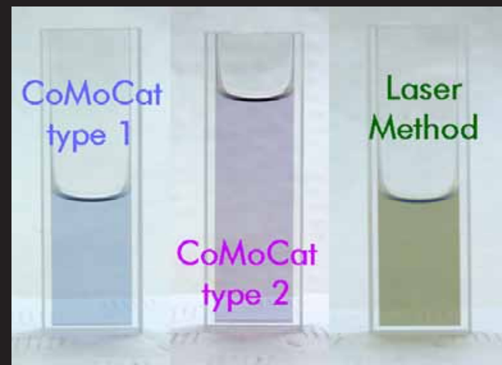
Nanotube Metrology

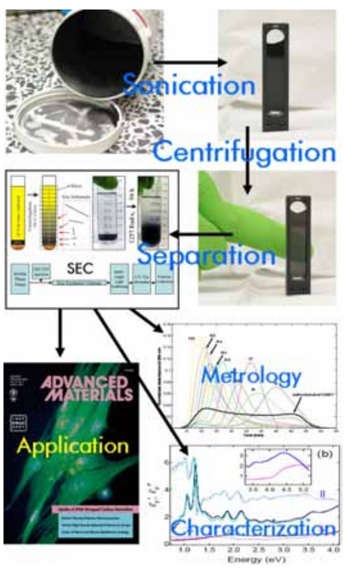
Objective

Our goal is to develop methods to produce well-characterized fractions of carbon nanotube suspensions with controlled parameters (length, type, charge, concentration and impurities) and to utilize them for measuring intrinsic nanotube properties and addressing emerging EHS concerns. By providing measurements that underlie this new class of materials, we allow vendors and buyers to trade with confidence and provide the final users with sound knowledge of the properties of the material.



NANOMATERIALS

Impact and Customers



- The global market for nanotubes has the potential to reach $5B by 2012 in electrical, mechanical, health and medical applications. We are developing the measurements infrastructure that underlies this new material.

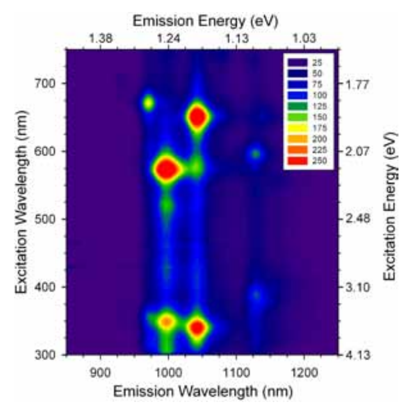
- Three biannual workshops on single-walled carbon nanotubes (SWCNTs), jointly sponsored by NIST and NASA, have led the way for dissemination of the NIST effort to both the industrial and academic communities. The output was a Recommended Practice Guide which launched the extensive ISO activities in SWCNTs. Seven documentary standards are in preparation by five countries.

- 2009 will see the release of three SWCNT Reference Materials (RMs), each designed to address measurement needs reported by the SWCNT community. A SWCNT soot RM, a purified SWCNT "bucky paper," and a set of length separated SWCNTs in aqueous dispersion will be released.

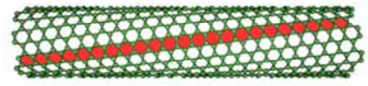
- We collaborate with industrial, academic and government researchers including Rice University, NASA and SouthWest Nanotechnologies Inc. by providing them with analysis of samples of unprecedented quality, by sorting samples into their component parts and by providing optical data.

Approach

In every SWCNT production technique many different types (called chiralities) and lengths of SWCNTs are produced. The properties of the SWCNTs are linked strongly to both of these parameters. Thus, in order to characterize the intrinsic properties of any specific SWCNT type or length, an initially polydisperse nanotube sample must be first purified of non-SWCNT carbon and metallic catalyst, and then separated by diameter or length to achieve robust results. Characterization by optical methods (absorption, fluorescence, Raman scattering), conductivity measurements, microscopy or other techniques then yields specific results.



Individual dispersion of the SWCNTs with DNA, or small molecule surfactants such as sodium deoxycholate, enables this purification and separation via nondestructive solution phase separation techniques. We use a variety of different techniques to separate SWCNTs by chirality or length, depending on the requirements of the characterization we wish to perform. Using techniques such as size exclusion chromatography, field-flow fractionation and ultracentrifugation (for either length or type separation), highly resolved SWCNT fractions are generated to allow for measurement development and individual property determination.

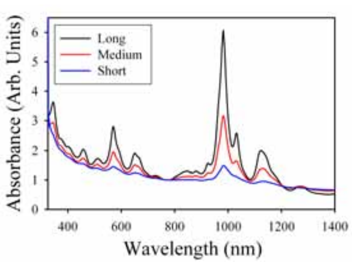


Accomplishments

Our systematic focus on controlling the nanotube population in a sample through the utilization and development of separation techniques differentiates the NIST effort in SWCNTs. Using well controlled populations ensures that we can accurately develop measurement techniques and characterize intrinsic SWCNT properties, resulting in greater confidence in measurements by nanotube manufacturers, device makers and academic researchers.

Controlling the SWCNT population in a sample begins with the dispersion process. In the dispersion process the SWCNTs are brought into an aqueous or organic solvent through the use of small molecules called surfactants. Our first research was to determine the most efficient methods for dispersion and dispersion metrology.

Utilizing small angle neutron scattering (SANS) to directly measure dispersion, we compared measurements from additional techniques such as multiple angle light scattering, dynamic light scattering, UV-visible-near infrared (UV-Vis-NIR) absorption and NIR fluorescence on the best dispersed surfactant – SWCNT systems, to develop the metrology of dispersion. This work identified the best dispersants as small single stranded DNA molecules, such as (GT)15, and the small molecule surfactant sodium deoxycholate.



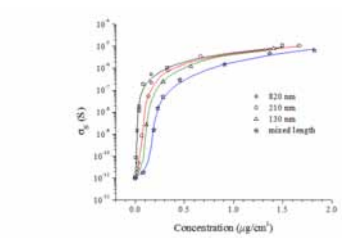
The effect of length on absorbance

Length Separation

We utilize three different techniques to perform length separation: size exclusion chromatography (SEC), field-flow fractionation (FFF), and centrifugation. Each technique offers a different, complementary balance between size resolution, mass throughput, and metrology development. Centrifugation based length sorting, invented at NIST, allows for the largest scale separation. FFF and SEC process smaller amounts of material, but allow for higher resolution of the separated fractions and for online measurement of the separation process. For all three techniques we have made significant advances to the separation science and metrology of SWCNTs.

We have also subjected the separated SWCNT length fractions, ranging from 1μm to less than 50 nm, to intense characterization. In 2007 this resulted in the publication of the previously unrecognized dependence of SWCNT optical properties on length. In 2008 we optimized the parameters for length separation via ultracentrifugation, began sorting populations by multiple vectors, i.e. length and electronic functionality, and used our separated materials to explore the effects of length on 2D percolation, templated self assembly, and the measurement of defect density on a nanotube.

The effort involving the 2D percolation of nanotubes was particularly interesting, as it provided an experimental comparison with 2D percolation theory. It also showed that sorted nanotubes, even of a shorter average length, may perform better than unsorted tubes due to their tendency to pack in a 2D (rather than a 3D) network.



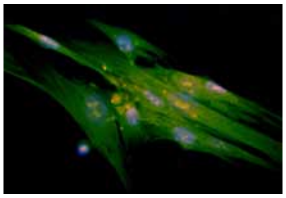
The effect of length on percolation

Reference Materials

Results from these scientific investigations have enabled the production in 2009 of three grades of Reference Materials (RMs). The lowest grade will be a raw SWCNT soot characterized for elemental composition. More purified materials will include a RM composed of a mat of purified SWCNTs from the raw soot, and a set of length separated fractions in aqueous dispersion, also purified from the raw soot base material. The absorbance spectra shown for the long, medium, and short fractions are representative of these solutions.

SWCNT Uptake and Toxicity

The development of SWCNT samples with different lengths, and the metrology of those samples, are enabling significant new investigations and collaborations. In concert with the biomaterials group, these samples were used for the first determination of the effect of length on the uptake of SWCNT by multiple cell lines, including human lung fibroblasts. In this study we found that only the shortest SWCNTs, those less than 200 nm, were absorbed at a significant rate by the cells. Thus the potential toxicity of these materials can likely be significantly reduced by the use of SWCNTs longer than this threshold.



A human cell containing SWCNTs

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Publications

Fagan JA, Becker ML, Chun J, Nie P, Bauer BJ, Simpson J, Walker ARH and Hobbie EK *Centrifugal Length Separation of Carbon Nanotubes* Langmuir, 24: 13880 (2008)

Simien D, Fagan JA, Luo W, Douglas JF, Migler K and Obrzut J *Influence of Nanotube Length on the Optical and Conductivity Properties of Thin Single-Wall Carbon Nanotube Networks* ACS Nano, 2:1879 (2008)

Becker ML, Fagan JA, Gallant ND, Bauer BJ, Bajpai V, Hobbie EK, Lacerda S, Migler KB and Jakupciak JP *Length-Dependent Uptake of DNA-Wrapped Single-Walled Carbon Nanotubes* Advanced Materials, 19: 939 (2007)

Fagan JA, Simpson JR, Bauer BJ, Lacerda S, Becker ML, Chun J, Migler KB, Walker ARH and Hobbie EK *Length-Dependent Optical Effects in Single-Wall Carbon Nanotubes* J. American Chemical Society, 129: 10607 (2007)