Supporting Information

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

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Derivation of equation

According to Beer-Lambert's law, the absorbance (A) of a specific (n,m) SWNT can be expressed in terms of its extinction coefficient (ε) and concentration (C). For an (n,m) metallic SWNT with absorbance $(A_{M_{(n,m)}})$, originating from the inter-band transition of the first van Hove singularity, eq (1) applies where the extinction coefficient $(\varepsilon(\lambda)_{M_{(n,m)}})$ is a function of the wavelength of incident light (λ) and L is the path length of incident light.

$$A_{M_{(n,m)}} = \int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda)_{M_{(n,m)}} C_{M_{(n,m)}} L d\lambda$$
(1)

Total absorbance of all metallic species in the sample $(A_{M,total})$ can be expressed according to eq (2), where x_M is the actual (molar) composition of metallic species, C_{total} is the total concentration of SWNT mixture, *L* is the path length of light and $\overline{\varepsilon}_M$ is the weighted extinction coefficient of metallic species.

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

$$= C_{total} x_{M,total} L \frac{\sum_{(n,m)} \left(x_{M_{(n,m)}} \int_{\lambda_1}^{\lambda_2} \varepsilon(\lambda)_{M_{(n,m)}} d\lambda \right)}{x_{M,total}} = C_{total} x_{M,total} L \overline{\varepsilon}_M$$
(2)

Total absorbance of all semiconducting species ($A_{SC,total}$) can be expressed in a similar manner as in eq (3),

$$A_{SC,total} = \sum_{(n,m)} A_{SC_{(n,m)}} = \sum_{(n,m)} \left(\int_{\lambda_{3}}^{\lambda_{4}} \varepsilon(\lambda)_{SC_{(n,m)}} C_{SC_{(n,m)}} L d\lambda \right)$$

$$= C_{total} x_{SC,total} L \frac{\sum_{(n,m)} \left(x_{SC_{(n,m)}} \int_{\lambda_{3}}^{\lambda_{4}} \varepsilon(\lambda)_{SC_{(n,m)}} d\lambda \right)}{x_{SC,total}} = C_{total} x_{SC,total} L \overline{\varepsilon}_{SC}$$
(3)

where, x_{SC} is the actual composition of semiconducting species in SWNT mixture.

Background correction of UV-vis-nIR absorption spectra

Background spectra for HiPco and laser SWNT are different from each other due to the different preparation conditions. To overcome this issue related to background for two different types of SWNT, background correction was performed for all samples as done in our previous study.¹ When SWNT are covalently functionalized with diazonium reagent, absorption spectra originating from Van Hove transition of SWNT decay due to electron transfer from SWNT to diazonium reagents. Therefore, the absorption spectrum of fully reacted SWNT represents the background spectrum originating from carbonaceous impurities besides SWNT. Based on this assumption, we fully functionalized HiPco and laser SWNT with para-hydroxybenzene diazonium and used those absorption spectra as backgrounds, as shown in Figure S1 below.



Figure S1. Original spectra and their corresponding background: (a) HiPco, (b) Laser SWNT

Background substracted absorption spectra of SWNT samples were deconvoluted into individual metallic and semiconducting SWNT, based on the peak assignments reported in the literatures. In the case of HiPco SWNT (as shown in Figure S2), absorption spectra in the range of 490 ~ 625 nm were assigned to metallic SWNT ($E_{11,m}$) and those in the range of 625 ~ 920 nm were assigned to semiconducting SWNT ($E_{22,sc}$). In the case of laser SWNT, absorption spectra in the range of 560 ~ 770 nm were assigned to metallic SWNTs ($E_{11,m}$) and those in the range of 770 ~ 1100 nm were assigned to semiconducting SWNTs ($E_{22,sc}$).



Figure S2. Peak deconvolution and assignment for HiPco (left) and laser (right) SWNT.

Device fabrication

Each separated sample was diluted in 1 wt. % sodium dodecyl sulfate aqueous solution and bathsonicated in order to minimize ambiguity due to multiple nanotubes and bundles. Silicon substrate with 100 nm thermal oxides was treated with 2 vol. % 3-aminopropyl triethoxysilane for better nanotube adhesion. 10 µL of SWNT solution taken using a glass capillary (Drummond Scientific) was sprayed over the substrate, followed by DI rinsing and N₂ drying the substrate. Nanotubes appeared to be slightly aligned along the gas flow. Detailed deposition procedure can be found in Hedberg et al.² AFM (Dimension 3100, Digital Instruments) was performed to check the SWNT coverage. The above steps were repeated until desired coverage $(0.3 \sim 0.7 \text{ nanotubes/}\mu\text{m}^2)$ was obtained. Figure S3a shows optical image of patterned Pd electrodes. Pads A-B, B-C and C-D serve as source/drain electrodes for device 1, 2, and 3, respectively. The devices are back-gate from the bottom silicon substrate. Scale bar represents 50 μ m. Figure S3b shows SEM image of the channel region (scale bar = 1 μ m). Gap sizes are 300 nm (device 1), 600 nm (device 2), and 900 nm (device 3). Electrical testing confirms that nanotubes bridge the gap in 491 out of 6,000 devices (overall hit rate = 8.2 %). Hit rates for each sample can be found in Table S1. Lower hit rates guarantee a higher chance of getting single-tube devices. Most nanotubes (447/476, 94 %) were found in the smaller gaps (300 nm and 600 nm) as expected. Total numbers of prepared substrate were 1, 2, and 2 respectively for the control, M-enriched, and SC-enriched samples. For each substrate, 600 devices (Pd electrodes, 300 nm thick) were patterned in 1 cm² area using e-beam lithography, with the direction of SWNT alignment taken into account. Gap sizes were 300 nm, 600 nm, and 900 nm for the device number 3n+1, 3n+2, and 3n+3 (n=0, 1, 2, ..., 199), respectively. The devices Ar (1000 sccm)/ H_2 (250 sccm) for 20 min to improve the electrical contact. were then annealed in 500 An automated probe station performed electrical testing on total of 3,000 devices with the silicon substrate serving as a back gate electrode.



Figure S3.

Table S1. Summary of hit rate, % electronic enrichment of metallic over semiconducting SWNT.

Separation	SWNT	Sample	Hit rate	Composition	
method	300101	Sample	Thi Tate	Metal	Semiconductor
Electro- phoresis	HiPco	Control	13.2 %	40.5 %	59.5 %
			(158/1200)	(64/158)	(94/158)
		SC-enriched	6.6 %	24.1 %	75.9 %
			(79/2100)	(19/79)	(60/79)
Density gradient	Laser Ablation	Control	16.5 %	47.5 %	52.5 %
			(99/600)	(47/99)	(52/99)
		SC-enriched	2.6 %	22.6 %	77.4 %
			(31/1200)	(7/31)	(24/31)
		Menriched	9.1 %	78.9 %	21.1 %
			(109/1200)	(86/109)	(23/109)

For each sample in Table S1 transfer characteristics at V_d =-1.5V from all the devices are shown below. Electronic type (metallic:M, semiconducting:S) and on/off current ratio values are also reported.

















Electrophoresis / HiPco / SC-enriched (sample1): M (9), SC (15)



Electrophoresis / HiPco / SC-enriched (sample2): M (10), SC (45)















Density gradient / Laser / SC-enriched (sample2): M (2), SC (8)











Figure S4. Transfer characteristics of all the 476 devices. Electronic type and on/off ratio values for each device are reported.

Percent of single-tube devices

AFM was performed on 26 metallic devices from one of the two M-enriched laser SWNT samples (sample 1, coverage ~ 0.3 nanotubes/ μ m², hit rate = 6 %) to estimate the number of nanotubes per device. It turned out that 16 of them (62 %) were single-SWNT devices, and 5 devices (19 %) had 2 SWNT across the gap. The devices with 3 and 4 nanotubes count 4 (15 %) and 1 (4 %), respectively. AFM images below are 5 μ m-wide.



	Device	# of SWNT	E-type
	10	3	М
	11	2	М
	13	1~2	М
L S	14	3	М
	15	1	М
	16	1	М
no SWNT crossing	17	1	Μ
does not cross			
	19	1	М
and a state of the	22	1	М



Figure S5. AFM images from 26 devices showing the number of nanotubes per device.

Per-tube mobility calculation

Per-tube field effect mobility (μ_{tube}) was calculated from $\mu_{tube} = L/(V_dC_t) \times (dI_d/dV_g)$.² L represents the channel length. Gate capacitance per unit length for the quasi-one dimensional SWNT channel ($C_t = 3.62 \times 10^{-13} F/cm$) was estimated from $C_t = 2\pi\varepsilon\varepsilon_o/ln(2h/r)$,³ where ε , ε_o , h, and r denote dielectric constant (3.9 for SiO₂), vacuum permittivity, dielectric thickness (100 nm), and nanotube radius (0.5 nm), respectively. μ_{tube} values were then calculated for 253 semiconducting devices.

AFM images showing no significant length variation between samples

We have performed AFM on five samples before patterning electrodes. There is no significant length variation between samples. The result confirms that the separation procedures (electrophoresis, and density gradient centrifugation) used in our study do not alter SWNT length distribution.



HiPco / Electrophoresis Separation / Control SWNT

HiPco / Electrophoresis Separation / SC-enriched SWNT





Laser / Centrifugation Separation / M-enriched SWNT



Laser / Centrifugation Separation / SC-enriched SWNT



Figure S6. AFM on all five samples used in this study

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