RAMAN METROLOGY TO ENABLE CARBON-BASED NANOMANUFACTURING

Angela R. Hight Walker
Physical Measurement Laboratory, National Institute of Standards and Technology

Optical techniques hold essential roles in revealing the detailed chemical and physical facets of carbon-based nanomaterials. Recent progress in the characterization of single-wall carbon nanotubes (SWCNTs) *via* three optical spectroscopic techniques: Raman scattering, UV-Vis-NIR absorption, and photoluminescence excitation, will be compared and contrasted. Our results highlight the power and uniqueness of optical techniques for nano-metrology. SWCNTs, each formed by a graphene sheet rolled into a hollow cylinder, are produced with often undesirable heterogeneity during the manufacturing process, *e.g.,* variations diameter and the rolling angle of the graphene sheet that determines its chirality [denoted by two integers *(n,m)*]. Each of these parameters affects the opto-electronic properties of SWCNTs, which, if not well understood and controlled, will hinder application development especially in electronics, photonics, and sensors. Researchers at NIST pioneered an aqueous two-phase extraction strategy to enrich SWCNTs with specific and predefined parameters. The separated SWCNT populations each possess distinctive electronic transitions that result in fingerprint absorption and fluorescence peaks and Raman modes. For Raman spectroscopy, when the laser excitation energy is matched to the electronic transition of a SWCNT, the intensity of Raman modes is enhanced tremendously resulting in a resonant Raman signal. Therefore, optical spectroscopic techniques are essential to evaluate the separation quality, purity, and identify the enriched component. Specifically, resonance Raman spectroscopy (RRS) is the most powerful technique to evaluate SWCNTs as it provides the metallicity, chirality, degree of bundling, dielectric environment inside or outside of the tube, defect density, impurity level, and the level of electron-phonon coupling. Using tunable laser sources spanning the entire visible range from 400 nm to 850 nm, we resonantly probe most of the chiralities of SWCNTs produced from any method.

Recent results will be highlighted including an under-recognized complexity in the evaluation of Raman spectra for the assignment of (*n,m*) population distributions[1]. Strong structural dependencies affect the intensity ratio of the RBM to G modes and can result in misleading interpretations. Also, in a separate work, the effect of dielectric environments on the nanotube properties were assessed through intentional endohedral filling[2]. These works, combined with an international effort among several national metrology institutes to enable quantitative assessment through Raman spectroscopy, are leading to protocols to reduce heterogeneity in nanomanufacturing.

[1]Piao, Y.; Simpson, J. R.; Streit, J. K.; Ao, G.; Zheng, M.; Fagan, J. A.; Hight Walker, A. R. Structure-dependence Resonant Raman Intensity Ratios for Semiconducting Single-wall Carbon Nanotubes. *ACS Nano,* 2016 10, 5259.
[2]Campo, J.; Piao, Y.; Lam, S.; Streit, J. K.; Hight Walker, A. R.; Fagan, J. A. Alkane Filled Single-wall Carbon Nanotubes: Endohedral Volume Control for Improved Nanotube Properties. *Nanoscale Horizons* 2016 1, 317.