Connecting Single Molecule Electrical Measurements to Ensemble Spectroscopic Properties for Quantification of Single-Walled Carbon Nanotube Separation

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The separation and sorting of single-walled carbon nanotubes (SWNTs) is one of the most significant challenges in this rapidly progressing field. A variety of methods including density gradient centrifugation[1] and free solution electrophoresis[2] invariably utilize Raman, photoabsorption, or photoluminescent spectroscopy to benchmark the resulting separation. However, it is not clear how to relate these qualitative numbers to absolute quantities of individual SWNTs. Moreover, for nanoelectronic applications, separation and purity standards need to be studied using single molecule electrical measurements, and ensemble spectroscopic assessments are thus far uninformative for this purpose. There is also recent evidence that solution phase processing of the types employed for the above separation methods induces undesirable defects on SWNTs that adversely affect their electrical performance.[3] However, there is currently no quantitative standard by which the degree of defect generation on individual SWNTs from solution phase processing is accessed.

Here, we directly compare, for the first time, the ensemble spectroscopic measurements to a systematic and statistically rigorous counting of individual metallic and semiconducting SWNT devices using a high throughput electrical probe station. The comparison allows us for the first time to report an accurate extinction coefficient ratio for metallic and semiconducting SWNTs from HiPco and laser oven preparations. This parameter should greatly aid in the analytical chemistry of separation methods for SWNTs. The systematic counting of metallic and semiconducting types from solution also allows us to examine the variances associated with device properties and therefore provide the first measure of potential defect generation during processing.

The peak areas in the photoabsorption spectrum of solution dispersed SWNTs can be connected to actual compositions of metallic and semiconducting types via statistics on single molecule SWNT devices that unambiguously classify them as metallic or semiconducting.[4] The total peak areas of all metallic species in the sample ($A_{M,total}$) can be expressed as the sum of the peak area ($A_{M,(n,m)}$) for an (n,m) metallic SWNT according to eq 1, where $x_{M,total}$ is the actual composition of metallic species, C_{total} is the total concentration of SWNTs, L is the path length, and $\bar{\varepsilon}_M$ is the weighted extinction coefficient of metallic species.

$$A_{M,total} = \sum_{(n,m)} A_{M,(n,m)} = \sum_{(n,m)} \left(\int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda)_{M,(n,m)} C_{M,(n,m)} L \, d\lambda \right)$$

$$= C_{total} x_{M,total} L \frac{\sum_{(n,m)} \left(x_{M,(n,m)} \int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda)_{M,(n,m)} \, d\lambda \right)}{x_{M,total}} = C_{total} x_{M,total} L \bar{\varepsilon}_M$$

$$(1)$$

The total absorbance of all semiconducting species ($A_{SC,total}$) can be expressed in a similar manner as in eq 2,

$$A_{SC,total} = \sum_{(n,m)} A_{SC,(n,m)} = C_{total} x_{SC,total} L \bar{\varepsilon}_{SC} \qquad (2)$$

An extinction coefficient (ϵ) varies with the (n,m) chirality and therefore with the wavelength of the incident light (λ)[4]; however, the summation of extinction coefficients over a collection of SWNTs and the wavelength of incident light should remain constant and be composition independent, an assertion examined below. Therefore, from eqs 1 and 2, a simplified relationship between the absorbance ratio and the actual composition of metallic over semiconducting SWNTs can be derived, as in eq 3,

$$\frac{A_{M,total}}{A_{SC,total}} = \frac{x_{M,total}}{x_{SC,total}} \bar{\varepsilon}', \quad x_{M,total} + x_{SC,total} = 1 \qquad (3)$$

where the constant $\bar{\varepsilon}'$ represents the extinction coefficient ratio of metallic over semiconducting SWNTs in an SWNT mixture. Once $\bar{\varepsilon}'$ is determined via single molecule calibration, the actual composition of each electronic type in the separated SWNT mixture can be easily calculated from absorption intensity alone.

We prepared SWNT samples having different compositions of metallic and semiconducting SWNTs from two distinct methods and two SWNT sources: (1) HiPco SWNTs separated via free solution electrophoresis as advanced by our group,[2] (2) laser ablated SWNTs separated by the density gradient developed by Arnold and co-workers.[1] A single pass separation was utilized in both cases to vary the compositions from ∼20 to ∼80% to generate an extinction coefficient ratio valid over a wide composition range. The absorption spectra of separated SWNTs together with their initial mixtures are shown in Figure 1a−b, indicating that semiconducting SWNTs (SC-enriched) for HiPco (Figure 1a) and both metallic (M-enriched) and semiconducting (SC-enriched) SWNTs for laser samples (Figure 1b) have been successfully enriched from initial mixtures (Control). For the accurate measurement of absorption intensities of SWNTs, background correction was performed for all samples as demonstrated previously.[5] Details are explained in the Supporting Information (Figure S1).

Then, from more than 6000 attempts, we fabricated and tested a total of 476 mostly single-tube FET devices from these same SWNT samples for electrical testing to estimate the actual composition of metallic or semiconducting SWNTs. Figure 1c shows AFM images of two representative single-tube devices.

We have first examined the on/off current ratio and identified the electronic type based on the following criteria. Semiconducting SWNTs have (1) an on/off ratio on the order of 10^1 or higher and (2) an off current on the order of 10^{-9} or lower. Tubes are metallic otherwise. Figure 1d shows typical transfer characteristics from 3 metallic (red) and 3 semiconducting (blue) devices at $V_d = -1.5$ V. The on/off ratio is as high as ∼10^6 for the semiconducting devices shown. From the transfer curves, percent distributions of on/off current ratios were plotted for HiPco (Figure 1e) and laser (Figure 1f) samples. The distribution is bimodal, centered at 10^1 and $10^5 - 10^7$ as discussed. Clearly, the distribution is skewed toward low (*high*) values for M-enriched (*SC-enriched*) samples, similar to the absorption spectra shown in Figure 1a−b. On/off ratios for SC-enriched samples vary presumably due to the wide distribution of SWNT chirality, and thus the band gap, as inferred by their
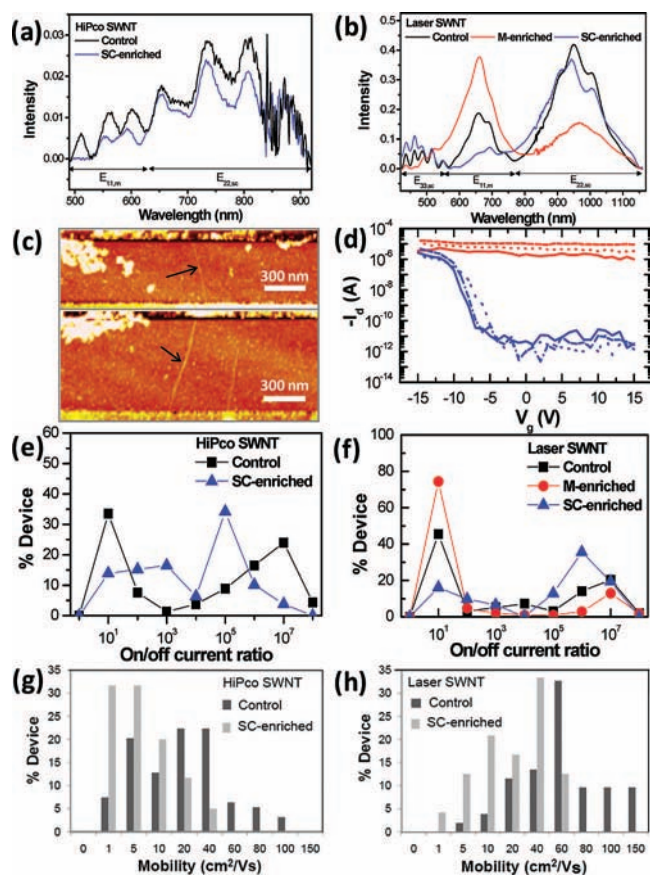
Figure 1. UV—vis—nIR absorption spectra of (a) HiPco SWNTs and (b) laser SWNTs. (c) AFM images of single nanotube in 300 nm (top) and 600 nm (bottom) channels. (d) Typical transfer characteristics from 3 metallic (red) and 3 semiconducting (blue). Distribution of on/off ratio from (e) HiPco SWNTs and (f) laser SWNTs. Histogram showing per-tube mobility distribution (μ_{tube}) for (g) HiPco and (h) laser SWNT devices.

Table 1. Summary of % Electronic Enrichment, Total Absorbance Ratio, and the Extinction Coefficient Ratio of Metallic over Semiconducting SWNTs

SWNT	sample	composition		ratio	
		M	SC	A_M/A_{SC}	$\bar{\varepsilon}_M/\bar{\varepsilon}_{SC}$
HiPco	control	40.5%	59.5%	0.240	0.353
	SC-enriched	24.1%	75.9%	0.112	0.353
laser	control	47.5%	52.5%	0.308	0.340
	SC-enriched	22.6%	77.4%	0.107	0.366
	M-enriched	78.9%	21.1%	1.307	0.350

mobility (μ_{tube}) was calculated for semiconducting devices (Figure 1g—h).[6,7] The μ_{tube} values for HiPco SWNT devices average lower at 20.2 ± 21.3 cm^2/Vs than at 64.0 ± 29.4 cm^2/Vs for laser SWNT devices. The μ_{tube} values are further lowered to 5.3 ± 7.5 cm^2/Vs for HiPco SWNT devices and 19.4 ± 15.2 cm^2/Vs for laser SWNT devices, after separation. Compared to the μ_{tube} from CVD-SWNT devices,[6,7] these values are lower by 2–3 orders of magnitude. We suspect that this is due to the defects introduced during solution processing as well as perhaps residual surfactant and density gradient modifiers on the SWNT surface, utilized in this study.[3,8] We note that this statistically rigorous data set, the first of its kind to appear in the literature to date, provides a basis to clarify the origin of the mobility decrease in future work.

In conclusion, we have successfully quantified the percent enrichment of each electronic type from separated SWNT samples for the first time, independently of potential spectroscopic artifacts. Preparation of large arrays of single-tube devices enabled this quantification. We measure and report for the first time an extinction coefficient ratio for metallic to semiconducting SWNTs of 0.352 ± 0.009, showing that it is independent of the separation method or starting material used in this study. We also found that this systematic classification of individual SWNTs allows us to assess defect generation during processing. Future studies will focus on the source of defect generation as well as a more detailed correlation between spectroscopic enrichment and actual electronic enrichment.

Supporting Information Available: Derivation of equations, background correction, details of device fabrication, transfer characteristics, calculations for percent of single-tube devices and per-tube mobility, and AFM images. This information is available free of charge via the Internet at http://pubs.acs.org.

absorption spectra (Figure 1a—b). Conversely, the on/off variation in an M-enriched sample is mainly from multiple tubes and tube—tube junctions. The area under each mode represents the relative enrichment of each electronic type. The percent enrichment of the desired electronic type is 78.9% (M-enriched laser), 77.4% (SC-enriched laser), and 75.9% (SC-enriched HiPco), as listed in Table 1. Assuming a uniform chirality distribution in as-produced SWNTs, the control sample is expected to show ~67% of semiconductors. The smaller actual values (52.5% for laser and 59.5% for HiPco) can be attributed to either multitube devices at high hit rates (Table S1) or an actual abundance of semiconductors in the SWNTs used in this study.

We finally estimated the extinction coefficient ratio of metallic over semiconducting SWNTs ($\bar{\varepsilon}'$) in eq 3 from their area ratio obtained from absorption measurement (Figure 1a—b) and actual composition obtained from electrical measurement, as listed in Table 1. The calculated extinction coefficient ratios from five samples are comparable with one another with an average value of 0.352 ± 0.009 (1 standard deviation, ~68.3% confidence). The fact that the ratios estimated from five different samples show similar values indicates that the $\bar{\varepsilon}'$ is constant, as we postulated, and is valid for quantifying the SWNT composition, irrespective of preparation methods used in this study. This systematic classification of individual SWNTs into metallic/semiconducting types from solution also allows us to assess potential defect generation during processing. From the linear region of transfer curves, per-tube field effect

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