Determining (n,m) compositions of SWCNT samples

Qualitative analysis

SWCNT samples almost always contain a number of (n,m) structural species, including semiconducting and metallic forms. The semiconducting SWCNT species present in a sample can be detected and identified by their fluorimetric signatures, which involve characteristic emission peaks in the near-IR and characteristic excitation peaks in the visible region. Two-dimensional excitation-emission scans were originally used to observe these features and qualitatively analyze for the semiconducting (n,m) species. The continuously wavelength- tunable excitation light needed for such scans is available only by using a monochromator to filter the output of a broadband lamp. Unfortunately, the resulting lamp-based excitation beam is low in power and impossible to focus tightly.

The NS1 instead uses three higher power diode lasers with fixed wavelengths carefully chosen to excite a broad range of semiconducting SWCNTs. But how can many (n,m) species be detected using only three wavelengths that do not match most of their absorption peaks? First, each (n,m) species has a dominant excitation band with broad Lorentzian wings that extend far from the resonance peak. In addition, there are secondary excitation features from vibronic side-bands and perpendicular spectral transitions that greatly expand the range of wavelengths capable of inducing near-IR emission. Finally the NS1's powerful excitation beams, efficient optical system, and sensitive near-IR detector let it capture emission spectra with very high signal-to-noise ratio and large dynamic range, clearly revealing the emission features of less abundant or inefficiently excited species. Specialized analysis software integrated with the NS1 automatically uses advanced models of nanotube spectroscopy and photophysics to interpret the data and generate an (n,m) inventory. This analysis takes only seconds, even for very dilute SWCNT samples.

Quantitative analysis

There are two levels of sophistication in finding the quantitative distribution of semiconducting (n,m) abundances in a SWNCT sample. The first is measuring and tabulating the near-IR emission intensities (normalized to excitation efficiency and laser power) of the species identified in the (n,m) inventory described above. The NS1 analysis software achieves this by careful global fitting of the three emission spectra. Each spectrum is simulated as a superposition of emission peaks from a large "basis set" of (n,m) species, with the relative species populations constrained to match among all three spectra. The simulation uses an advanced model that includes precise peak positions, widths, and shapes for

each species' excitation and emission spectrum. These parameters are held in surfactant-specific templates that reflect the minor spectral changes induced by different nanotube environments. Instrumental factors such as the wavelengths and powers of the excitation lasers are included to compensate for differences in excitation efficiency among the (n,m) species. Efficient algorithms allow quick computation of the fitting results. They give a distribution equivalent to that obtained from measuring peaks in a two-dimensional excitation-emission scan, but with the advantages of much faster data acquisition and higher sensitivity.

The second level of quantitative interpretation goes beyond the assumption (implied above) that all (n,m) species give equal fluorescence signal strengths if they are present at equal mass concentrations. Instead, the (n,m) distribution deduced from the first level is adjusted using a set of correction factors that reflect the differing intrinsic fluorimetric brightness of different species.
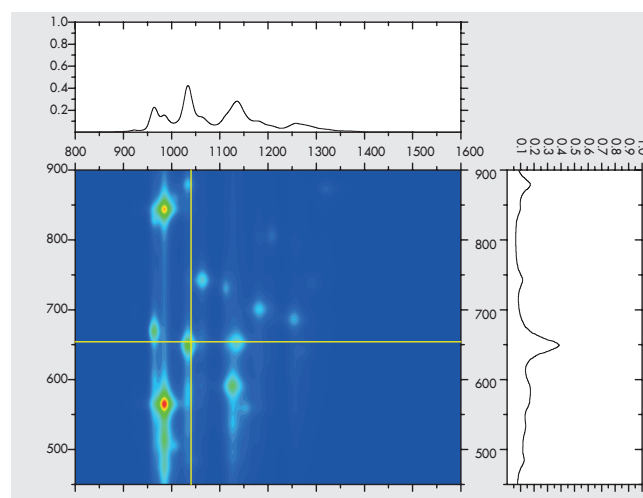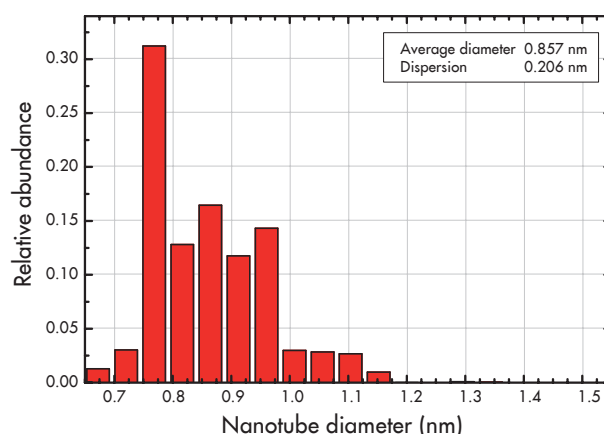
Diameter Distribution from Fluorescence Analysis

Determining (n,m) compositions of SWCNT samples

These (*n*,*m*)-specific factors are the product of absorption cross-section at the excitation peak multiplied by quantum yield for NIR emission. They are found from state-of-the-art calibrated photophysical measurements on individual SWCNTs. As future research findings suggest refinements in these correction factors, they will be promptly updated in revised versions of the NS1 software. By applying the photophysical correction factors during fluorimetric analysis, the NS1 system provides a reliable (*n*,*m*) distribution showing the relative mass abundances of semiconducting SWCNT species in the sample. No other bulk method can provide such quantitative analyses.

The (*n*,*m*) distribution deduced by measuring and interpreting the three near-IR emission spectra is displayed in automatically generated, publication-ready graphs (shown below):

- a graphene sheet map in which the line thickness of each hexagon is proportional to the deduced species abundance
- a diameter histogram computed from the abundance distribution
- an excitation-emission contour plot synthesized from the deduced abundance distribution and relevant spectral parameters.