THE MOLAR FRACTION OF CARBON NANOTUBES IN SOOT

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Determining the fractional yield *Y* (molar % or wt carbon %) of single wall carbon nanotubes (SWNT) [1] in carbon soot has been a long-standing problem that hinders progress to finding optimal growth conditions. In most cases, when yields have been reported, electron microscopy (SEM or TEM) has been used to provide an estimate for the yield. Researchers who have been engaged in the analysis of these microscope images are aware of the difficulty and pitfalls of counting "sticks" (nanotube bundles) and "balls" (e.g., carbon nanospheres and carbon coated metal particles), particularly in low-yield samples in which the tube bundles are obscured by a nanoparticle coating. In this paper, we describe a convenient method based on Raman scattering and SEM to estimate Y.

Most of the SWNT material used in this study was grown by the electric arc discharge method [2] using a Ni-Y catalyst (CarboLex, Inc.). Samples were prepared in the form of films deposited onto 2 x 1 x 0.1 cm^3 Pyrex glass substrates. About 15 ml of spectroscopically pure ethanol was mixed with a standard amount (20 mg) of carbon soot containing SWNT. The soot was dispersed in ethanol by ultrasonic agitation for about 15 min. This suspension was then poured to a height of ~1 cm into a 20 ml beaker containing a substrate at the bottom. Next, the alcohol was evaporated in air in an oven set at 110°C for about an hour, leaving a thin-film deposit on the substrate. Films prepared in this way exhibit excellent spot-to-spot reproducibility of the optical data. Unpolarized Raman scattering spectra were collected at room temperature using four excitation wavelengths (Ar^+: 488 nm, 514.5 nm; Kr^+: 647.1 nm; Nd-YAG: 1064 nm). As reported earlier [3], the dominant peaks in the Raman spectrum are the radial breathing (R) mode band (~160-180 cm^{-1}) and tangential (T) mode band (1500-1600 cm^{-1}) of the SWNT, both broadened inhomogeneously due to a distribution (~1-2 nm) in the nanotube diameter [3].

We found that long-term, ultrasonic agitation (for several hours) of the SWNT bundles suspended in ethanol changes the relative intensity of the R and T bands. Experiments with 1064 nm excitation showed that this was primarily driven by a gradual loss of the R band intensity. Therefore we use the intensity of the T band to determine the SWNT yield.

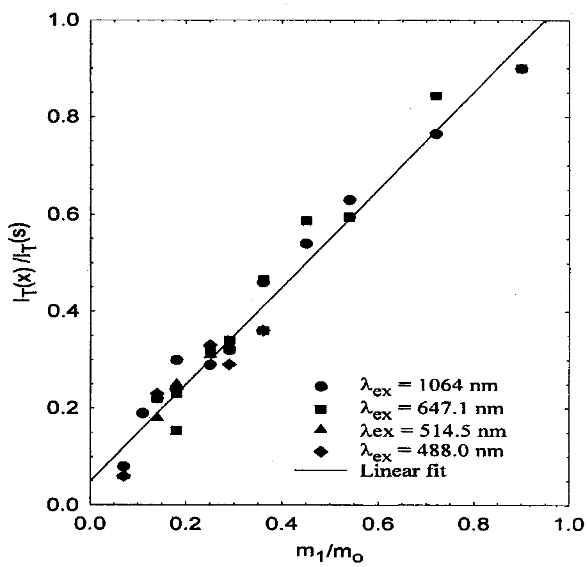

Fig.1. The T band intensity ratioed to that of a standard 90 wt% SWNT film plotted as a function of the mass fraction of m_1/m_0, where m_1 is the mass of the 90 wt% carbon SWNT component in the sample.

A series of thin film samples (designated "x") were prepared by mixing m_1 (mg) of high-yield (Y_1~90%) soot with m_2 (mg) of low yield soot (Y_2~6%), so that a constant total mass $m_0=m_1+m_2=20$ mg was used for depositing films on substrates following our protocol. A standard film (designated "s") was made using 20 mg of Y_1~90% soot (see Fig. 2). The Raman spectra of the *s* and *x* films were recorded successively by shuttling the films into the laser beam using an optical translation stage. In this way, no significant changes in the optical alignment occurred. In Fig. 1 we display the T-band intensity ratio for the *x* and *s* films $[I_T(x)/I_T(s)]$ vs. (m_1/m_0) for four laser excitation wavelengths. As can be seen from the figure, this intensity ratio is linear in (m_1/m_0). The straight line in the figure is the result of a linear least-squares fit to the data.

We demonstrate below that the linear dependence of $[I_T(x)/I_T(s)]$ on (m_1/m_0) is consistent with the fact that the integrated Raman scattering intensity I_T of the T band is proportional to the molar fraction of carbon as SWNTs in the film. The molar fraction $f_{SWNT}(x)$ of SWNT in the test film (x) may be written as

$$f_{SWNT}(x) = Y_1\,(m_1/m_0) + Y_2\,(m_2/m_0)\,, \qquad (1)$$

where m_0 is the atomic mass of carbon, and Y_1 and Y_2 are the molar fractions, or yields, of the SWNT in the high (Y_1) and low (Y_2) yield soot. Assuming $I_T \sim f_{SWNT}$, for constant optical conditions, equation (1) gives

$$I_T(x)/I_T(s) = [(Y_1 - Y_2)/Y_1]\,(m_1/m_0) + (Y_2/Y_1), \qquad (2)$$

where $m_0=(m_1+m_2)$. It should be noted that all factors due to the optics cancel out of the ratio. Thus, a plot of $[I_T(x)/I_T(s)]$ vs. (m_1/m_0) should be linear with a slope = $(Y_1-Y_2)/Y_1$ and exhibit an intercept on the vertical axis of (Y_2/Y_1). This is precisely the form of the experimental data displayed in Fig. 1. We therefore conclude that $I_T \sim f_{SWNT}$ is approximately satisfied in our films. From a high resolution (HR) SEM analysis (see Fig. 2), we find $Y_1 \sim 90$ wt% for the high-yield soot; a value for $Y_2 \sim 5$ wt% was obtained from the intercept in Fig. 1. Thus, the slope of the straight line fit to the data (Fig. 1) is expected to be (0.9-0.05)/0.90~0.944, about 6% smaller than the value 1.002 obtained from the least-squares fit. Considering the scatter in the data, the agreement with the model assumptions is very good.

The HRSEM image shown in Fig. 2 was analyzed using the National Institute of Health's (NIH) *Image* software [4]. Regions of carbon nanospheres were identified and the ratio of the total rectangular image area selected to the nanosphere image area was computed automatically by the software, which recognizes the irregular shape of the clustered or individual nanoparticles via the contrast in the image. This procedure was repeated on three representative areas of each image (Fig. 2). Taking the average of the computed nanosphere areas to the corresponding selected rectangular areas, we find Y=90±2%. In order to establish confidence in this HRSEM calibration for Y, we compared values for Y by HRSEM and Raman spectroscopy in three other, high yield films. The results we obtained are: Y(Raman, SEM) = (95, 95), (88, 90) and (90, 92), giving an accuracy of better than ±2%. A more detailed analysis of the SEM image shows that the area ratio provides a reliable estimate for the wt% yield of SWNT in the soot [5].

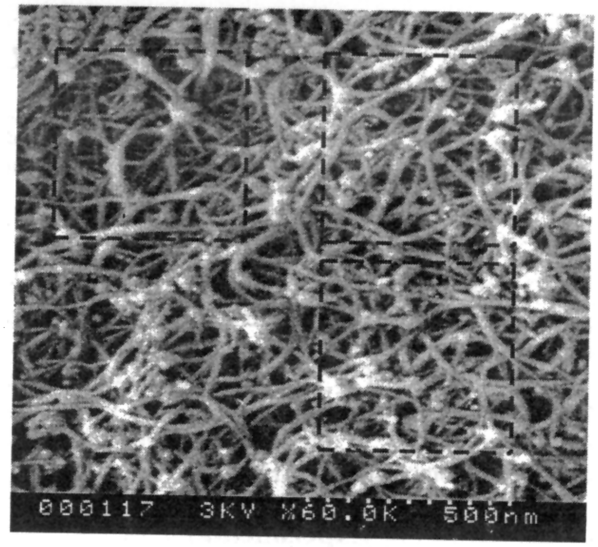

Fig. 2. HRSEM image of our standard (90 wt% SWNT) film; note the scale bar at the bottom of the image.

Acknowledgments

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References

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