Probing Carbon Nanotube-Surfactant Interactions with Two-Dimensional DOSY NMR

Supporting Information

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Sorting metallic and semiconducting carbon nanotubes of similar surface area: Arc-discharge P2-SWCNTs (Carbon Solutions, Inc) were added to an aqueous solution of 1.5 % (weight/volume) sodium cholate at a loading of 8 mg/mL and horn sonicated (Fisher Scientific Model 500 Sonic Dismembrator) using a 3 mm diameter tip at 20% amplitude for 1 hour (~12 W power). The dispersion was centrifuged in 2 mL Eppendorf vials at 15,000 rpm for 1 hour and 45 minutes in a tabletop centrifuge in order to sediment out large bundles of SWCNTs, metal catalyst particles, and amorphous carbonaceous materials. The top 1.5 mL of supernatant was retained for sorting.

As previously described,[S1] a narrow diameter distribution of unsorted SWCNTs was obtained by centrifuging the SWCNT dispersion in 1.5 % w/v sodium cholate (SC). Specifically, 12 mL centrifuge tubes were loaded with 1.5 mL of 60 % iodixanol, and a linear density gradient of 20 % to 45 % ioxidanol was formed on top using a linear density gradient maker (Hoefer SG 15). The purified, unsorted nanotube dispersion was layered on top of the linear density gradient using an open-top 10 mL syringe and a 23G1 needle, allowing the solution to drip out on its own in order to avoid disturbing the gradient. All layers contained 1.5 % w/v SC. The solutions were centrifuged for 14 hours at 41,000 rpm in a Beckman Coluter SW 41 Ti swing bucket rotor. Fractions of 0.5 mm were extracted from the centrifuge tubes using a piston gradient fractionator (Biocomp Instruments) and analyzed using UV-vis spectroscopy (Agilent Cary 5000).

Appropriate narrow diameter distribution fractions were retained for use in semiconducting and metallic enrichments. Following established procedures,[S2] semiconducting SWCNTs were obtained by loading 12 mL centrifuge tubes with 1.5 mL of 60 % iodixanol and a linear density gradient from 15 % to 30 % iodixanol. The entire tube contained a co-surfactant ratio of 1:4 sodium dodecyl sulfate (SDS) to SC and an overall surfactant loading of 1 % w/v (0.2 % w/v SDS and 0.8 % w/v SC). For ~1.3 nm diameter metallic SWCNTs,[S1] centrifuge tubes were loaded with 1.5 mL of 60 % iodixanol and a linear density gradient of 20 % to 35 % iodixanol. The entire tube contained a co-surfactant ratio of 3:2 SDS:SC and an overall surfactant loading of 1.25 % w/v (0.75 % w/v SDS and 0.50 % w/v SC). The narrow diameter distribution of unsorted SWCNTs was brought to a concentration of 32.5 % ioxidanol and a co-surfactant ratio of 1:4 SDS:SC or 3:2 SDS:SC through the addition of appropriate amounts of iodixanol, SDS, and SC. This solution was injected at the interface of the linear gradient and the 60 % iodixanol layer for semiconducting sorting and approximately 5/6th of the way down the linear gradient for metallic sorting. Injection was carried out using a syringe pump (Harvard Apparatus Pump 11) at a rate of 0.1 mL/min. A solution of 1:4 SDS:SC or 3:2 SDS:SC in deionized water was carefully layered on top of the gradient using an open-top 10 mL syringe and 23G1 needle until the tubes were full to prevent collapsing during centrifugation. The solutions were centrifuged for 14 hours at 41,000 rpm in a SW 41 Ti rotor, and 0.5 mm fractions were collected and analyzed using UV-vis spectroscopy.

Diameter determination for metallic and semiconducting SWCNT solutions: For semiconducting SWCNTs, the diameter was determined from Raman spectroscopy (Nanophoton Raman-11) of a thin film and ground state absorption spectroscopy (Agilent Cary 5000) in solution. Semiconducting SWCNT thin films were prepared on glass slides using the previously established vacuum filtration and acetone transfer method.[S3] For Raman measurements, the S_{33} semiconducting transitions were excited using a 582 nm laser. The wavenumber of the peak corresponding to the radial breathing mode (RBM) was

correlated to the diameter of semiconducting SWCNTs using the relation w = A/d + B, where w is the wavenumber of the radial breathing mode, A = 234 cm^{-1}, B = 10 cm^{-1}, and d is the SWCNT diameter in nanometers.[S4] The average diameter was determined to be 1.4 nm from the RBM peak in Figure S1 at ~173.5 cm^{-1}.
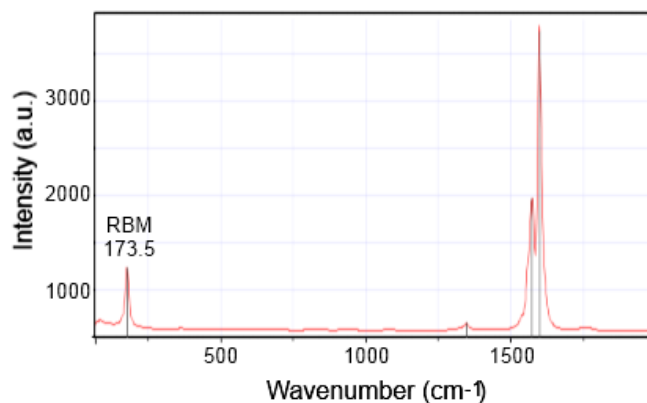

Figure S1. Raman spectrum of semiconducting carbon nanotubes with a narrow diameter distribution. The single radial breathing mode peak (RBM) at 173.5 nm confirms an average diameter of 1.4 nm.

The S$_{22}$ transitions seen in the ground state absorption spectrum in Figure S2 were fit to a series of Lorentzian peaks. The chirality of SWCNT corresponding to each of these peaks was determined through an empirical Kataura plot of the S$_{22}$ semiconducting transitions as observed in absorption experiments of surfactant-dispersed SWCNTs in aqueous solutions.[S5] From these chiralities and the relative areas of the Lorentzian peaks, an average diameter of 1.4 nm ± 0.1 nm is calculated.
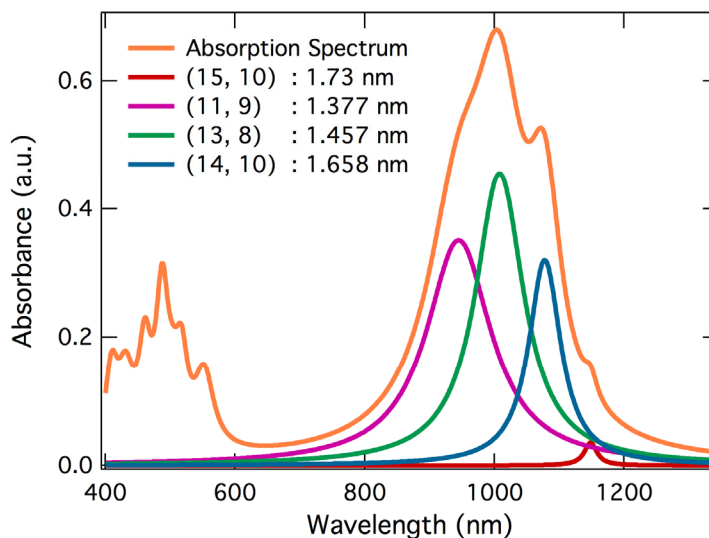
Figure S2. Ground state absorption spectrum of semiconducting SWCNTs, where the S_{22} transition is fit to a superposition of Lorentzian lineshapes. The chirality, labeled by its indices (n, m), and diameter of the SWCNT corresponding to each peak is listed in the legend of the graph as (n, m) : diameter.

While RBM relations also exist for metallic SWCNTs, the commonly excited M11 transitions for SWCNTs with diameters between 1.2 and 1.7 nm are clustered closely together between 650 nm and 800 nm at smaller intervals than the differences between available laser lines. Thus, accurate determination of the diameter distribution of metallic arc-discharge SWCNTs is difficult from Raman alone as all M11 transitions cannot be properly excited. Instead, we utilized a previous method by which the metallic SWCNT diameter is determined through UV-vis spectroscopy by fitting the M11 transition to a superposition of Lorentzian peaks (Figure S3). [S1] From this, the diameter was determined to be 1.3 nm ± 0.1 nm.
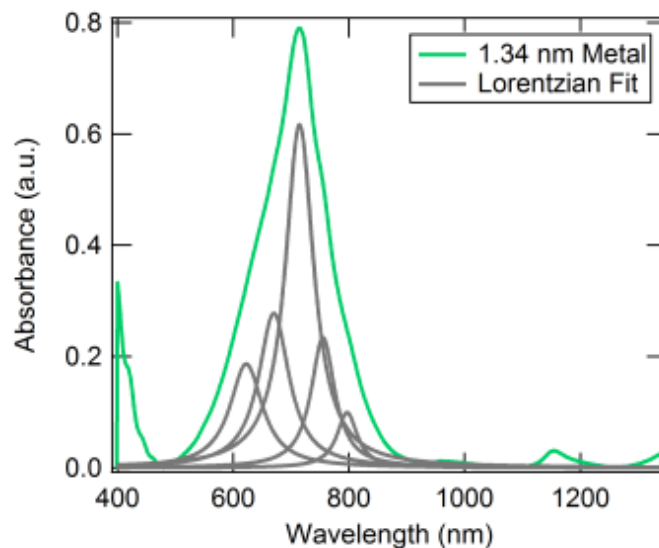
Figure S3. Ground state absorption spectrum of metallic carbon nanotubes with a narrow diameter distribution. The narrow range of the superposition of Lorentzian peaks leads to an uncertainty in diameter of 0.1 nm.

Determination of length distribution of metallic and semiconducting SWCNTs: Fractions of metallic and semiconducting SWCNTs were injected into dialysis cassettes (Slide-A-Lyzer 0.1 – 0.5 mL, 20,000 MWCO) and dialyzed in a 1750 mL bath of 1% SDS in deionized water for several days to get rid of excess iodixanol and sodium cholate. The bath was changed once a day for three days, and solutions were removed and briefly centrifuged (15,000 rpm for 1 min) to sediment large bundles of SWCNTs. The top 1 mL of supernatant was carefully decanted. The solutions were diluted 10x in deionized water to ensure isolation of single SWCNTs on the samples. Silicon wafers with a 300 nm thermally grown oxide were diced into 1 cm x 1 cm squares, sonicated in acetone, rinsed in IPA, and placed in a solution of 0.05 mM of 3-aminopropyltri(ethoxysilane) (APTES) in IPA. After 15 mins, substrates were removed, rinsed in IPA, and blow dried using a nitrogen air gun. The diluted SWCNT solutions were drop cast onto the substrates and allowed to sit for 15 mins. The droplets were blow-dried off the substrates, and the

samples were subsequently rinsed in deionized water and blow dried using nitrogen. Samples were

annealed at 400 C for 20 mins to burn off excess surfactant.

The samples were characterized by AFM using a Bruker Dimension FastScan AFM. Scans of 5

micron by 5 micron were taken over various areas of the substrate, and the length of the SWCNTs was

determined by tracing a line along the shape (either from height or phase) and determining the number

of pixels. At least 80 SWCNTs were counted for each of the semiconducting and metallic CNT

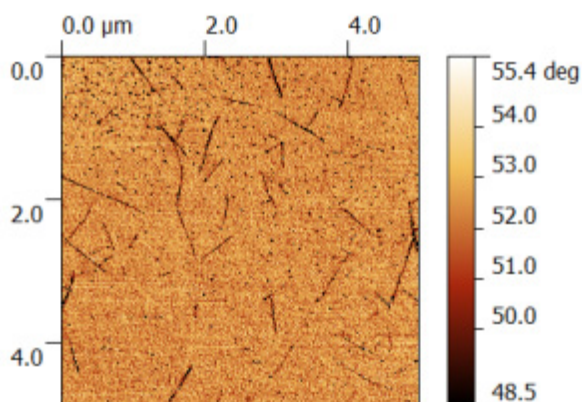distributions. A representative phase image is presented in Figure S4.

Figure S4. Representative AFM phase image used to quantify the length distribution of DGU-sorted

SWCNT samples

The length distributions shown in Figure 1B of the main text were fit to log-normal distributions

of the following form:

$$\text{counts} = A * e^{-\left(\frac{\ln(\text{length}/x_0)}{w}\right)^2} \tag{S1}$$

where the parameters for semiconducting SWCNTs were $A = 14$, $x_0 = 500$, $w = 0.9$, and the parameters

for metallic SWCNTs were $A = 11$, $x_0 = 500$, and $w = 1.1$.

Preparation of samples for 2D DOSY NMR: Surfactant-only samples were prepared by weighing SDS and SC powders to achieve the appropriate weight ratio and adding deuterium oxide. For SWCNT samples, fractions of metallic and semiconducting SWCNTs were injected into dialysis cassettes (Slide-A-Lyzer 0.1 – 0.5 mL, 20,000 MWCO) and dialyzed in a 1750 mL bath of either 1 % (w/v) 3:2 SDS:SC or 1:4 SDS:SC in deionized water. The bath was changed once a day for three days in order to exchange surfactants and remove excess iodixanol. The cassettes were then transferred to a 180 mL bath of either 1 % (w/v) 3:2 SDS:SC or 1:4 SDS:SC in deuterium oxide and dialyzed for 48 hours without changing the bath to replace water with deuterium oxide. Samples were removed and pipetted directly into NMR tubes for further experiments. The time between separation and dialysis and the total time of dialysis were kept strictly constant to ensure minimal and/or equal bundling of the SWCNTs before characterization.

It should be noted that the exchange of deuterated water for H_2O during dialysis also results in the removal of the majority of the density gradient medium, iodixanol, though a small amount may continue to be adsorbed on the SWCNT-surfactant complex. Iodixanol may play a role in electronic-structure discrimination during the DGU process, but its presence was not detected in the NMR data. Thus, we are not able to comment on the role of iodixanol in electronic-type discrimination.

DOSY NMR experiments: ^{1}H NMR spectra were measured using a Bruker Avance-III 600 MHz spectrometer. DOSY spectra were recorded using Bruker's "dstebpgp3s" program with a diffusion delay (D) of 0.15 s and gradient length (δ) of 2500 μs for each sample. T1, and the 90° pulse width, were independently measured prior to running the DOSY experiment, and the spectra were recorded with a delay of 15 s (greater than 5x T1) between scans in order to guarantee sufficient relaxation of the magnetization. The gradient strength was varied from 5 % to 95 %. The data were processed using the Bayesian DOSY Transform (BDT) within the MestReNova 7.0.2 software package, where the processing

parameters for the BDT were set with the Resolution Factor equal to 10, two repetitions, and 128 points in the diffusion dimension.

Peak identification: Figure S5 shows the ^{1}H NMR spectra for SDS and SC used to identify the surfactants in subsequent experiments. Here, the red traces are the spectra recorded from the single surfactant samples, and the blue traces are from the 1:4 SDS:SC surfactant-only solution. Figure S5A shows the traces for SC while Figure S5B shows the traces for SDS in the single-surfactant and two-surfactant solutions. In a similar manner, traces in other samples were compared to identify the two surfactants.
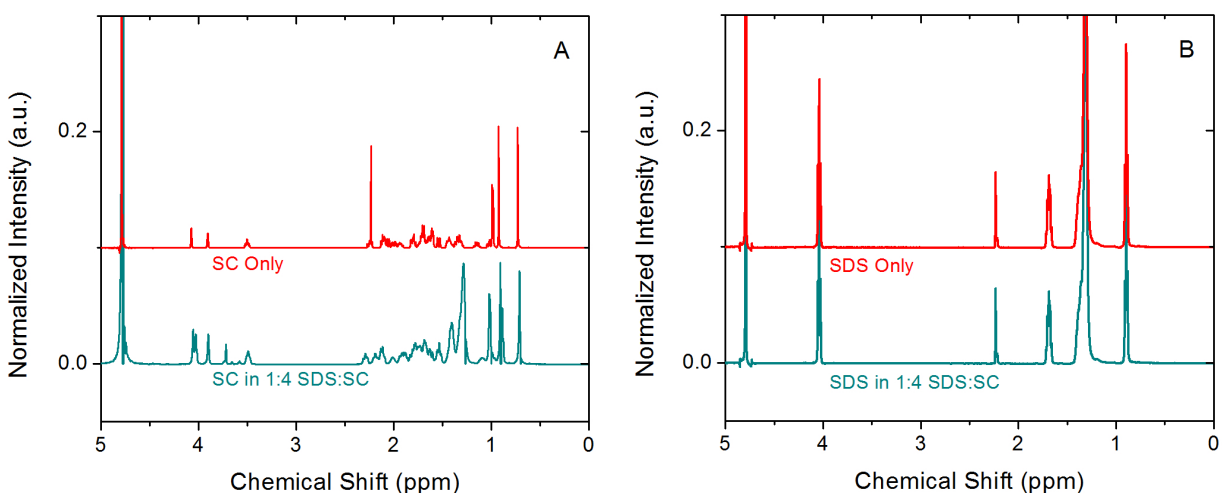

Figure S5. Chemical shift (ppm) vs intensity for ^{1}H NMR spectra of SC (A) and SDS (B). The red traces show the single surfactant proton spectrum while the blue traces are taken from the co-surfactant ratio 1:4 SDS:SC to identify the two surfactants.

Calculation of micelle size: Micelle size was calculated from the peak diffusion constant in the 2D DOSY spectra using the Stokes-Einstein relation given by:

$$D \frac{kT}{6\pi\eta r} \tag{S2}$$

where D is the diffusion constant (cm^2s^{-1}), kT is thermal energy (4.11×10^{-21} J at room temperature), η is the solvent viscosity (1.25×10^{-9} J·s·cm^{-3}), and r is the micelle radius (cm). The peak diffusion constants of 1.69, 2.10, and 1.52 cm^2s^{-1} for the SDS, SC, and SDS+SC free micelles lead to the calculated micelle radii of 1.03, 0.83, and 1.15 nm.

2D DOSY NMR plots of SWCNTs in co-surfactant solutions: Figure S6 shows the full 2D DOSY NMR plots for the 1:4 SDS:SC and 3:2 SDS:SC solutions with semiconducting and metallic SWCNTs, analogous to Figure 2 of the main text. The integration of all chemical shifts versus diffusion coefficient is plotted on the left (leading to the traces plotted in Figure 4 of the main text), while the integration of all diffusion coefficients versus chemical shift is plotted on the top. Table S1 summarizes the peak diffusion constants extracted from the plots in Figure S6 (and those in Figure 4 of the main text).
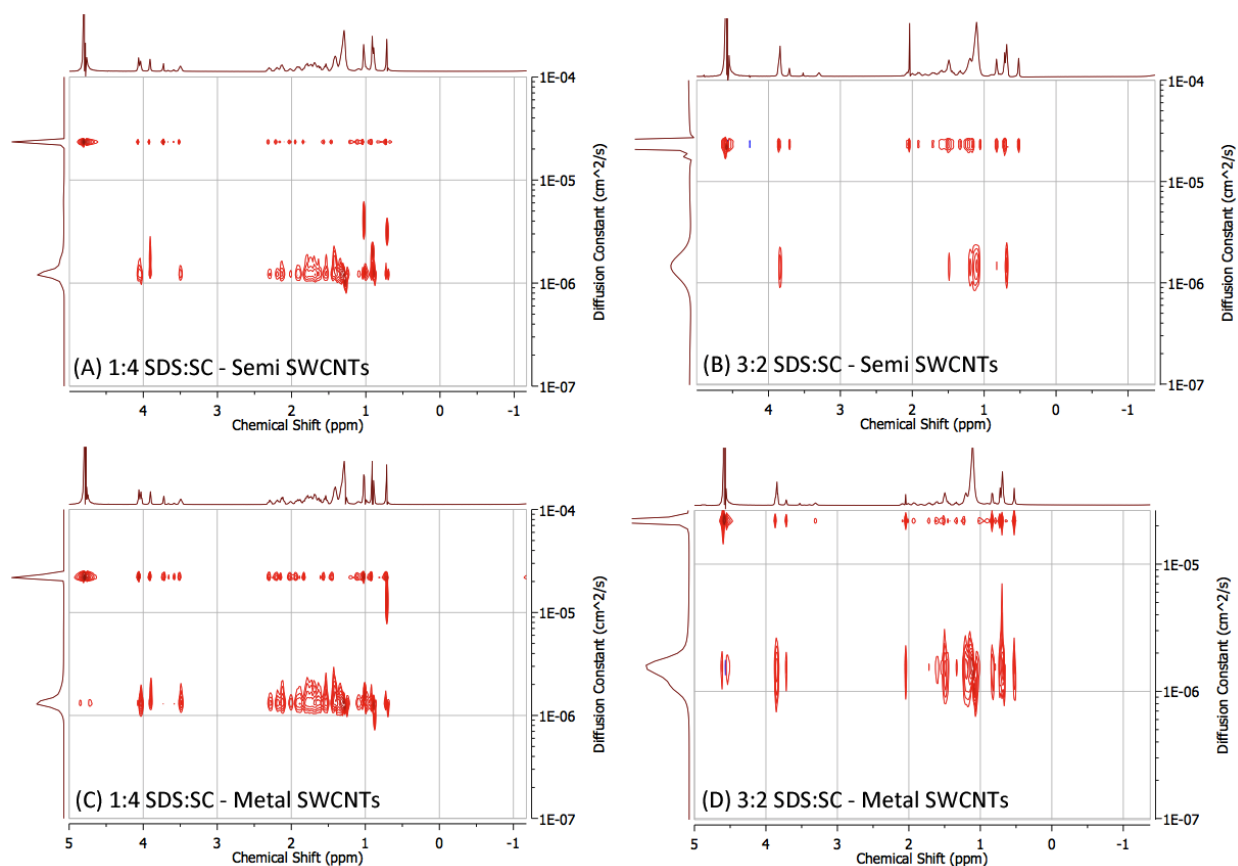
Figure S6: 2D DOSY NMR plots of chemical shift (ppm) versus diffusion constant (cm^2s^{-1}) for semiconducting SWCNTs in (A) 1:4 SDS:SC and (B) 3:2 SDS:SC and metallic SWCNTs in (C) 1:4 SDS:SC and (D) 3:2 SDS:SC. In all plots, the species diffusing faster than 10^{-5} cm^2s^{-1} is H_2O arising from impurities in the deuterated water and sonicated single surfactant molecules unable to form micelles that interact with H_2O.

Table S1. Summary of peak diffusion constants of SDS and SC with and without metallic and semiconducting SWCNTs in 1:4 SDS:SC and 3:2 SDS:SC surfactant ratios

Sample	Surfactant Ratio (SDS:SC)	SDS Diffusion (10^{-6} cm^{2}s^{-1})	SC Diffusion (10^{-6} cm^{2}s^{-1})
Surfactant Only	1:4	1.69	2.10
Semi SWCNTs	1:4	1.22	1.53*
Metal SWCNTs	1:4	1.30	1.51*
Surfactant Only	3:2	1.52	1.52
Semi SWCNTs	3:2	1.36	1.36
Metal SWCNTs	3:2	1.73	1.44

*Values are approximate due to broad distribution

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[S2] Arnold, M. S.; Green, A. A.; Hulvat, J. F.; Stupp, S. I.; Hersam, M. C. *Nature Nanotechnol.* **2006**, *1*, 60.

[S3] Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. *Science*, **2004**, *305*, 1273.

[S4] Dresselhaus, M. S.; Dresselhaus, G.; Saito, R.; Jorio, A. *Phys. Rep.* **2005**, *409*, 47.

[S5] Weisman, R. B.; Bachilo, S. M. *Nano Lett.* **2003,** *3*, 1235.