Fluorescence Spectroscopy of SWCNTs: Bridging the Gap between Single-particle and Bulk Studies

Sergei M. Bachilo, Jason K. Streit, Saunab Ghosh, and R. Bruce Weisman

Department of Chemistry and R. E. Smalley Institute for Nanoscale Science and Engineering
Rice University,
Houston, Texas 77005 USA

Conventionally, single-walled carbon nanotubes (SWCNTs) and other samples have been studied using two separate types of fluorescence spectroscopy. One type, bulk or ensemble spectroscopy, is very effective for detecting and characterizing SWCNTs in condensed phase samples. The other approach uses fluorescence microscopy to reveal features of individual nanotubes. Both methods have their strengths and weaknesses. Bulk spectroscopy intrinsically provides excellent statistical sampling but can reveal only averaged properties. For example, it cannot distinguish samples with many weakly emitting nanotubes from those with lower concentrations of strongly emitting SWCNTs. This distinction is clear from microscopic measurements on individual nanotubes, but it can be tedious to observe enough particles for a statistically accurate result.

We will present progress in developing new spectroscopic methods that can fill the gap between these regimes. Imperfections in microscope optics are used to achieve spectral analysis of many individual SWCNTs in parallel. Microscope objectives designed for use at visible wavelengths often show severe axial chromatic aberration in the NIR, making objects emitting at different NIR wavelengths appear to focus at different depths. After this aberration has been calibrated for a particular objective lens, the depth at which an emissive nanoparticle appears brightest and best focused is used to deduce its peak emission wavelength. The method is demonstrated using a dilute, structurally polydisperse SWCNT sample deposited onto a microscope slide. Discrete emission centers in this sample have different peak wavelengths corresponding to specific nanotube structural species. A set of images was recorded at stepped focus settings and analyzed to find the focal depth of each nanotube. The chromatic aberration calibration curve converted these depths into peak emission wavelengths with a spectral precision of approximately 3 nm, allowing identification of each nanotube's species. Data compiled from such images gives both a composite intensity spectrum and also a particle-number spectrum. The resolution between different (n,m) species in this approach may actually exceed that from bulk spectra because only the peak wavelength of each emitter is used in the compilation. This can be useful for characterizing mixed samples with spectral congestion. Data are also obtained showing the distributions of brightness within and between SWCNT species. Thus, this “microscopic,” spectrometer-free spectroscopy can provide additional information about the SWCNT samples, combining some benefits of single-particle and ensemble methods.