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3rd NASA-NIST Workshop on Nanotube Measurements

Co-Sponsored by NASA and NIST

September 26-28, 2007
NIST, Gaithersburg, MD, USA

PURPOSE

The NASA-NIST Workshop Series devoted to Single Wall Carbon Nanotubes is to focus the community's attention on the issues of nanotube quality and characterization. Leading experts convene to discuss forefront efforts in the areas of dispersion, purity, and characterization. The output of the second meeting was a Recommended Practice Guide, which formed the basis for the current ISO documentary standards activities in single wall carbon nanotubes.

We will discuss emerging nanotube applications and environmental, health and safety concerns which are driving the need for high quality, well characterized nanotubes. We will seek community feedback on efforts to develop both documentary standards and standard reference materials that are based on these advances. Workshop attendees will learn cutting edge techniques in purification and characterization, guide the development of nanotube standards and reference materials, learn the latest on nanotube applications and potential risks and how they drive the need for standardization.

OUTPUT

The goal for this third meeting is to capture and disseminate rapid advances in the development of high quality standard materials and sophisticated characterization methods.

ORGANIZING COMMITTEE

NIST	NASA
Kalman Migler (Chair)	Sivaram Arepalli (Co-Chair)
Angela Hight Walker	Peter Lillehei
Carol Laumeier	Edward Sosa
Stephanie Hooker	Leonard Yowell

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FINAL AGENDA

3rd NASA-NIST Workshop on Nanotube Measurements

September 26-28, 2007
Gaithersburg, MD

Wednesday, September 26th

8:00 AM	**Registration and Continental Breakfast**	

Session One - Plenary Talks

Session Chairs: Sivaram Arepalli and Kalman Migler

9:00	NIST Welcome	Jim Turner
9:15	NASA Welcome	TBA
9:30	"SWCNT growth by the CoMoCAT method. Kinetic Modeling, Characterization of Catalysts and Nanotube Product"	Daniel Resasco University of Oklahoma and Southwest Technologies
10:00	"Use of Relative Purity in the Processing and Applications of Single-Walled Carbon Nanotubes"	Robert Haddon University of California Riverside and Carbon Solutions Inc
10:30	**Break**	

Session Two - Development of High Quality Materials

Session Chair: Stephanie Hooker

11:00	"Sorting Single-Walled Carbon Nanotubes by Their Physical and Electronic Structure using Density Differentiation"	Mark Hersam Northwestern University

11:30	"Metallic vs. Semiconducting SWNT Separation using Dielectrophoresis"	Matteo Pasquali Rice University
12:00 PM	"Applying Biomolecular Recognition for Carbon Nanotube Separation"	Jennifer Cha IBM
12:30	**Lunch**	

Session Three - Characterization Methods I

Session Chair: Edward Sosa

1:30 PM	"Qualitative and Quantitative Analysis of Bulk SWNT Samples using Near-IR Fluorimetry"	Bruce Weisman Rice University
2:00	"A Novel Floating Catalyst Synthesis and Electron Diffraction Characterization of High Purity Individual SWCNTs"	Esko Kauppinen Helsinki University of Technology
2:30	"Developing Carbon Nanotube Standards at NASA"	Pasha Nikolaev NASA-JSC
3:00	**Break**	

Session Four - Characterization Methods II

Session Chair: Angela Hight Walker

3:30	"Raman Spectroscopy and Nanotube Standards"	Ado Jorio Universidad Federal de Minas Gerais
4:00	"Optical Characterization of Length Sorted Single Wall Carbon Nanotubes"	Jeffrey Fagan NIST
4:30	"Quantifiable Assessment of SWNT Dispersion in Polymer Composites"	Peter Lillehei NASA Langley
5:00	**Poster Session and Reception**	

Thursday, September 27th

8:00 AM Continental Breakfast

Session Five - Application Specific Materials and Measurement Needs

Session Chair: Daniel Resasco

8:30	"Strategies for Improved Properties in Nanotube / Polymer Composites"	Karen Whiney University of Pennsylvania
9:00	"Characterization of SWNT Thin Film Electrodes of Precisely Tuned Metal/Semiconductor Ratios with Optical and THz Spectroscopies"	Jeffrey Blackburn National Renewable Energy Laboratory
9:30	"Optical Modulation of Single Walled Carbon Nanotubes for Sensor Applications"	Michael Strano MIT

10:00 Break

10:30 Breakout Session I - Roadmapping Future Characterization Needs

(Cheol Park, Leonard Yowell, Eric Hobbie, and Angela Hight Walker)

12:00 PM Lunch

Session Six – Nanotube Standards

Session Chair: Ado Jorio

1:30	"International Efforts in Nanotube Standards"	Clayton Teague NNCO
2:00	"A Needs-based Assessment of Nanomaterials and the United States Measurement System "	Clare Alloca NIST
2:30	"Summary of NNI Workshop on Standards for EHS Concerns"	Dianne Poster NIST

2:40 Break

3:00	**Breakout Session II – Needs for Reference Materials and Documentary Standards**	
	(Pasha Nikolaev, Sivaram Arepalli, Kalman Migler and Stephanie Hooker)	
5:00	Bus back to Holiday Inn	
6:00	Social hour and drinks	
7:00	Dinner at Holiday Inn	

Friday, September 28th

8:00 AM **Continental Breakfast**

Session Seven – Health Applications and Concerns: the Need for Well-Characterized Materials

Session Chair: Marcus Cicerone

8:30	"Pulmonary Toxicity of Single-Walled Carbon Nanotubes *in vivo:* Mechanisms and Consequences "	Anna Shvedova NIOSH
9:00	"Carbon Nanotubes in Medicine Where We are and Where We Need to Be	Valerie Moore University of Texas Health Science Center
9:30	"SWNT Interactions with Biological Systems: Focus on Length"	Matt Becker NIST

10:00 **Break**

Session Eight – Miscellaneous Characterization

Session Chair: Esko Kauppinen

10:30	"Atomic-Level Characterization of Carbon Nanotubes"	Kazu Suenaga AIST

Session Nine – Wrap up Session

Session Chairs: Sivaram Arepalli and Kalman Migler

11:00 **Reports from Break out Sessions**

12:00 PM **Lunch and Adjourn**

1:30 **Post Meeting Lab Tours**

SESSION ONE

PLENARY LECTURES

Wednesday AM

SWNT Growth by the CoMoCAT Method: Kinetic Modeling, Characterization of Catalysts and Nanotube Product

Dan Resasco

University of Oklahoma and SouthWest Nanotechnologies

In the past few years, we have investigated the disproportionation of CO on supported CoMo catalysts and have given evidence that this reaction can produce single-walled carbon nanotubes (SWNT) with high selectivity to the wanted product as opposed to other less desired forms of carbon, such as graphite nanofibers. In fact, the commercial CoMoCAT™ process, based on this reaction, currently makes SWNT with narrow diameter and chirality distributions. In this contribution, we will describe a kinetic model that attempts to capture mathematically the various stages of the nanotube synthesis, including: a) catalyst carburization and activation; b) CO dissociation on the catalyst surface; c) nucleation and growth; d) termination. We will also describe the experimental protocol that we use to characterize the quality of the SWNT obtained by this process. The protocol includes TEM, Raman spectroscopy, optical absorption (UV-vis and NIR), TGA, TPO, AFM, and electrical conductivity.

Use of Relative Purity in the Processing and Application of Single-Walled Carbon Nanotubes

Robert Haddon

University of California Riverside and Carbon Solutions Inc

SESSION TWO

DEVELOPMENT OF HIGH QUALITY MATERIALS

WEDNESDAY AM

Sorting Single-Walled Carbon Nanotubes by Their Physical and Electronic Structure using Density Differentiation

Mark C. Hersam

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The utilization of single-walled carbon nanotubes (SWNTs) in large quantities for molecular electronics, optoelectronics, biosensors, and medical applications will require SWNTs of the same physical structure, electronic type, and band gap. Since current methods of synthesis produce mixtures of nanotubes with different physical structures and electrical properties, the development of strategies for the post-production separation of these one-dimensional materials is highly desirable. In this work, we demonstrate a scalable method for separating SWNTs by their diameter and electronic type (i.e., semiconducting versus metallic) using density gradient ultracentrifugation (DGU). Since DGU is a technique commonly utilized in biochemistry to separate and isolate different sub-cellular components, DNA from RNA, and even different sequences of DNA by their compositions, we initially focused on the bulk sorting of DNA wrapped SWNTs in aqueous density gradients [1]. This process led to enrichment of SWNTs by diameter – especially in the small diameter regime (i.e., SWNT diameter = 0.7 – 1.0 nm). However, DNA wrapping possessed several undesirable characteristics including prohibitive expense in large scale production, irreversible wrapping, and inefficient wrapping for SWNTs with diameters exceeding 1 nm. Consequently, subsequent work has focused on DGU of surfactant encapsulated SWNTs [2]. In particular, bile salt surfactants, such as sodium cholate (SC), have overcome the drawbacks of DNA. Furthermore, additional control over the density-structure relationship has been achieved by using co-surfactant mixtures of SC and sodium dodecyl sulfate (SDS). For example, highly efficient metal versus semiconductor separation has been achieved with SDS and SC co-surfactant mixtures. Characterization of the resulting sorted SWNT samples includes optical absorption spectroscopy, photoluminescence spectroscopy, atomic force microscopy, and direct charge transport measurements. Since DGU produces relatively large quantities of monodisperse SWNTs, this talk will conclude with our most recent efforts to realize enhanced performance in SWNT devices, such as thin-film field effect transistors and transparent conductors, using SWNTs sorted by DGU.

[1] M. S. Arnold, S. I. Stupp, and M. C. Hersam, “Enrichment of single-walled carbon nanotubes by diameter in density gradients,” *Nano Letters*, **5**, 713 (2005).

[2] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, and M. C. Hersam, “Sorting carbon nanotubes by electronic structure via density differentiation,” *Nature Nanotechnology*, **1**, 60 (2006).

Metallic vs. Semiconducting SWNT Separation using Dielectrophoresis

Manuel J. Mendes, Noe Alvarez, Howard K. Schmidt and Matteo Pasquali

Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, 6100 Main Street, Houston, Texas 77005, USA

We theoretically investigated the behavior of individualized single-wall carbon nanotubes (SWNT) in a dielectrophoretic flow device. The SWNTs motion was simulated by a Brownian Dynamics (BD) algorithm which includes the translational and rotational effects of shear flow, brownian motion, dielectrophoretic and electrophoretic energies. The device geometry is chosen to be a coaxial cylinder, because it yields effective flow throughput and all the fields can be described analytically everywhere.

The BD code is combined with a Nelder and Mead optimization algorithm that numerically searches for the best conditions that enable a global maximum in the separation performance, for any type of SWNT or solution parameters. Modeling results show that a 99.1% performance can be expected with typical SWNT parameters.

We also show spectroscopic measurements of early experimental tests which demonstrate the feasibility of metallic vs. semiconductor separation at electric field frequencies in the MHz range. This was achieved using a nonionic surfactant (Pluronic F108) and a mixture of anionic (SDS) and cationic (CTAB) surfactants.

Additionally, these results may also reveal crucial knowledge on the influence of the surfactants on the SWNTs effective conductivity.

Applying Biomolecular Recognition for Carbon Nanotube Separation

Jennifer Cha
IBM

SESSION THREE & FOUR

CHARACTERIZATION METHODS

WEDNESDAY PM

Qualitative and Quantitative Analysis of Bulk SWNT Samples using Near-IR Fluorimetry

R. Bruce Weisman
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and Center for Biological and Environmental Nanotechnology
Rice University
Houston, Texas 77005

Since the discovery of structure-dependent near-IR emission from semiconducting single-walled carbon nanotubes (SWNTs), fluorimetric analysis has emerged as a practical and valuable tool for characterizing SWNT samples. Because the wavelengths of E_{22} absorption and E_{11} (near-IR) emission are now known for all (*n*,*m*) structures, fluorimetry provides secure qualitative analysis of the semiconducting species present in bulk samples. However, quantitative determination of relative or absolute species concentrations remains far more challenging. Two types of information are needed to make fluorimetric analysis quantitative: (1) the intrinsic differences in photophysical parameters (absorptivities and emissive quantum yields) in perfect nanotubes as a function of structure, and (2) the role of extrinsic factors, or imperfections, that can influence fluorescence intensities. These extrinsic factors may include the presence of quenching sites (structural defects, ends, or chemical derivatizations), the extent of sample aggregation, and the influence of specific suspending agents. The first measurements of absolute fluorescence action cross sections will be reported for twelve species of SWNTs in aqueous SDBS suspension. We believe that these action cross sections, which are the products of E_{22} absorptivity times fluorescence quantum yield, describe the intrinsic fluorimetric efficiencies of SWNTs in the absence of extrinsic quenching effects. The measured action cross sections range from 1.7 to 4.5 x 10^{-19} cm^2/C atom and show systematic, relatively mild variations correlated mainly with optical band gap. The determination of these values represents a major step toward quantitative fluorimetric analysis of bulk SWNT samples.

A Novel Floating Catalyst Synthesis and Electron Diffraction Characterization of High Purity Individual SWCNTs

Esko I. Kauppinen[1, 2]

[1] NanoMaterials Group, Laboratory of Physics and Centre for New Materials, Helsinki University of Technology, Finland & [2] VTT Biotechnology
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We present two floating catalyst methods for the selective synthesis of high purity individual SWCNTs, using pre-made iron catalyst particles by a hot wire based PVD method or grown *in situ* via ferrocene vapour decomposition in the presence of CO. When adding trace amounts of H_2O and CO_2 to the synthesis conditions, the tube growth rate i.e. length can be controlled. In addition, SWCNTs can be decorated during their synthesis with covalently bonded fullerenes, which novel hybrid material we call the carbon NanoBud^{TM}[1]. The formation of nanotube bundles can be controlled by the number concentration of catalyst clusters, by their activity to grow tubes, as well as time given for individual tubes to collide during their growth in the floating catalyst reactor. We show that individual tubes can be collected onto any substrate at ambient temperature, which opens possibilities to directly intergrate SWCNT floating catalyst synthesis into novel nanoelectronics manufacturing processes. Individual tubes e.g. on the holey carbon TEM grids are needed to their chirality determination.

In addition, we present a new method for direct chirality determination of the carbon nanotubes from their electron diffraction patterns. The unique method is based on a novel concept of the non-dimensional "*intrinsic layer-line spacing*" which we introduced [2] with an intention to establish a measurement standard for electron diffraction analysis of SWCNTs. The method is absolutely calibration-free. Uniquely, errors due to the nanotube inclination are specified and tilt angles of nanotubes with respect to the electron beam are simultaneously calculated so that the tilt effect on the calculation is eliminated. Moreover, the introduced method enables several effective procedures to cross-check the results by using the abundant information contained in the diffraction patterns. Due to the fact that only the layer-line distances and the interval between the zeros along the equatorial line are involved in the measurement, this method has no significant limitations, and has proven to be an easy, fast and trustworthy method for chirality determination of SWCNTs. The method can be extended to structural analysis of other nanotubes having structures similar to carbon nanotubes, such as boron nitride nanotubes.

Reference

[1] A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tománek, and E. I. Kauppinen, (2007) A Novel Hybrid Nanomaterial, *Nature Nanotechnology* **2**(3), **156-161**

[2] H Jiang, A G Nasibulin, D P Brown and E I Kauppinen: *Carbon* **45** (2007) 662.

Acknowledgements

Albert G. Nasibulin, Hua Jiang, David P. Brown, Sergey D. Shandakov, David Gonzales, Paula Quiepo, Anton Anissimov, Andrei Ollikainen, Gunther Lientschnig, Abdou Hassanien, Peter V. Pikhitsa, Mansoo Choi, Guilio Lolli, Daniel E. Resasco, Arkady V. Krasheninnikov, David Tomanek, Delphine Chassaign and Risto Nieminen are acknowledged for collaboration as well as Academy of Finland, TEKES and EU for funding.

Developing Carbon Nanotube Standards at NASA

Pasha Nikolaev[1], Sivaram Arepalli[1], Edward Sosa[1], Olga Gorelik[1] and Leonard Yowell[2]

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2. NASA Johnson Space Center
Houston, Texas 77058

Single wall carbon nanotubes (SWCNTs) are currently being produced and processed by several methods. Many researchers are continuously modifying existing methods and developing new methods to incorporate carbon nanotubes into other materials and utilize the phenomenal properties of SWCNTs. These applications require availability of SWCNTs with known properties and there is a need to characterize these materials in a consistent manner. In order to monitor such progress, it is critical to establish a means by which to define the quality of SWCNT material and develop characterization standards to evaluate of nanotube quality across the board. Such characterization standards should be applicable to as-produced materials as well as processed SWCNT materials. In order to address this issue, NASA Johnson Space Center has developed a protocol for purity and dispersion characterization of SWCNTs (Ref.1). The NASA JSC group is currently working with NIST, ANSI and ISO to establish purity and dispersion standards for SWCNT material. A practice guide for nanotube characterization is being developed in cooperation with NIST (Ref. 2). Furthermore, work is in progress to incorporate additional characterization methods for electrical, mechanical, thermal, optical and other properties of SWCNTs.

Ref. 1: Carbon **42**, pp. 1783-1791 (2004)
Ref. 2 : http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes_Guide.htm

Raman Spectroscopy and Nanotube Standards

Ado Jorio

Universidad Federal de Minas Gerais (UFMG) and Brazilian National Institute of Metrology (Inmetro)

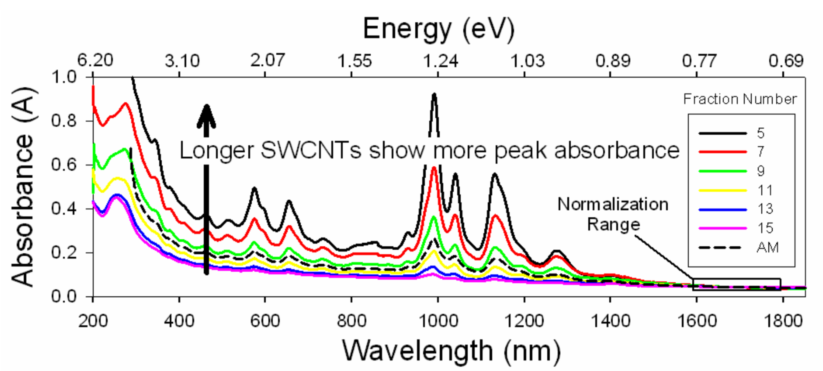
The use of resonance Raman spectroscopy for the characterization of single-wall carbon nanotube (SWNT) samples will be discussed. Focus will be given on the determination of carbon nanotube diameter and diameter distribution in an ensemble. The controversial determination of the constants relating radial breathing mode frequency and tube diameter will be discussed, leading to a proposal of a SWNT reference standard.

Optical Characterization of Length Sorted Single Wall Carbon Nanotubes

Jeffrey A. Fagan, Barry J. Bauer, Matthew L. Becker, Jeffrey R. Simpson, Kalman B. Migler, Angela R. Hight Walker and Erik K. Hobbie.

National Institute of Standards and Technology
Gaithersburg, MD
3rd NASA-NIST Workshop on Nanotube Measurements
September 26th 2007

The optical properties of length sorted single wall carbon nanotubes (SWCNT) will be presented. The strength of the intrinsic nanotube optical features are found to vary strongly with the length of the SWCNT regardless of the separation technique. Spectra and a discussion of the observed length dependence will be presented both for size exclusion chromatography sorted nanotubes, and for nanotubes length fractionated by their transient motion when centrifuged in a dense liquid. Length enhancement of the optical properties is observed for all types of nanotube materials, with specific experimental results to be presented for HiPCO and CoMoCat process SWCNTs.



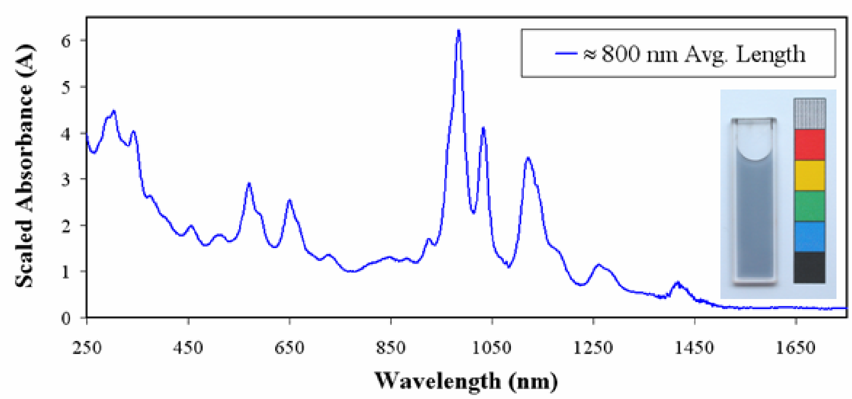


Figure: (TOP) Absorption of SEC sorted DNA-wrapped carbon nanotubes of several lengths. The size of the optical transitions are observed to increase linearly with length above a constant background. (Bottom) Absorption spectra of a dialyzed centrifugation sorted carbon nanotube solution containing SWCNTs ≈ 800 nm in length. The inset shows the lavender-gray color of the solution that is the result of the enhanced optical transitions.

Quantifiable Assessment of SWNT Dispersion in Polymer Composites.

Peter T. Lillehei, Cheol Park, Jae-Woo Kim, Luke J. Gibbons, Kristopher E. Wise, Emilie J. Siochi.

Optimal utilization of single walled nanotubes in structural-multifunctional platforms demands an understanding of the fundamental principles that govern their behavior at the nanoscale. It has been previously established that the single most critical aspect related to the functional performance of SWNT composites is the degree to which the nanotubes are dispersed. However, the lack of a quantitative assessment of the SWNT dispersion has hampered the understanding of the structural-functional relationship. This talk will describe the tools and the procedures that we have developed to quantitatively assess the SWNT dispersion in polymer composites. Using this data enables us to probe the nanoscale structure and then predict the bulk scale functional performance.

SESSION FIVE

APPLICATION SPECIFIC MATERIALS AND MEASUREMENT NEEDS

THURSDAY AM

Strategies for Improved Properties in Nanotube / Polymer Composites

Karen I. Winey

University of Pennsylvania
Philadelphia, PA 19104-6272

Polymer nanocomposites refer to multi-component materials in which the major constituent is a polymer or blend thereof, and the minor constituent has at least one dimension below ~ 100nm. Using this definition there have been commercially important polymer nanocomposites for decades. Nonetheless, there are new opportunities to extend the range of functionality and utility of existing polymers by introducing nanoscale fillers. These opportunities are particularly evident with carbon nanotubes that access a new size and aspect ratio regime. Specific strategies from our work on nanotube / polymer composites will be presented: the effect of nanotube alignment on electrical conductivity, the evidence for nucleation and templating of crystalline polymers on nanotubes, the benefit of grafting polymers onto nanotubes, and the importance of polymer molecular weight in transferring mechanical load. Our recent studies highlight the need to characterize polymer conformation in the nanotube / polymer composites, because extensional flow aligns both carbon nanotubes and polymers and this alignment dramatically influences the properties of the nanocomposites. Also, methods continue to be required to quantitatively characterize nanotube dispersion at multiple length scales, so as to be effective when the nanotubes are dispersed individually in a polymer matrix and when the nanotubes form micro-scale structures.

Characterization of SWNT Thin Film Electrodes of Precisely Tuned Metal/Semiconductor Ratios with Optical and THz Spectroscopies

J.L. Blackburn, M.C. Beard, T.M. Barnes, J vandeLagemaat, T.J. McDonald, T. Coutts, M.J. Heben

National Renewable Energy Laboratory, Golden, CO, 80401

Thin films of carbon single wall nanotubes (SWNT) have recently attracted attention as possible replacements for indium tin oxide electrodes in a variety of applications, including photovoltaics (PV) and light emitting diodes (LEDs). Advantages of the nanotube films include flexibility, enhanced infrared transparency, thermal stability, better wetting of organic layers, low cost, material availability, and the potential for fully printable device design. While several initial reports have demonstrated devices based on conductive thin SWNT films, much basic research remains to be done to understand important issues, such as the effects of dopants on the optical and electrical properties, the thermal stability of various dopants, and the effect of nanotube type (metal or semiconductor) on the optical and electrical properties.

The recent work of Arnold et al. has paved the way for simple separation of metals (m-SWNTs) and semiconductors (s-SWNTs), as well as separation by diameter. We have adapted this separation strategy, along with simple film deposition methods, to produce highly conductive transparent SWNT films with precisely tunable m- and s-SWNT contents. Such films allow for detailed studies into type-dependent properties critical to the application of SWNT thin films in opto-electrical devices. In this report, we explore the optical and electrical properties of conductive transparent SWNT films with preceisely tuned metal/semiconductor ratios. We demonstrate the use of optical and terahertz spectroscopy to determine optical constants, doping level, and conductivity, all of which are dramatically affected by SWNT type. Terahertz spectroscopy is a non-contact method that provides complimentary information to traditional contact electrical measurements.

Optical Modulation of Single Walled Carbon Nanotubes for Sensor Applications

Michael Strano
MIT

SESSION SIX

NANOTUBE STANDARDS

THURSDAY PM

International Efforts in Nanotube Standards

Clayton Teague

NNCO

A Needs-based Assessment of Nanomaterials and the United States Measurement System

Clare M. Allocca

Senior Scientific Advisor to the Director
National Institute of Standards and Technology
Gaithersburg, MD

The National Institute of Standards and Technology (NIST) is engaged in a needs-based assessment of the state of the United States Measurement System (USMS). The focus of the assessment was on measurement problems that pose technical barriers to technological innovation, a major source of the nation's industrial competitiveness and economic well-being. Report results will be reviewed, and implications for the world of nanomaterials will be explored. Identified measurement needs in the field of nanomaterials will be presented, as well as some potential resources for these measurements. Additionally, the NIST USMS addresses innovation-limiting measurement needs in three ways: by allowing potential providers of solutions to specific measurement problems to be engaged and mobilized; by bringing the attention of stakeholders to systemic issues in the functioning of the U.S. measurement system as a whole; and by serving as a catalyst for the identification of other needs and issues of the USMS. Finally, the future plans for the USMS will be discussed in the context of nanomaterials.

Summary of NNI Workshop on Standards for EHS Concerns

Dianne Poster
NIST

SESSION SEVEN

HEALTH APPLICATIONS AND CONCERNS: THE NEED FOR WELL-CHARACTERIZED MATERIALS

Friday AM

Pulmonary Toxicity of Single-Walled Carbon Nanotubes *in vivo:* Mechanisms and Consequences.

Anna A. Shvedova, Ph.D., D.Sc., FATS,
Pathology & Physiology Research Branch/NIOSH/CDC, & Department of Physiology and Pharmacology, WVU, Morgantown, WV

Occupational and/or environmental exposures to engineered nanomaterials may be associated with potential adverse health effects. While the toxicity of nanomaterials has not been fully characterized limited studies conducted to date indicate an urgent necessity for detailed toxicological assessments. Single-Walled Carbon Nanotubes (SWCNT) - new materials with particularly broad technological applications - have unique physico-chemical, electronic and mechanical properties. This may result in unusual interactions with cells and tissues, thus necessitating studies of SWCNT cytotoxicity and health effects. We found that SWCNT in doses relevant to potential occupational exposures may exert their toxic effects in the lung of exposed animals in vivo. We characterized an unusual and robust inflammatory and fibrogenic response and correlated it with the progression of oxidative stress. We also established that SWCNT exposure lead to impaired pulmonary function. Realistic exposures to SWCNT are likely to occur in conjunction with other pathogenic influences, e.g., microbial infections. We established that compromised bacterial clearance is characteristic of the lungs of SWCNT-exposed mice, the fact of significant biomedical and clinical importance. This talk will address key issues of respiratory toxicity of aspired *vs* inhaled SWCNT in relation to their ability to cause pulmonary injury and trigger pro-fibrotic mechanisms and pathways. We will discuss the issues of SWCNT toxicity with respect to current regulations of protection and their adequacy in occupational settings
Acknowledgements: supported by NIOSH OH008282, NORA 92700Y. **Disclaimer:** The findings and conclusions in this report are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

Key Words: occupational exposure, free radicals, lung fibrosis, neutrophils, transition metals.

Carbon Nanotubes in Medicine: Where We are and Where We Need to Be

Valerie Moore

University of Texas Health Science Center, Houston TX

Carbon nanotubes are infiltrating the medical community promising extraordinary advances in applications like tissue engineering, therapeutic agent delivery, biochemical sensors, and contrast agents. As these applications move forward the chemical research community must keep in mind the history and culture of the biomedical community. Biomedical researchers work with well-characterized, high-purity molecules. Carbon nanotubes are not to this point yet. Reading the nanotube literature, it is hard to draw conclusions about nanotube benefits or hazards. For each publication showing biocompatibility there is one demonstrating toxicity. The one theme throughout literature is a need for standards in characterization. This presentation will provide an overview of carbon nanotubes in biomedical research and highlight the areas where standards for characterization have the greatest potential impact.

SWNT Interactions with Biological Systems: Focus on Length

Matt Becker

NIST

SESSION EIGHT

MISCELLANEOUS CHARACTERIZATION

FRIDAY AM

Atomic-Level Characterization of Carbon Nanotubes

Kazu Suenaga

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Physical and chemical properties of carbon nanotubes can be drastically altered by its atomic defects and chirality. Imaging of the carbon networks has been recently made possible by pushing the HR-TEM to the extreme of its possibilities. In this presentation the atomic-level characterization of carbon nanotubes and their derivatives by means of the HR-TEM will be demonstrated. It includes (i) the stability and mobility for vacancy, interstitial and topological defects in carbon nanotube [1, 2, 3], (ii) the chirality and handedness assignment of individual carbon nanotubes [4, 5], and (iii) the embedded molecules within nanotubes such as single chains of carbon atoms [6, 7].

Partially supported by JST-CREST, ERATO and NEDO.

1. A. Hashimoto et al., *Nature* 430 (2004) 870
2. K. Urita et al., *Phys. Rev. Lett*., 94 (2005) 155502
3. K. Suenaga et al., *Nature Nanotech*. 2 (2007) 358
4. Z. Liu et al., *Phys. Rev. Lett*., 95 (2005) 187406
5. M. Koshino et al., *Science*, 316 (2007) 853
6. Z. Liu et al., *Nature Nanotech*. 2 (2007) 422

POSTER SESSION

WEDNESDAY EVENING
NIST

P 01

Functionalization of Single-Walled Carbon Nanotubes at Room Temperature. Identification and Quantification of the Functional Groups

Yadienka Martínez-Rubí,[1] Jingwen Guan,[1] Shuqiong Lin,[1] Christine Scriver,[2] Ralph E. Sturgeon[2] and Benoit Simard*[2]

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In the addition of radical to SWNTs by the thermal decomposition of peroxides the reaction times can vary between hours and days as has been previously reported. We have developed a rapid and efficient procedure to functionalize SWNT where free radicals generated at room temperature by a redox reaction between reduced SWNTs and diacyl peroxide derivatives were covalently attached to the SWNT wall. We performed the reaction in the presence of sodium naphthalene, a radical-anion salt that can reduce the SWNTs. In this way the negatively charged SWNTs are exfoliated prior the reaction with the peroxides and at the same time the decomposition of the acyl peroxides, bearing different functionalities, is catalyzed. The reaction takes place at room temperature and is completed in a few minutes. The redox reaction can be repeated to adjust the degree of functionalization. Using this procedure we were able to anchor acid and amine functionalities to the wall of SWNTs. This repetitive process also affords the possibility of anchoring functional groups of different types; one type per cycle, to produce multifunctional SWNT. The functionalized derivatives were characterized by Raman, XPS and FTIR. Additional evidence of covalent amine-functionalize SWNT was obtained by MALDI-TOF. The total percentage of carboxylic acid groups in acid-functionalized SWNT was determined by analyzing the Na content in the SWNT-COO^-Na^+ salt using ICP-AES.

P 02

Size Separation of Single Wall Carbon Nanotubes by Flow-Field Flow Fractionation

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Flow-field flow fractionation (Fl-FFF) is used to separate single wall carbon nanotubes (SWNTs) dispersed in aqueous medium by the use of DNA. On-line measurements are made of SWNT concentration, molar mass, and size using UV-Vis absorption detection and multi-angle light scattering (MALS). Separations are made for unfractionated SWNTs as well as SWNT fractions made previously through size exclusion chromatography (SEC). The SEC fractions are well resolved by Fl-FFF. SWNT hydrodynamic volume from calibrations with polymer latex particles in Fl-FFF are compared to calibrations of hydrodynamic volume from the SEC fractions derived from dissolved polymers. Rod lengths of SWNTs are calculated from on-line measurements of MALS and are compared to rod lengths from hydrodynamic models from latex sphere calibrations. Experiments on samples with different fracturing time for SWNTs through extended sonication suggest that Fl-FFF is an efficient tool to characterize SWNTs.

P 03

Impedance Measurement of Single Wall Metallic Carbon Nanotubes

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Carbon nanotubes are being considered for the next generation of electronic devices that can be scaled down to nano-dimensions. The electrical transport properties of carbon nanotubes are especially attractive since they are not affected by surface scattering or surface roughness when the feature size of the interconnects shrinks [1]. We describe impedance measurements of individual single wall metallic carbon nanotubes (CNTs) in the frequency range of 40 Hz to 100 MHz. Model calculations for carbon nanotubes [2] predict that a drop in impedance should occur due to damping of the plasmon wave at a crossover frequency $f_c = 1/\pi R_{DC} C_{QE}$, where R_{DC} is the resistance and C_{QE} are the combined quantum and electrostatic capacitance of the tube. In our earlier work, we showed that the broad-band impedance measurement can be used to separate resistance from the capacitance of individual CNTs assembled as a conducting channel of a 3-terminal field-effect-transistor (FET) structure [3].

Our present work is aimed at further elucidating the effect of contact barriers on the crossover frequency and the measurement of capacitance of CNTs. We utilized a resistance - capacitance (RC) lumped element circuit model to extract the capacitance of the tube and the corresponding contact resistance. The resistance values are approximately symmetric in respect to $\pm$ DC bias, indicating symmetric contacts that can be attributed to forward-biased Schottky barriers at each contact. After deposition of platinum at the nanotube-electrode interface, the measured resistive component of the impedance decreases significantly, from 1.2 MΩ to about 230 kΩ, while f_c shifts to higher frequencies. The theoretical R_{DC} value of a perfect non-interacting CNT is about 12.5 kΩ. In the case of a high-damping limit, R_{DC} may approach about 100 kΩ [2, 4, 5], which compares favorably with our results. The extracted CNT capacitance, C_{CNT}, of about 4×10^{-14} F/μm, is independent of the total resistance. However, the C_{CNT} values are larger than theoretically predicted quantum capacitance of a perfect tube. We observed a sharp conductor-insulator transition at a crossover frequency, f_c, above which the circuit response becomes capacitive. Our results agree qualitatively with the theoretical impedance characteristic of a perfect metallic CNT and furthermore, they imply that the crossover frequency due to quantum capacitance would fall in the range of about 100 GHz.

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P 04

Large-Scale Combustion Synthesis of Single-Walled Carbon Nanotubes and their Characterization

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In recent years, well-controlled premixed combustion has been established as a major industrial process for the manufacturing of nanostructured carbonaceous materials including spheroidal fullerenes such as C_{60}, C_{70} and C_{84}. Addition of catalyst and operation at non-sooting conditions allows for the selective synthesis of single-walled carbon nanotubes (SWCNT). The use of iron pentacarbonyl and alternative catalyst precursors will be described. A standard procedure for materials characterization and quality control using Raman spectroscopy, thermogravimetric analysis (TGA) and scanning transmission electron microscopy (SEM) has been developed. Additional insight has been gained by means of transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), atomic force microscopy (AFM) and UV-Vis-NIR absorption spectroscopy. Correlations between process conditions and properties such as length have been established. Time-resolved sampling in the flame with subsequent characterization has shed light on the SWCNT formation mechanism. Selective synthesis of SWCNT in a semi-industrial reactor used routinely for fullerene manufacture has been demonstrated recently. Challenges of SWCNT purification and dispersion will be discussed.

P 05

Multimodal Nanoscale Imaging to Interrelate Physical, Chemical and Optical Properties of Hybrid Complexes of Single Walled Carbon Nanotubes and Semiconductor Quantum Dots

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The need for technologies enabling hybrid nano-device assemblies using assorted nano-material building blocks has been paramount for the last decade in a variety of fields such as optoelectronics, nanooptics, advanced telecommunication engineering, and nanomedicine. Such nanoscale building blocks include metal nanoparticles such as gold or silver nanospheres, rods and shells, carbon nanotubes (CNTs), semiconductor nanocrystals or quantum dots (QDs), and organic linker molecules such as DNA and antibody-antigen pairs. The ultimate purpose of engineering these hybrid devices is to achieve desired functions through the assembly of nanoscale building blocks. Their functions are usually dependent upon the nanoscale details of their assembly structures, which can be characterized by optical measurement techniques capable of enhanced spatial resolution beyond the diffraction limit. On the other hand, an integrated approach employing diffraction-limited spectroscopic imaging techniques and time-resolved measurements provide rich information on the interactions among the different building blocks. Although the spatial resolutions of these imaging techniques are diffraction-limited, the synergistic employment of the techniques allows assessment of nanoscale structural information. Here, we demonstrate the capability of integrated diffraction-limited imaging techniques to reveal nanoscale details in hybrid assemblies of fluorescent colloidal QDs and single walled carbon nanotubes (SWCNTs). Hybrid QD-SWCNT complexes were self-assembled by DNA hybridization, where the surface of QDs and CNTs were functionalized with complimentary sequences of DNA. Integrated multimodal imaging techniques including confocal fluorescence spectroscopic and lifetime microscopy, polarization dependent confocal Raman microscopy, and atomic force microscopy of the hybrid complexes reveal rich nanoscale information on the distribution of each element and the assembly structure. The nanoscale proximity between QDs and CNTs in the complex results in significant reduction of the fluorescence lifetime of QDs bound to SWCNTs.

P 06

Processing of High-Purity Single-Walled Carbon Nanotubes as Standard Reference Materials and Conductive Thin Films

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Single-walled carbon nanotubes (SWNTs) with very high purity are necessary to reveal their intrinsic properties and assess their functionality for the development of new applications. Moreover, methods to evaluate the purity of SWNTs and the development of solid-phase SWNT standard reference materials are essential to both fundamental and applied research. Here we report a scalable purification technique for SWNTs synthesized by high-power laser vaporization, the development of solid-phase SWNT standard materials, and the production of transparent conductive SWNT thin films. The purified SWNTs contain metal residue less than 1% and carbonaceous purity among the highest ever reported. The purity of purified SWNTs was evaluated by using SEM, TEM, TGA, and solution phase NIR spectroscopy techniques. SWNTs were synthesized by high-power (600 W) laser ablation facility of carbon targets with Ni and Co as catalysts at 20 gram/run quantities. The purification was carried out at 10 gram/batch quantities and involved nitric acid refluxing, controlled-pH water-extraction, and hydrogen peroxide treatment. Standard SWNT reference materials are produced both by depositing purified SWNTs on TEM grids and as transparent thin films on optically transparent substrates. The TEM grids are essential for relative purity comparisons, while transparent thin films of purified SWNTs are useful for optical spectroscopic analysis and sheet resistance assays. SWNT thin films were produced by dispersion/filtration/transferring methods. Typical sheet resistances of SWNT films are lower than 100 ohm/sq with transmittance of 65%, which is comparable to the best reported SWNT thin films.

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P 07

Purity of Carbon Nanotubes: Separating the Nanotube from the Dispersant in Thermal Decomposition Profiles

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The study evaluated the drop-casting method as a means of depositing carbon nanotube dispersions onto quartz crystal microbalances (QCMs) to determine thermal properties of carbon nanotubes (CNTs). A QCM is an extremely sensitive mass sensor, capable of measuring mass changes in the nanogram range. By examining the properties of specimens at this finer scale, additional evidence can be gained on the extent of homogeneity within the larger bulk sample. Drop-casting involves pipetting a small amount of the dispersion onto the surface of the crystal; the current deposition method employs an airbrush to spray a chloroform-CNT dispersion. Compared to spraycoating, drop-casting is superior in terms of speed, ease of use, and amount of material required. Interactions between some widely used CNT-dispersants (chloroform, toluene, dimethylformamide) and pipette tips suggest that an aqueous dispersion is more appropriate. Triton X-114 is an effective dispersant, but unlike organic solvents that vaporize leaving little residual chemical, Triton X significantly alters the thermochemical response of the sample. To isolate the interference due to the surfactant, experiments were conducted to determine the surfactant's thermal profile over the desired heating range. Relating the thermal decomposition of the separate components of the dispersion, an equation eliminating the effect of the Triton X was generated by analyzing the CNT-Triton X heating curve. By providing both an easy to use dispersant and a calibration curve for thermal response, manufacturers and end-users of carbon nanotubes can more easily examine the purity of their materials without concern for exact concentrations during sample preparation.

P 08

Quality Control of Bulk Single Wall Carbon Nanotube Materials

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We report on our experience using a preliminary protocol for quality control of bulk single wall carbon nanotube materials produced by the electric arc-discharge, laser ablation and CVD method. The first step in the characterization of nanotube material is mechanical homogenization. Quantitative evaluation of purity has been performed using the procedure based on solution phase near-infrared spectroscopy (NIR) [1]. Our results confirm the need of pure standard SWNT samples which can be applied in the purity evaluation process by NIR. Especially, for different production methods new reference samples are required.

Single walled carbon nanotubes due to their high-aspect ratio and high electrical conductivity are recognized as the best electrical additives in several composites. However, the electrical conductivity strongly depends on the content of nanotubes and the carbonaceous impurities. Therefore the determination of electrical conductivity in bulk material is an important issue in the characterization of SWNT. We propose a device to characterize the electrical properties of SWNT by measuring the electrical conductivity of SWNT sheets made of SDS suspension and of powder of as prepared material. Presenting results compare electrical conductivity of several CNT materials supplied by different producers with other carbon materials.

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P 09

Quantitative Spectral Simulation and Analysis of Excitation-Emission Matrices for Semiconducting SWNTs

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Current models of the semiconducting bandgap properties of single walled carbon nanotubes (SWNT) can be used to make quantitative structural identification of individual species based on their light-energy absorption and photoluminescence emission profiles. One of the most convenient ways to gather the needed spectral information is to generate an excitation-emission matrix (EEM) wherein the spectrum of the exciting light is scanned over a chosen region of interest simultaneously with given intervals comprising the emission spectral region of interest. EEMs need to be corrected for both excitation inhomogeneities as well as for the radiant sensitivity of the instrument components, primarily the emission detector. Quantitative spectral analysis involves calibrating the instrument with NIST traceable correction factors for the excitation source and emission sensitivity. This study reports on the most recent updates to our established method for interpreting EEMs based on analytical lineshape simulations using our patented double-convolution algorithm. The upgraded method allows one to choose and or define the analytical lineshape(s) to deconvolute instrumental responses from the natural lineshape of the spectral emission. The lineshape function parameters can be fully constrained, globally linked, fixed as well as pre-defined using distinct initial guess scenarios. The model fitting parameters can be compared to calibrated spectral libraries of SWNT physical properties. Physical parameters of interest can include the n, m parameters, the diameters, excitonic sidebands, line-widths (as indicators or bundling) and the relative amplitudes as indicators of 1) energy transfer processes among individual SWNTs in bundles as well as 2) reabsorption properties of the sample. The revised user interface was designed to serve as the preferred method for interpreting EEMs in the standardized protocols currently being proposed to the ASTM and ISO international standard bodies.

P 10

Resonance Raman Spectroscopy of Aligned and Length-Separated Single Wall Carbon Nanotubes

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Many potential advanced-technology applications of single wall carbon nanotubes (SWCNTs) require homogeneity of physical properties not found currently in bulk SWNT samples. This work demonstrates mechanical alignment and length separation characterized via vibrational spectroscopy. We measure resonance Raman scattering (RRS) using continuously tunable laser excitation, from NIR thru UV, coupled to a triple grating spectrometer. This experimental setup permits observation of resonant low-frequency modes, such as the nanotube radial breathing mode (RBM), through higher frequency graphite modes. Our samples include HiPco, CoMoCat, and arc-discharge SWCNTs wrapped with single-stranded DNA or other molecules to achieve dispersion in aqueous solutions. They exhibit an exceptionally low degree of SWCNT bundling and clustering, in the limit of nanodispersion, as determined by small-angle neutron scattering.

Aligned samples are produced by casting dispersed SWCNT solutions in polyacrylic acid (PAA) which are then mechanically stretched into optically-transparent polymer composite films. Polarized RRS (VV orientation) reveals significant nematic alignment of SWCNTs in these stretched films. Extraction of the nematic order parameter, together with absorption and ellipsometry measurements, provides a measure of the intrinsic complex dielectric permittivity. A comparison of the measured dielectric to simple models illustrates the importance of including excitonic effects in SWCNT optical properties.

Size-exclusion chromatography collects length fractions ranging in size from less than 100 nm to approximately 600 nm. Multi-angle and dynamic light scattering, atomic force microscopy, and transmission electron microscopy characterize the length distribution of the fractions. All observed vibrational modes, including the RBMs, D-band, G-band, M-band, iTOLA, and D*, exhibit a monotonic increase of Raman scattering intensity with increasing nanotube length. We discuss these results in terms of optical scattering models and the resonant behaviour of the vibrational modes. The increased Raman scattering intensity from longer length-separated fractions affords investigation of SWCNT features not typically observed.

P 11

Simulation of Nanoscale Spheres and Rods in Field-Flow Fractionation (FFF)

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For nanotubes to achieve their full potential in applications, it is desirable to be able to separate them according to their various physical properties. One possible technique for achieving this is field-flow fractionation (FFF). Classical flow-FFF is a separation technique in which a perpendicular cross flow is imposed upon a channel flow of dilute particulates[1]. The cross flow exits through a porous accumulation wall which is impermeable to the particulates. Competition between various flow mechanisms drives particles of unlike size to different average positions in the cross flow direction. Separation is achieved due to the different residence times of the particles based upon their position in the parabolic velocity profile in the throughput direction. FFF can also be combined with other techniques such as dielectrophoresis to produce separations based on electronic, as well as size based properties.

A number of different mechanisms can be exploited to achieve separation in flow-FFF. Normal mode separation applies to particles which are small enough to undergo significant Brownian motion, and whose size is small compared to the cross flow gap size. In this case, smaller particles, which are more diffusive, have an average position closer to the centerline and elute faster than larger particles. Steric mode separation occurs when the particle layer in FFF is strongly compressed along the accumulation wall. In this case, larger particles are more highly entrained by the throughput flow and elute more quickly than smaller ones. This turnaround is called the steric inversion. The steric transition is the intermediate range in which normal mode FFF begins to change over to steric FFF due to increasing particle diameter.

In this work, a Brownian dynamics simulation for modeling the separation of both spheres and rodlike particles in FFF is developed. For spheres, the particle motions are governed by a Langevin equation which takes into account the drag force due to fluid flow and the Brownian force [2,3]. The rods are modeling as prolate spheroids and the particle motions are governed by a similar Langevin equation with orientation dependent drag and diffusion coefficients, and the Jeffrey equation with rotational diffusion. Modeling and experimentation of particle separation for spheres under conditions spanning the normal to steric transition was examined. Elution fractograms as a function of particle size, and throughput and cross flow flowrates are shown and compared with experimental data and theory. Both the simulation results and experimental data for mean elution time are in good agreement with the steric inversion theory of Giddings [4]. The steric transition occurs when the particle diameter is in the range of 300 to 600 nm (for the given experimental conditions). For rods, the simulation shows that nanotube scale particles elute by a normal mode mechanism up to aspect ratios of about 500, based on a particle diameter of 1 nm. At larger sizes, the rods begin to deviate from normal mode theory, but in the opposite sense as for spheres. While the steric effect for spheres causes larger spheres to elute faster than predicted by normal mode theory, an inverse steric effect occurs for rods in which larger rods move increasing slower than that predicted by the theory. This is due to alignment of the rods in low velocity region along the accumulation wall. Spheres and rods of equivalent diffusivity elute at the same rate up to sphere:rod sizes of approximately 90 nm:500 nm (based on 1 nm diameter). After this point, the negative deviations for the spheres and the positive deviations for the rods lead to increasingly greater differences in mean elution times.

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P 12

Single Walled Carbon Nanotubes for Space Flight Applications

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Single walled carbon nanotubes (SWCNTs) are currently being investigated for use in a variety of spaceflight applications. Unique properties of SWCNT such as high surface area, exceptional mechanical strength, high thermal conductivity and interesting electrical properties make them attractive materials for state of the art technologies. This presentation focuses on the use of SWCNTs in advanced life support technologies, advanced repair systems, multifunctional composites, ionizing radiation monitors and shields, as well as type specific SWCNT production. Details of advanced characterization needs associated with such technologies are also discussed.

P 13

Effect of Aggregate Structure and Length of Carbon Nanotubes on the Rheological Properties of Nanotube/Epoxy Suspension

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The addition of carbon nanotubes to polymer matrices has yielded significant improvement in thermal and electrical properties. The state of dispersion of carbon nanotubes significantly influences the electrical and rheological properties of polymer/nanotube composites. It is critical to understand the effect of shear flow on the state of dispersion of nanotubes, which in turn determines the electrical properties of the dispersion. Current work describes rheological measurements and associated optical microstructure observations of multiwall carbon nanotubes (MWCNTs) suspended in an epoxy resin matrix. Above a critical concentration of nanotubes, we observe a progressive increase in the zero shear viscosity with increasing nanotube concentration, which we correlate with an increase in nanotube aggregate interaction. With increasing shear rate, shear thinning behavior was observed due to the yielding and ultimate de-aggregation of a nanotube network. We also studied the effect of nanotube length on the scaling behavior of the viscosity and elastic shear modulus of the epoxy nanotube suspension.

P 14

The Characterization of Solutions of Single Wall Carbon Nanotube Complexes

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The application of single wall carbon nanotubes (SWCNT) in current and future applications crucially depends on the ability to process SWCNT in a solvent to yield high quality dispersions characterized by individual SWCNTs and with a minimum of SWCNT bundles. Many different approaches for solubilizing SWCNT have been reported, but there is no general comparison of the relative quality and efficiency of these methods. We report here on a quantitative comparison of the relative ability of oligonucleotides, peptides, lignin, chitosan, cellulose, ionic liquids and organo-sulfate surfactants to solubilize SWCNT in water. Optical absorption and fluorescence spectroscopy provide quantitative characterization of these suspensions. Oligonucleotides (GT_{30}, GT_{20}, AC_{30}, AC_{20}, $C_{10\text{-}30}$ and carboxy methylcellulose (CMC-250K) exhibited among the best overall quality suspensions of the various complexation agents studied in this work. The information presented here provides a good base for further study of SWNT purification and applications.

P 15

The Reduction of Bundling in Single-Walled Carbon Nanotubes via Density Gradient Separation

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We use an isopycnic density gradient separation method[1] to examine the reduction of bundling in single-walled carbon nanotubes (SWNT) through absorption and photoluminescence measurements. The samples consisted of aliquots taken at different positions in the centrifugal force gradient. Our work shows that the leading edge of the continuum absorption is sharpened as the fractions become less dense. We believe that this may be due to a reduction of the bundling peak in the ultraviolet frequency regime. The inherent optical absorption baseline was also reduced, as seen by a systematic decrease in the baseline curvature as the fractions became less dense. Relative photoluminescence increased for the least dense aliquots when compared to the starting decant. This is a strong indication that the density gradient separation method is enriching the percentage of individual tubes in those fractions[2]. In addition, we have performed experiments demonstrating that isopycnic separation can also be performed in non-iodixanol based mediums as long as the densities are comparable.

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