Nanometrology Links State-of-the-Art Academic Research and Ultimate Industry Needs for Technological Innovation

Ado Jorio and Mildred S. Dresselhaus

Carbon Nanotubes as Prototypes for Nanometrology

The rapid development of nanoscience and the growing interest in applying nanomaterials to societal needs is now creating an interesting challenge and opportunity for both the research community and industry. While the scientific community is pointing out the potential of nanomaterials for new technologies, the industrial community has not yet organized itself on how to best achieve the potential benefits which nanoscience and nanotechnology promise. This situation urges that increasing attention be given to the development of nanometrology science. Scientific and industrial metrology are expected to provide quantitative tools to foster technological growth and innovation by providing calibrated measurement procedures and standard reference materials to promote nanobased products with reliable performance. However, the fundamental aspects for the development of protocols and standards in nanomaterials, that is, for building the basis for nanometrology, are still largely undefined. This multidisciplinary field is not only drawing from the basic sciences across many disciplinary fields such as chemistry, physics, materials science, biology, and engineering, but it is also offering an opportunity for linking state-of-the-art academic research and ultimate industrial needs for technological innovation.

Since 2005, carbon nanotubes have evolved into the most intensively studied materials in the nanoworld.[1] Now, it seems clear that the carbon nanotube field is on the verge of approaching a "phase transition critical point," which means the field is now mature enough to make a phase transition from nanoscience to nanotechnology. Much activity is already occurring or starting in industrial research laboratories, including start-up companies, large established corporations, and everything in between. Still, neither do large-scale industrial suppliers nor customers at any level clearly understand how to define the nanotube-based products they are selling or buying.

For the past few years, the international ISO Standards Committee has been meeting annually, addressing nanometrology issues and needs. The increasing international involvement in nanometrology can be noted by an increase in the number of countries in attendance at the ISO standards meeting and in the increased national level of effort in nanometrology within many of the participating countries. Recently (2007), the ISO Standards Committee has given particular emphasis to nanotubes as a prototype material for establishing nanometrology standards. The emphasis on nanotube metrology as an early strategy for developing standard reference materials is a current challenge, thus signaling the need for the nanotube research community to become more engaged in working jointly with metrology experts in advancing nanometrology science.

Furthermore, international conferences are now starting to establish a connection between metrology and academic nanoscience research, focusing on nanotube metrology. Organized by the international nanotube scientific community, the MSIN07 conference[2] was held at Inmetro, the Brazilian National Institute of Metrology, in Rio de Janeiro on June 22, 2007. This meeting was organized as a satellite of the annual International Nanotube Scientific Conference NT07 that brought together, in Ouro Preto, Brazil, more than 400 scientists working in the nanotube field. Organized by the metrology community, the 3rd NASA-NIST Workshop on Nanotube Measurements[3] was held in the United States at the National Institute of Standards and Technology, Gaithersburg, Md., on September 26–28, 2007. Both the MSIN07 Conference and the 3rd NASA-NIST Workshop on Nanotube Measurements were efforts to bring the nanoscience research community together with metrology experts to advance the development of the nanometrology science field.

The distinction between metrology in general and metrology on the nanoscale is widely recognized by the research community[4] and stems from the different properties of materials on the nanoscale as compared to their bulk counterparts. For example, the density of electronic states at the nanoscale, which governs essentially all of the electronic and optical properties of nanomaterials, is very different for three-dimensional (bulk), two-dimensional (quantum wells), one-dimensional (quantum wires), and zero-dimensional (quantum dots) levels. Furthermore, nanomaterials have a large surface/volume area, which, for example, promotes catalytic activity. In this context, a 2 nm gold nanoparticle has high chemical reactivity as a catalyst, in contrast to gold in bulk form which is quite inert chemically. Since the properties of nanomaterials are strongly size-dependent and are largely still in the discovery stage, the development of the science of nanometrology is especially challenging. Furthermore, since both the measurement process and the environment of a nanomaterial often perturb the properties of the nanosystem, establishing robust measurement protocols is also very challenging (see Figures 1–2).

In the following, we try to put nanotube metrology in context. We adopt the framework of a recent review of nanotube appli-

Material Matters is a forum for expressing personal points of view on issues of interest to the materials community.

cations[1] which considers both large-scale and niche nanotube applications in three categories: applications which (1) have already been commercialized, (2) show promise for commercialization within the coming decade, or (3) show promise for commercialization on a longer time scale. Considering nanometrology within this framework is thought to be helpful in developing a strategy for implementing nanometrology research and development (R&D) programs to both support existing industrial needs and promote the development of nanotechnology-related companies in the future.

Addressing Present Needs

There is already a thriving and growing nanotube industry, utilizing the unique properties of carbon nanotubes, including both large-scale and niche applications.[1] Examples of large-scale applications include nanotube composites for sporting goods (exploiting the high strength and stiffness of nanotubes), structural composites for use in residential and commercial building construction, in aircraft and space vehicle construction, as well as for automotive and other industrial applications. Nanotube composites tend to exploit both the superior strength-to-weight properties of nanotubes and their electrical conductivity for electrical shielding and device applications. Nanotubes are used in lithium ion batteries to exploit nanotube resiliency in order to increase the dimensional stability of electrode structures during battery charging and discharging cycles, thereby enhancing battery performance and increasing battery lifetime.

In addition to the large-scale applications, niche applications are now also being commercialized in several areas, including medical devices (such as catheters) and measurement tools (such as scanning probe tips). The scanning probe tips represent an example of an important new opportunity for nanometrology in providing a new category of tools for enhancing measurement capabilities at the nanoscale. The commercial catheter application is an example of a vast new opportunity area for nanotubes in biomedical niche applications. Nanotubes could operate as sensors within cells, or could be used for neuroscience probes, or for implanted nanobiomedical measurement systems for medical monitoring or interventions. Therefore, development of the new nanometrology field is providing tools for fundamental measurements, nanomaterials for calibration of properties measurements, and nanomaterials and tools for nanobio probes.

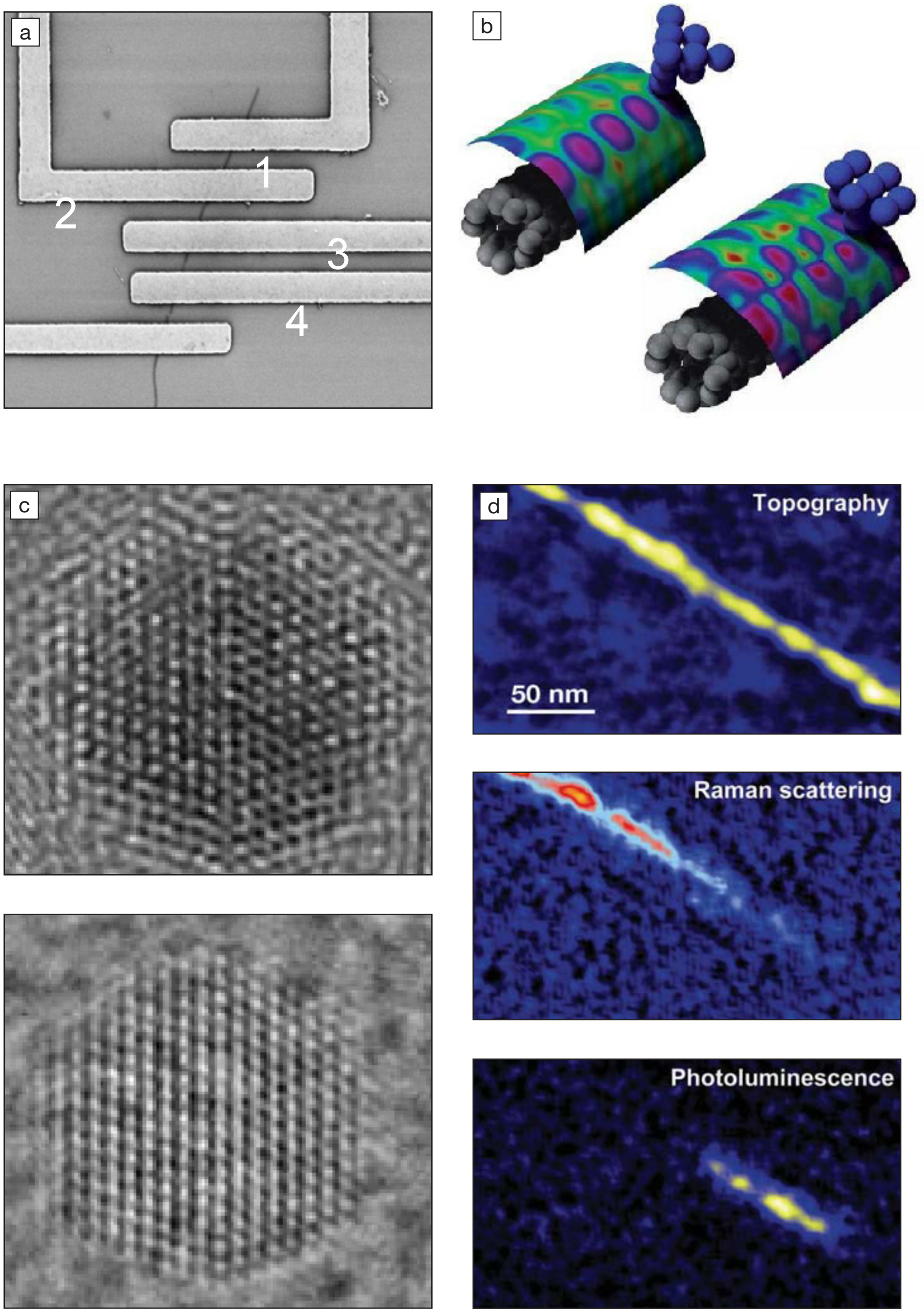

Figure 1. Nanometrology Challenge 1 addresses how to extract information from a material that is extremely small and delicate, and will be perturbed by the probes used for the measurements. (a) For resistance measurements of materials, the four-contact geometry is used to avoid the interference of the resistance from the measurement system. However, in the case of nanotubes, the four-contact geometry does influence the system since the contacts themselves change the nanotube conductivity.[8] (b) Scanning tunneling spectroscopy can map the density of electronic states on the surface of a nanomaterial, as shown in the color code surfaces drawn on top of the tubes. However, the response depends on the atomic structure of the tip, as seen by comparing the two images.[9] (c) Comparison between two atomic resolution transmission electron micrographs without (upper panel) and with (lower panel) electron lens aberration correction. This correction provides true imaging at the atomic levels.[10] (d) Topography (top), near-field Raman (middle), and near-field photoluminescence (bottom) images from a single-walled carbon nanotube. The spatial resolution of tens of nanometers shows optical processes that are localized and different in two adjoining tube segments. The results may be explained by the junction of two different (*n*,*m*) tubes resulting in different optical responses.[11]

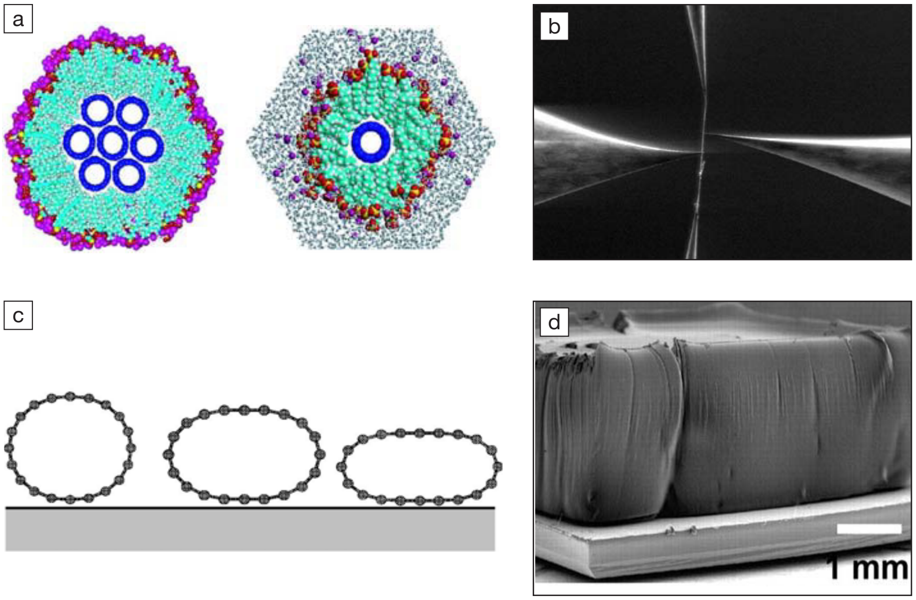

Figure 2. Nanometrology Challenge 2 addresses how to extract information from a material that is extremely small and delicate, and will be perturbed by its environment. (a) Sonicating single-walled carbon nanotubes (SWNTs) in sodium dodecyl sulfate-aqueous solution was shown to disperse SWNT bundles (left) into isolated single-walled carbon nanotubes (right).[12] This dispersion procedure has been largely used by the research community to do experiments on unbundled individual tubes. (b) It is possible to make transport measurements through a carbon nanotube avoiding tube-substrate contact (see Web site http://www.zyvex.com/Products/ PPS1_001a.html). Different experiments on freely suspended carbon nanotubes have been made with tubes suspended by a tip or crossing trenches between two substrate posts. However, one cannot avoid the contact made by the nanotube with the tip or whatever is used to suspend the nanotube. (c) A SWNT sitting on a substrate can flatten because of tube-substrate interaction. The flattening will depend on substrate type and tube properties, such as its diameter. Flattening can change the electronic structure, causing, for example, a semiconducting-to-metal transition.[13] (d) Ultra-long SWNTs grown vertically aligned from a Si/SiO_2 substrate by the water-assisted chemical vapor deposition method. Here the individual tubes are enclosed in a forest of nanotubes and may thereby be shielded from the external environment.[14] Surprisingly, this structure is highly hygroscopic.

With 2.5×10^5 kg/yr of multiwalled carbon nanotubes (MWNTs) and 6.4×10^3 kg/yr of single-walled carbon nanotubes (SWNTs) now being produced worldwide in a rapidly growing industry, there is a need for developing metrological standards for both MWNTs and SWNTs as materials, and standards for measuring their performance-enhancement properties.

Graphite and graphite-based products have an estimated market of $13 billion, and carbon nanotubes offer superior properties for some of the current products of the graphite-based industry. The metrology programs at NIST and the National Aeronautics and Space Administration (NASA) have thus far focused mainly on present needs for metrology. A major issue that is strongly pursued by the U.S. nanotube metrology program is the evaluation of the purity and the uniformity of the nanotube dispersion of typical nanotube materials purchased from suppliers. In this context, typical commercial nanotube samples have been measured from a metrological standpoint by a variety of techniques and at various size scales. At the macroscopic scale, thermogravimetric analysis (TGA), ultraviolet visible near-infrared (NIR) absorption, and NIR fluorescence measurements were investigated comparatively. For microscopic characterization, scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDAX), and Raman spectroscopy were used, and finally at the nanoscopic scale, transmission electron microscopy (TEM) characterization was employed. Statistical comparisons were made between TGA analysis working at the milligram scale and quartz crystal micro-balance studies working at the microgram scale regarding SWNT content relative to that of other carbonaceous materials, addressing inhomogeneity at the milligram scale. Multistep manipulation processes seem likely to introduce sample inhomogeneity. Raman characterization based on the D-band/G-band intensity ratio showed a large scatter from one region to another in samples purified by a "standard procedure" and demonstrated that the present purification process which is used commercially for the removal of amorphous carbon and catalytic particles also modifies the SWNT properties themselves. Near-IR absorption measurements demonstrated that the percentage of nanotube to other carbon material in typical commercial samples tended to be significantly overestimated by producers (perhaps by a factor of 2). To promote utilization of the on-going standards work at an early stage and as it continues to evolve, a Recommended Practice Guide has been made available on a NIST Web site.[5] The metrology work done so far shows the need for significant improvement in the purification of commercial nanotubes and in the uniform dispersion of nanotubes throughout commercial samples.

Therefore, despite the progress that has been made thus far, research is needed to establish a simple and reliable protocol (or measurement standards) for the specification of the nanotube content, purity, and dispersion characterization within a given sample that is offered for sale. A variety of different characterization techniques giving complementary information is now being applied to develop characterization protocols for making characterization measurements on actual samples and for controlling industrial processes involving nanotubes. Most of the work that has been done by the academic community addresses nanotubes with diameters in the range of 0.7–1.5 nm, with a clear lack of protocols on how to address larger diameter SWNTs and MWNTs which is where many of the industrial products are now focused. At the same time, researchers have to consider that the present needs of industry also require standards for *property* measurements, not usually addressed by the academic research community, such as nanotube resiliency for battery applications, strength/weight ratio measurements for sporting goods applications, metallicity or conductivity enhancement for electrical shielding for building materials, and related applications. In the case of nanomaterials, reliable measurement protocols need to be established by nanometrology experts to assist industry with developing reliable specifications of their nanobased products.

Nanometrology for Near- and Long-Term Applications

The research community has identified a number of near-term application areas for carbon nanotubes with both large-scale and niche applications. Nanometrology science needs to develop along certain directions that can be identified now, addressing nanotube structure, properties, and environmental effects. The structure of a perfect SWNT is defined by its diameter (d_t) and chiral angle (θ), or equivalently by the nanotube (n,m) indices,[1] but environmental effects and defects can play a very important role in the properties of nanotubes used in device applications based on nanotubes.

TEM and scanning probe microscopy (SPM) are well recognized as important tools for nanometrology. The ability to image the nanomaterial by TEM is very important and has a large impact on understanding nanotube properties. Not only does SPM provide a complementary tool to TEM for structural characterization, but SPM can also be used to characterize both electrons and phonons. The large emphasis on electron microscopy in the nanotube field can be related to two factors. The first is the historical importance of TEM as a fruitful structural characterization tool for nanotubes. The second is the major advance that has occurred in the very recent past in greatly increasing the resolution of TEM instruments by the introduction of aberration-corrected optics in the latest TEM instruments. Present instruments can deliver atomic resolution images with enhanced contrast and image stability without compromising resolution by using low acceleration voltages (e.g., 80 keV), which is required for TEM measurements on carbon materials without inflicting radiation damage to the samples. It is now possible to image SWNT handedness, heptagon-pentagon defects, dynamic dislocations, and linear chains of carbon atoms growing inside the cores of SWNTs. A calibration-free method based on electron diffraction for determining the (n,m) structure for individual SWNTs is now available,[1] which includes measurement of the tilt angle between the nanotube axis and the electron beam when indexing the electron diffraction pattern for rapid and robust (n,m) determination. While the achievements of electron microscopy are impressive and keep evolving, interestingly there is no protocol for calibrating length measurements in a TEM instrument over the full range of sample lengths from atomic lengths to the largest sample sizes seen in current TEM instruments.

A major concern for nanomaterials characterization is the effect on the measurements of the probes, either electron probes, scanning tips, or electrical contacts for transport measurements (see Figure 1). Nanotransport can, in principle, distinguish metallic from semiconducting SWNTs in a current versus voltage (I–V) plot. It is, however, difficult to make an ohmic contact to a nanotube, since most contacts have a Schottky barrier that must be overcome in order for current to flow. Furthermore, experiments show that if four contacts are applied along the length of a nanotube, the resistance $R_{12} + R_{23} + R_{34}$ is not equal to R_{14}, because nanoscale transport measurements of this type themselves are perturbed by the leads or contacts. Moreover, transport measurements on MWNTs present an additional challenge in making good electrical contacts to all the walls of the MWNT. Thus nanotransport measurements offer serious metrological challenges in developing reliable and reproducible measurement procedures.

> *…nanotransport measurements offer serious metrological challenges in developing reliable and reproducible measurement procedures.*

Optics offers as a very important set of tools for nanomaterials characterization since light provides a chargeless and massless probe. Resonance Raman spectroscopy (RRS) provides a powerful metrological tool for distinguishing metallic (M) from semiconducting (S) tubes, for determining the diameter distribution of SWNTs in a given sample, and for determining the (n,m) values for individual nanotubes. Photoluminescence (PL) has developed rapidly as a nanotube characterization tool because it is very attractive for identifying the (n,m) indices for semiconducting nanotubes in a solution sample. Rayleigh scattering shares with PL the advantage of a much stronger signal than RRS. Near-field microscopy has been used to show the topography, the Raman spectra, and the photoluminescence from the same tube, thus providing, at the same time, information about the morphology as well as the electronic and vibrational properties of nanotubes. The technique can be used to locate individual defects spatially in a nanotube by looking for an abrupt change in the spectral signature of a given (n,m) tube as the spectrum is scanned spatially. At present, the spatial resolution record for near-field optics is ~10 nm and a goal for this technique would be eventually to achieve atomic resolution.

There are three major problems concerning the applicability of optics as an accurate metrological tool. First, although it is possible to assign, when using the RRS or PL techniques, the amount of light coming from specific (n,m) tubes in a sample, the quantitative determination of the (n,m) population within a nanotube sample is hindered at present by the absence of an independent experimental method for the determination of the magnitude of matrix element governing the excitonic absorption and emission intensity from SWNTs. Calculations of Raman frequencies and RRS matrix elements are now at an advanced stage for SWNTs,[1] but understanding lifetime effects and dark singlet and triplet states are still at an early stage. Second, environmental effects due to substrates, wrapping agents, functionalization, strain, or other mechanisms are expected to strongly influence the optical response (see Figure 2). This is especially important for nanotubes where the excitonic nature of the excited states makes them highly sensitive to their dielectric environment. Controlling environmental effects is vital for a variety of applications of functionalized nanotubes for sensors and biomedical applications. Third, the presence of defects on the tube structure is also expected to strongly influence their optical properties, since defects change the local structure and act as trap states for excitons. The accumulated experience from TEM experts show that it is not difficult to find a defect within a ~100 nm segment of SWNTs grown by usual chemical vapor deposition processes. However, the type of defect (an impurity, a vacancy, or an interface) is important in changing the optical behavior. Accurate and accessible measurement techniques for detailed defect characterization are not yet available. An in-depth study of defects in nanostructures is very important, since defects will influence not only optics, but also the various mechanical and transport properties.

The uncertainty behind all measurements in the carbon nanotube field is certainly decreasing the speed of both scientific and technological development. For example, the radial breathing mode (RBM) frequency (ω_{RBM}) provides a simple spectroscopic signature of SWNT diameter (d_t). The experimental results in the literature have been fitted with the relation $\omega_{RBM} = \mathbf{A}/d_t + \mathbf{B}$, but the values for **A** and **B** vary from one publication to another. The empirical constant factor **B**, supposedly associated with environmental effects, prevents the expected limit of a graphene sheet from being achieved, where the ω_{RBM} should go to zero when d_t approaches infinity. Trying to understand the physics behind **B**, or more generally the consistency between the nano and bulk scales, means trying to obtain an in-depth understanding behind the size-dependent effects of nanomaterial properties. Carbon nanotubes and graphene are unusual insofar as their quantized behavior (which is important for nanosystems) in transport can even be observed at room temperature. Because of the close connection between graphene and carbon nanotubes (since a carbon nanotube is a graphene layer rolled up in a seamless way to form a cylinder), many similar potential applications can be envisioned for graphene and carbon nanotubes. However, their different geometries give rise to distinct properties for these two types of carbon materials and, therefore—separate though related—metrology programs for graphene and nanotubes will be needed. Since graphene research and potential nanotube applications are developing very rapidly, the time seems ripe for starting a graphene metrology program now.

Biomedical Applications

Discussion of biomedical applications has been addressed in two contexts. One is the great opportunities envisaged for carbon nanotubes in the biomedical area for applications such as tissue regeneration, cancer cell treatment, drug delivery, neuron activation, and use in implants for medical sensing and treatment devices. The second context concerns toxicological studies involving issues such as monitoring the movement of nanotubes through the body, their elimination from the body, their accumulation within the body of an animal (or human), and the preferred locations by the biological system for this accumulation. Toxicology studies are needed to assess health effects due to the presence and accumulation of nanotubes in specific organs, for example the lungs (as might result in black lung disease in coal miners). The efforts have to go from the development of strategies for characterizing the aerosol properties of nanotubes, up to the strategies to mitigate illness caused by the presence or accumulation of nanotubes. One such strategy that has shown promise in mice is the functionalization of nanotubes with nitrogen.[1]

It is felt by the nanotube community that the bionanotube area needs special consideration for three reasons. First, the topic of biomedical nanotube research is so large, diverse, and important that it needs more time and careful attention than it presently receives at general nanotube conferences. Second, different researchers with different areas of expertise are involved in the research on the various topics which fall under the bionanotube heading. Finally, the biomedical-nanotube area is so diverse that researchers now working in this field worldwide do not know each other, nor are they well-acquainted with the nanotube research community. For all these reasons, it was decided that a bionanotube workshop would be held next year (2008) as a satellite conference to NT08 in Montpellier, France, in addition to the second satellite conference on nanometrology of nanotubes MSIN08.[6,7] Liaison between the metrology and bionanotube satellite workshops would also be encouraged to advance the development of bionanotube metrology science that would be needed for the implementation of a viable metrology program in the nanotube area.

> *…the time seems ripe for starting a graphene metrology program now.*

Conclusion

The metrology studies on carbon nanotubes began late, and developments in the field appear to be substantially behind advances in commercializing carbon nanotubes. The most basic materials characterization of the nanotube content, purity, and dispersion requires serious attention and standard reference materials need to be developed for various aspects of nanotube metrology. To address present industrial needs, protocols are required for characterizing basic concepts like (n,m) and tube length distribution, metallic-to-semiconducting nanotube ratio in a sample, the presence of structural defects, surface area, and optical efficiency. In addition, nanometrology needs to be developed for quantifying, and therefore improving sophisticated concepts that, once adopted, will be engineered for enhancing specific properties that are exploited in industrial products. The development of standards at present is at such an early stage that it is not yet clear how these standards should be developed, and how these standards should be used.

At the same time, it is clear from the metrology workshops which have been held so far that present and future nanometrology efforts will foster competitiveness and create a favorable environment for both scientific and industrial development. Nanotubes are prototype nanostructures and should interface with the broader nanoscience metrology programs as shown by the recent international efforts of the ISO program. Specific software for the analysis of TEM, SPM, and PL experiments on SWNTs are already on the market. The high resolution of the TEM and SPM measurement techniques can be utilized to study in detail the interplay between structure, electronic properties, and local perturbations. Optics provides a powerful pathway as a fast and reliable approach for nanotube characterization, as demanded for applications, but the optical efficiency is highly dependent on tube morphology and environment. Fruitful outcomes should be achieved when combining SPM and TEM with optical spectroscopy techniques, giving researchers the opportunity to correlate vibrational modes with local changes in the microscopic structure or chemical attachment of functional groups on individual SWNTs. Systematic characterization by multiple techniques is important for metrology science, but is not directly applicable to large-scale industrial needs where easy and quick tests are necessary. Consistency between properties measured on the nano and bulk scales have to be pursued for a clear understanding of size effects. Although a lot of work has already been done on these topics, many promising and important research directions remain to be pursued. Attention should now also be given to the metrology for the bio- and biomedical nanotube research area, addressing the needs of applications in this area. Attention also needs to be given to developing the toxicological aspects of this kind of nanoscience. Developing nanometrology thus presents both a large opportunity and challenge for the successful transformation and exploitation of nanoscience into nanotechnology.

Acknowledgments

The authors acknowledge Prof. Kauppinen Esko and Dr. Abdou Hassanien for comments on the manuscript. A.J. acknowledges financial support under Universal Grants (CNPq and Fapemig) and by Rede Nacional de Pesquisa em Nanotubos de Carbono (MCT and CNPq). M.S.D. acknowledges support under NSF Grant DMR 07-04197.

References

1. A. Jorio, M.S. Dresselhaus, G. Dresselhaus, *Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications* (Vol. 111, Springer Series in Topics in Appl. Phys., Springer-Verlag, Berlin, 2007).

2. *First International Workshop on Metrology, Standardization and Industrial Quality of Nanotubes (MSIN07)*, (Inmetro, Rio de Janeiro, Brazil, June 22, 2007); http://www.inmetro.gov.br/msin07.

3. *Third NASA-NIST Workshop on Nanotube Measurements*, (NIST, Gaithersburg, September 26–28, 2007); http://polymers.nist.gov/

Nanotube3/Workshop3.htm.
4. National Research Council, *Condensed-Matter and Materials Physics: The Science of the World Around Us*, (The National Academies Press, 2007).
5. National Institute of Standards and Technology, *T.M.S. an Engineering Laboratory*; http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes_Guide. htm.
6. *Second International Workshop on Metrology, Standardization and Industrial Quality of Nanotubes (MSIN08)*, (Le Corum, Montpellier, France, June 28, 2008); http://www.cnrs-imn.fr/NT08/Satellites.html.
7. *First International Workshop on Carbon Nanotube Biology and Medicine (NTBM08)*, (Le Corum, Montpellier, France, June 28, 2008); http://www.cnrs-imn.fr/NT08/Satellites.html.
8. Y.-M. Lin, "Challenges and Achievements on the Transport Measurements of Carbon Nanotubes," presented at the First International Forum on Metrology, Standardization and Industrial Quality of Nanotubes. www.inmetro.gov.br/msin07/abstract_Lin-MSIN07.pdf.
9. H. Hovel, M. De Menech, M. Bodecker, C. Rettig, U. Saalmann, and M.E. Garcia, *Eur. Phys. J. D.* (2007) DOI: 10.1140/epjd/e2007-00226-2. Figure reprinted with permission. ©2007 by EDP Sciences.
10. B. Freitag, B. Groen, M. Otten, and D. Hubert, "Novel Developments in High Resolution Electron Microscopy for Ultimate Nanotube Metrology," presented at the First International Forum on Metrology, Standardization and Industrial Quality of Nanotubes; www.inmetro.gov.br/msin07/abstract_hubert-MSIN07.pdf.
11. A. Hartschuh, *Nachrichten aus der Chemie* **55** (2007) p. 495. Reprinted with permission.
12. M.J. O'Connell, S.M. Bachilo, C.B. Huffman, V.C. Moore, M.S. Strano, E.H. Haroz, K.L. Rialon, P.J. Boul, W.H. Noon, C. Kittrell, J. Ma, R.H. Hauge, R.B. Weisman, and R.E. Smalley, *Science* **297** (2002) p. 593. Reprinted with permission from AAAS.
13. M.S.C. Mazoni and H. Chacham, *Appl. Phys. Lett.* **76** (2000) 1561. Figure reused with permission. ©2000 American Institute of Physics.
14. K. Hata, D.N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, *Science* **306** (2004) p. 1362. Reprinted with permission from AAAS.

***Ado Jorio** is an associate professor in the Department of Physics at the Universidade Federal de Minas Gerais and a researcher at Instituto Nacional de Metrologia in Brazil.*

***Mildred S. Dresselhaus** is an Institute Professor of Physics and Electrical Engineering at the Massachusetts Institute of Technology.*