, and non-nanotube carbonaceous impurities. Research into purification has yielded major advancements in the processing of the raw soot. Liquid dispersion (6-8), dry and wet methods for selectively removing non-SWCNT carbon, as well separation by length (9-11), chirality (12-15), electronic type (15-17) and optical handedness (18-20) are all areas of significant and ongoing efforts. Despite these efforts, the SWCNT community still does not have an agreed-upon set of methods for decisive evaluation of an unknown material; nor is there consensus regarding the explanations for certain commonly measured properties.

Although not yet released, the development of nanomaterial documentary standards, such as those in development by the International Organization for Standardization (ISO), and earlier efforts like the NIST recommended practice guide (21) among others, address the need for common measurement protocols. Nevertheless, to tie these methods to known values, and to ensure comparison between laboratories, consumers, and suppliers, reference materials (RMs) of known composition and/or properties are an additional requirement.

Development of SWCNT Reference Materials

One output from NIST work on SWCNTs will be a suite of SWCNT reference materials. The reference materials will include a raw SWCNT soot, characterized for composition, a purified SWCNT "buckypaper", and a set of three length-sorted populations in aqueous dispersion. It is expected that these materials will meet many of the needs for improving commerce in SWCNTs. The characterization and applicability of these SWCNT materials to post complementary metal oxide semiconductor (CMOS) technologies forms the remainder of this contribution.

Characterization of SWCNT Soot

Although production of SWCNT "forests" grown on surfaces is increasing in importance, the primary morphology in which SWCNTs are produced and purchased is in the form of a dry soot. Production by electric arc reactors, laser ablation, high-pressure decomposition, and fluidized bed reactors all produce SWCNT material in this morphology. Despite the desire to simply conduct commerce of the raw soot without additional processing in this form, raw soot is the most challenging format for characterization of the nanotube properties for several reasons. The largest issue for the commerce and use of SWCNT materials in the raw soot form is a typical lack of homogeneity on several length scales. Although manufacturers are improving their production processes, it is still typical for production to be done in relatively small volume batches from which large orders are generated by mechanical mixing. Moreover, there can be significant batch-to-batch variation in process variables, either due to evolving process control or the continuing iterative optimization of a reactor. The fact that several of the production methods inherently produce regions of SWCNT light and SWCNT rich soot within the reactor that have intrinsic differences in their mechanical properties can also cause significant batch to batch variation.

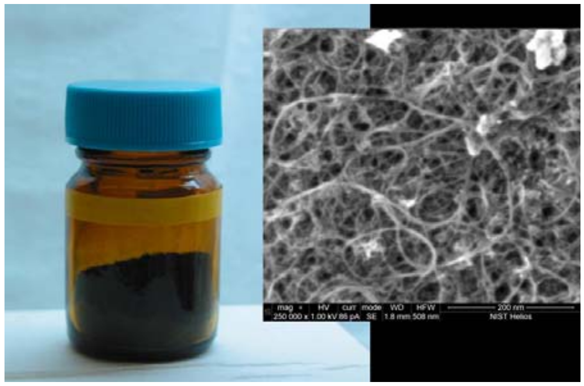

Figure 1. A bottle of the SWCNT powder bottled for reference material use, and a representative SEM image of a similar SWCNT soot obtained from the same manufacturer.

In a reference material, homogeneity and stability are the principal requirements. Primary characterization of the NIST soot will be for homogeneity in, and values of, the elemental composition as determined by prompt gamma activation analysis (PGAA) and instrumental neutron activation analysis (INAA). Secondary confirmation of the total metal content will be provided by thermogravimetric analysis (TGA). These measurement techniques allow for the complete elemental composition analysis of the soot, as well as information about the required unit size for homogeneity. Unfortunately not enough information is currently known to extract the fractional percentage of carbon in SWCNT form from these techniques. Raman, ultraviolet-visible-near infrared (UV-visible-near infrared (NIR)), and NIR fluorescence spectroscopy measurements, as well as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images will be also be performed to provide informational values. Interpretation of these values will allow for an estimate of the fractional SWCNT content, although the unambiguous interpretation of composition by these techniques is currently unresolved. Additional characterization by other techniques is also under consideration.

Homogeneity of the soot will be stated as a confidence interval in the reported values. Based on the independent measurement of the composition by three techniques, the soot RM qualifies for labeling as a NIST Standard Reference Material (SRM), which is equivalent to the more common terminology of “certified reference material” in many other countries. The product number for the soot material will be SRM 2483, and the material itself will be sold as individual bottles containing (0.26 to 0.27) g of soot in an amber glass bottle. For this material the primary customer bases are expected to be industrial suppliers and consumers of raw SWCNT soot, as well as the environmental, health, and safety (EHS) community. Critical needs for these communities are reference samples of known composition for metrology development and measurement-based comparison. The EHS community requires knowledge of the soot composition for evaluating the components of the soot for their toxicological and environmental effects.

Characterization of Purified SWCNT Buckypaper

To allow for comparison in characterization techniques and for calibration of measurement tools NIST is also producing a buckypaper format sample of the raw soot (SRM 2483), purified to have an increased mass fraction of SWCNTs. Purification of the nanotube powder is performed through aqueous phase processing. This purification occurs in three steps. First, the nanotubes are dispersed in an aqueous surfactant solution (2 % by mass sodium deoxycholate) through tip sonication, which produces nearly complete individualization of the SWCNTs from each other and contaminant impurities. Second, the SWCNT dispersion is centrifuged at high speed; under centrifugation, the denser catalyst particles and non-nanotube carbon selectively sediment to a pellet at the bottom of the centrifuge tube, which results in purification of the supernatant for SWCNT carbon. Lastly, the collected supernatant, estimated at greater than 90 % nanotubes, is filtered against a membrane and washed repeatedly to remove the surfactant. This results in a "bucky paper" RM format. Primary characterization of the resulting RM (RM 8282) will include TGA and Raman spectroscopy. Additional characterization techniques are still under assessment.

Extension to Graphene. RM 8282 is perhaps closest to one of the possible reference materials for graphene. Scientific advancement in the graphene area is currently proceeding rapidly, but one of the areas in which interest has been conveyed to NIST is for solution deposited graphene layers. Technically, processing of a graphene RM from a dispersed suspension would be similar to production of RM 8282 although the dispersant fluid would likely be different. Feedback is welcome on the desirability of such an RM.

Characterization of Liquid Dispersions

Lastly, NIST is producing a set of RMs containing three different length distributions of nanotubes dispersed in aqueous surfactant solution. This set of RMs will enable companies, regulators, and laboratories *to evaluate the effects of the nanotubes themselves, with minimal carbonaceous and catalytic impurities*, as well as to elucidate the effects of nanotube length on the material properties. Especially at the nanometer length scale, the absolute size of the nanoparticles, the aspect ratio, and the surface area are critical parameters in determining the materials physical and optical properties. (11,22) Critically, these characteristics impact the interaction of the nanomaterial with the biological environment.

Characterization of the dispersed and length separated SWCNTs will be for the length distribution using multiple independent techniques such as atomic force microscopy (AFM), transmission electron microscopy (TEM) and dynamic light scattering (DLS). Separate measurements including UV-vis-NIR absorbance and fluorescence spectrophotometry, as well as Raman scattering will be used to evaluate the optical response. All of these measurements are expected to result in informational values. Although measurement of the length distribution will be sampled independently by the different techniques, prior experience with measurements in nanoparticles indicate that the difference in what is intrinsically being measured by the separate techniques will likely lead to close but distinct values.

The length-sorted RM (RM 8281) set may still undergo slight changes as the processing is completed. However, the RM is projected to consist of three 5 mL transparent glass ampoules, each containing 2.5 mL of one length fraction, at a nanotube concentration between 0.02 mg / mL and 0.2 mg / mL. Test gamma irradiation of a demonstration set of length separated samples indicated that the nanotubes can be packaged without a preservative agent while still guaranteeing sterility of the individual vials.

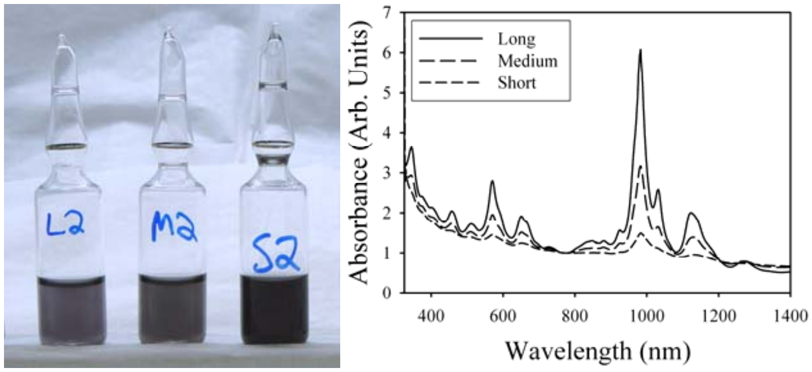

Figure 2. A mockup set of bottles containing different length populations of dispersed SWCNTs prepared from the raw RM soot, and approximate absorbance spectra of the dispersed populations in production. The standard uncertainty in the spectra, equal to one standard deviation, is less than the line width in the figure.

Due to the highly size-dependent nature of nanotube properties, we expect that the first areas of impact of this RM will be in the areas of nanotube electronics and bio-studies, including toxicity and cellular-nanotube interactions. This RM is expected to be purchased both for applied and scientific research activities, and will also be the basis for the development of diameter distribution determination metrics through a round-robin test being organized through the Versailles project on Advanced Materials and Standards (VAMAS). Furthermore these samples will be appropriate for calibration of certain instruments used in nanotube measurements and for conducting representative experiments on high-quality materials.

Implications for Post CMOS Applications

Carbon nanomaterials, particularly graphene and SWCNTs, are interesting to the semiconductor industry due to the approach of fundamental material limits in the materials currently in use. As the semiconductor industry is a multi-billion dollar industry, the importance of having reliable and quantifiable replacement materials is obvious. Currently the furthest advanced application of nanomaterials towards replacing or enhancing CMOS processes involve growth aligned nanotubes, however this may change as liquid processing techniques, which can offer more control over the nanotube properties, develops. As competing technologies emerge, the nanotube reference materials under development at NIST will help guide enhanced production and characterization for this demanding application.

Conclusions

Carbon nanotube RMs under development at NIST, with expected release dates in 2009, will provide the quantitative comparisons and common reference points necessary to encourage the further technological development of these materials. Particularly as competing strategies develop for post CMOS technologies, the NIST materials will provide important reference points for accurate comparison.

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