Supplementary Information

Separation of Double-Wall Carbon Nanotubes by Electronic Type and Diameter

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1. Additional RZU Fractions

Fig. S1 Additional RZU fractions not included in Fig. 1 of the main text. F2 and F8 are mostly featureless and are thought to contain nanotube aggregates and other carbonaceous impurities. F4 features a mixture of sharp and broad electronic transitions, suggesting the presence of both small and large diameter SWCNTs.

2. ATPE Method Validation



Fig. S2 Comparison of NIR fluorescence intensity for the parent SWCNT-DWCNT sample before (black) and after (red) being processed in an aqueous two-phase system. Constant emission intensity indicates that no inner nanotubes are extracted during the separation process. Spectra were acquired with 650 nm excitation.

Recent studies have demonstrated that the inner SWCNT shells of DWCNTs can be successfully extracted and collected through a combination of intense sonication followed by density gradient ultracentrifugation.¹⁻² The extraction process is thought to be enabled by low inter-shell frictional forces³⁻⁵ and from nanotube cutting induced by strong sonication.⁶⁻⁸ In light of these observations, we explored the possibility of inner shell removal facilitated by the differential affinity of the inner and outer nanotubes for the two different polymer phases. To monitor the relative concentrations of smaller diameter SWCNTs, NIR fluorescence measurements were acquired for the parent SWCNT-DWCNT sample both before and after ATP separation. Surfactant conditions were set at 0.1 % DOC and 0.6 % SDS so that the smaller diameters would have a greater affinity for the bottom dextran phase while the larger outer diameters would have a higher affinity for the top PEG phase. Fig. S2 shows that strong fluorescence is observed from the sample before separation, likely arising from individual SWCNTs produced during the growth process or by SWCNTs extracted from DWNCTs through the sonication procedure used for dispersion. Sample fluorescence does not increase (including both top and bottom phases of the ATP system), however, even after 10 repeated cycles of mixing and centrifugation in the two-phase polymer system. Since inter-wall coupling is thought to greatly suppress inner-shell fluorescence,⁹⁻¹⁰ a constant emission signal indicates that no additional inner SWCNTs are removed through ATPE. This validates the technique as a viable DWCNT separation method.

3. Raman Characterization of DWCNT APTE Diameter Sort



Fig. S3 Raman characterization of DWCNT samples isolated through RZU and further separated using ATPE. RBM modes of diameter-sorted larger bandgap semiconducting fractions were acquired using 514 nm (a) and 633 nm (b) excitation. RBM modes of diameter-sorted smaller bandgap metallic fractions were acquired using 633 nm (c) and 785 nm (d) excitation. Light blue shaded regions denote RBM intensities relating to DWCNT outer walls. In general, RBMs of both the inner and outer walls are found to shift to smaller wavenumbers (i.e. larger diameters) with decreasing SDS concentration used during ATP extraction (from bottom to top in each plot). The trend is in good agreement with the corresponding absorption spectra found in Fig. 3 of the main text. Raman spectra are normalized and vertically offset for easy comparison.

4. AFM Characterization



Fig. S4 (a) Representative AFM image from which diameter (b) and length (c) distributions are computed for the RZU and ATPE sorted 3BTB sample.

5. Size Exclusion Chromatography (SEC) of Cheap Tubes SWCNT-DWCNT Parent Material



Fig. S5 Absorption spectra of 14 different SEC fractions. To highlight differences in peak-to-baseline ratio, spectra are normalized to 1 at 900 nm.

SEC was performed following a previously published procedure.¹¹ Briefly, a GE ÄKTA Purifier HPLC system in conjunction with SEC columns (21.2mm × 250 mm, Sepax Technologies Inc., Newark, DE) packed with 5 µm silica-based beads were used for fractionation. Three columns with pore size of 2000 Å, 1000Å, and 300 Å were used in series, with a flow rate of 4 mL/min, and a typical injection volume of 4 mL of CNT dispersion. The samples were eluted with either 1% SC or 1% SDC. Fractions of 5 mL were collected and named sequentially from A1 to A15, followed by B1 to B15.

Although both arising from the same raw nanotube source, recent studies have shown that DWCNTs possess average lengths that are longer than their SWCNT counterparts.¹²⁻¹³ To test

whether this was true for our nanotube material, the parent Cheap Tubes SWCNT-DWCNT suspension was length sorted via SEC. Fig. S5 shows absorption spectra of 14 sequential SEC fractions. To compare peak-to-baseline ratios, all spectra are normalized by background absorption at 900 nm. If DWCNTs have average longer lengths, then we would expect the DWCNTs to elute out first followed by the SWCNTs. We find, however, that all SEC sorted fractions contain a mixture of both sharp and broad absorption features in the spectral region of (900 to 1300) nm, suggesting the presence of both small diameter SWCNTs and large diameter SWCNTs. We conclude from this data that the SWCNTs and DWCNTs in our samples possess similar average lengths. We also note that the peak-to-baseline ratio steadily decreases with increasing fraction number, consistent with the previous observed trend of higher absorption baselines for shorter nanotube samples.¹¹ This is thought to be due to a higher density of structural defects and kinks found in the shorter nanotube populations.

6. Metallic Fraction Extracted from a Single-Step Redox Separation of the Parent SWCNT-DWCNT Material



Fig. S6 Absorbance spectra of the last fraction extracted from a redox separation of the parent SWCNT-DWCNT mixture. This fraction is thought to contain a mixture of small and large diameter quasi/metallic SWCNTs along with smaller bandgap DWCNTs.

7. Analytical Ultracentrifugation (AUC)

In AUC, sedimentation velocity (SV) experiments are applied to determine a sedimentation coefficient, *s*, defined as the terminal velocity of the particle normalized by applied acceleration. This constant describes the sedimentation rate of a particle in a particular medium and can be related to various properties such as size, shape, and density:

$$s \equiv \frac{u}{\omega^2 R} = \frac{V_p(\rho_p - \rho_s)}{6\pi a \eta_s (f/f_0)}$$

(S1)

where u is the sedimentation velocity, ω is angular velocity, R is radial distance from the center of rotation, V_p is particle volume, ρ_p is particle density, ρ_s is solution density, a is the radius of a mass equivalent sphere, η_s is solution viscosity, f is the frictional coefficient of the sedimenting solute, and f_0 is the frictional coefficient of an equivalent mass sphere. Through eqn (S1), it is evident that by measuring s for the same population of particles (thus keeping ρ_p , V_p , and f/f_0 constant) in different solutions of varying density and viscosity, the unknown densities of the particles can be extracted.

7.1 Absorption Spectra of Fractions Analyzed by AUC



Fig. S7 Comparison of absorbance spectra for the RZU-3BTT and REDOX-3BT samples analyzed using AUC. The similarity of the spectra suggests that the two samples are of comparable average diameter.

7.2 AUC Data Analysis

Radial absorbance scans acquired in AUC experiments were analyzed using SEDFIT version 14.6e.¹⁴ The c(*s*) model was used to calculate the distribution of sedimentation coefficient, s, values that best fit the experimental data over a range from (0 to 50) Sv with a resolution of 0.17 Sv (300 points). The frictional coefficient was allowed to float during initial analysis and was fixed at an average value during subsequent analyses. This value was 5.5 for the anhydrous particle and 2.0 for the buoyant particle. The regularization parameter, P, was set to 0.95. Initial guesses for the partial specific volume, $\bar{\nu}$, of the surfactant-coated DWCNT were

calculated for an estimated model DWCNT using literature parameters. Based on the absorbance spectra, a model DWCNT comprised of a (15,8) outer SWCNT and a (7,6) inner SWCNT with an (exterior wall carbon center to carbon center) diameter of 1.58 nm was chosen as representative for the calculation. From geometric factors, and the previously reported packing density of DOC on an open (i.e. filled with the bulk solvent) SWCNT of similar size,¹⁵ an initial estimate of 0.6283 cm³/g was calculated. This value was iterated in the data analysis of the density of the sedimenting solute is determined.

AUC data from some experiments were also analyzed using the two-dimensional spectrum analysis (2DSA) in Ultrascan.¹⁶ When compared, *s* values calculated using the 2DSA analysis in Ultrascan fell within the *s*-distributions extracted using the c(s) model in SEDFIT (Fig S8). For more information on AUC data analysis and the models utilized in each fitting program, readers are asked to consult the following sources. ^{15, 17-18}



Fig. S8 Comparison of s extracted from 2DSA analysis in Ultrascan with the s-distributions extracted from the c (s) analysis in SEDFIT. The c (s) distributions from SEDFIT are denoted by

black lines and *s* values extracted from Ultrascan are plotted as blue symbols. Note that the two panels are of different samples, REDOX-3BT and RZU-3BT from left to right respectively.



7.3 Verification of Dilute Regime for AUC Analysis

Fig. S9 Average sedimentation coefficient of the REDOX-3BT sample evaluated at different sample optical densities (*i.e.* concentrations) as well as at different wavelengths. Black symbols denote *s*-values extracted from samples prepared to have various optical densities at $\lambda = 277$ nm. Samples with OD higher than 0.8 at $\lambda = 277$ nm were evaluated at $\lambda = 480$ nm, a wavelength at which the OD of the sample would be 1/3 the OD at 277 nm. Blue symbols denote samples prepared to have an OD = 0.2, 0.4, and 0.8 at $\lambda = 277$ nm but were evaluated at $\lambda = 355$ nm. Filled symbols represent average *s*-values extracted from data analysis in SEDFIT and open symbols represent average *s*-values extracted from data analysis in Ultrascan. The data shows that the sedimentation coefficient of the REDOX-3BT sample is independent of concentration in the regime evaluated. It also shows that regardless the wavelengths chosen to probe the sample ($\lambda = 277$ nm, 355 nm, or 480 nm), the population of particles analyzed remains constant. Finally, the data in this figure also show that average sedimentation coefficients determined using the 2DSA analysis in Ultrascan or the c (*s*) model in SEDFIT are very close in value. The solutions for all experiments was 10 g/L DOC in H₂O.

7.4 AUC Solution Characterization

Table S1 Densities and viscosities for 1 % DOC solutions of varying $\rm H_2O/D_2O$ and $\rm H_2O/iodixanol.$

Solution	ρ _s (g/cm³)	η (mPa-s)
1% DOC H ₂ O	1.00044	1.060
1% DOC D ₂ O	1.10663	1.316
1% iodix 1% DOC H ₂ O	1.00566	1.084
2% iodix 1% DOC H ₂ O	1.01097	1.108
3% iodix 1% DOC H ₂ O	1.01634	1.134
4% iodix 1% DOC H ₂ O	1.02107	1.158
6% iodix 1% DOC H ₂ O	1.03139	1.215
9% iodix 1% DOC H ₂ O	1.04801	1.315
12% iodix 1% DOC H_2O	1.06474	1.431

7.5 Densitometry Measurements for Buoyant Density Determination



Fig. S10 *s*-distributions for RZU-3BTT sample in solutions containing varying concentrations of iodixanol (10 g/L DOC).



Fig. S11 *s*-distributions for REDOX-3BT sample in solutions containing varying concentrations of iodixanol (10 g/L DOC).

7.6 Estimation of DOC Linear Packing Density for the RZU-3BTT sample

A model (7,6) @ (15,8) DWCNT was chosen for the estimation of linear packing density, which possesses an outer-wall diameter similar to that of the analyzed samples. A schematic of the model DWCNT is shown in Figure S12.



Figure S12. Schematic of a (7,6) @ (15,8) DWCNT. As seen here, a DWCNT is composed of two SWCNTs concentrically oriented with respect to each other. The diameter of a DWCNT is equal to the diameter of the outer SWCNT.

First, calculate the mass (*m*), volume (*V*), and density (ρ) for bare DWCNT:

- a. Assume concentric (15,8) and (7,6) SWCNTs; the (15,8) SWCNT has 189.6 carbon atoms/nm and (7,6) SWCNT has 105.8 carbon atoms/nm
- b. Mass/nm of bare DWCNT, *m*_{DWCNT}, is:

$$m_{DWCNT} = \frac{\left(\frac{carbons}{nm}in \ (15,8) \ and \ (7,6) \ SWCNTs\right) x \ MW_{carbon}}{Avogadro's \ Number} = \frac{(189.6 + 105.8) \ carbons}{nm} \left(\frac{12.011 \ g}{mol}\right) \left(\frac{1 \ mol}{6.022 x 10^{23} \ atoms}\right) = \frac{5.897 \ x \ 10^{-21} g}{nm}$$

c. Volume/nm of DWCNT, V_{DWCNT} , is: $V_{DWCNT} = \pi (r_o^2 - r_i^2) L = \pi [(0.962 \text{ } nm)^2 - (0.271 \text{ } nm)^2)](1 \text{ } nm) = 2.677 \text{ } nm^3$ d. Thus, density of bare DWCNT (meaning DWCNT with no DOC) is:

$$\rho = \frac{mass}{volume} = \frac{5.897 \times 10^{-21} g}{2.677 \ nm^3} \left(\frac{10^7 nm}{1 \ cm}\right)^3 = 2.237 \frac{g}{cm^3}$$

From previous experiments, it is known that the density of DOC is 1.295 g/cm³.

- a. The mass of one DOC molecule, m_{DOC} , is: $m_{DOC} = 414.5695 \frac{g}{mol} \left(\frac{1 \ mol}{6.022 \times 10^{23} \ molecules} \right) = 6.88 \ x \ 10^{-22} \frac{g}{DOC \ molecule}$
- b. Thus, the volume occupied by one DOC molecule, V_{DOC} , is:

$$V_{DOC} = \frac{m}{\rho} = \frac{(6.88 \times 10^{-22} g) cm^3}{1.295 g} = 5.313 \times 10^{-22} cm^3 = 0.5313 nm^3$$

Using the relation below, the linear packing density (LPD) of DOC can be estimated from the experimentally determined anhydrous density value measured for the RZU-3BTT sample:

$$\rho_{an} = \frac{(LPD * m_{DOC} + m_{DWCNT})}{(LPD * V_{DOC} + V_{DWCNT})} = \frac{(LPD * (6.88 x 10^{-22}g) + 6.083 x 10^{-21}g)}{(LPD * 0.5313 + 2.677) x 10^{-21} cm^3}$$

After plugging in the experimentally measured ρ_{an} value of 1.702 g/cm³, we calculate a LPD of 6.2 DOC/nm.

7.7 Estimating SWCNT/DWCNT Composition from Anhydrous Densitometry Data

To estimate the composition of SWCNTs and DWCNTs found in the REDOX-3BTT sample, *s*-distributions obtained from the ρ_{an} measurements were deconvoluted into contributions from both SWCNT and DWCNT sedimentation. DWCNTs were assumed to possess a ρ_{an} similar to that of the RZU-3BTT sample (1.702 g/cm³) while ρ_{an} for the SWCNTs was calculated based on the model of a (15,8) SWCNT and a linear DOC packing density of 6.2 DOC molecules/nm, see below:

$$\rho_{SWCNT-DOC} = \frac{(m_{SWCNT} + m_{DOC})}{(V_{SWCNT} + V_{DOC})} = \frac{(6.2 x (6.88 x 10^{-22} g) + 3.79 x 10^{-21} g)}{(6.2 x 0.5313 + 1.692) x 10^{-21} cm^3} = 1.616 \frac{g}{cm^3}$$

s-distributions for both SWCNTs and DWCNTs were generated from eq (1) in the main text, assuming a normal distribution of lengths centered around 400 nm and ranging from 200 to 1000 nm (Fig. S4). The mass of the sedimenting particle was calculated based on the mass of the DWCNT or SWCNT along with the mass of the DOC adsorbed on each type of particle. For data modeling, it was assumed that the linear packing density of DOC on the DWCNTs and SWCNTs was 6.2 DOC/nm. The partial specific volume, \bar{v} , is equal to ρ_{p}^{-1} ; thus, $\bar{v} = 0.588$ cm³/g for the DWCNT-DOC particles and $\bar{v} = 0.619$ cm³/g for the SWCNT-DOC particles. The friction coefficient of the DWCNTs and SWCNTs was calculated using slender body theory (Batchelor) as previously applied for carbon nanotubes:³

$$f = 6\pi\eta L \frac{Y^3 + 0.614Y^2 + 0.638Y + 0.0135}{2Y^4 + 0.614Y^3 + 0.544Y^2 - 0.136}$$
 (Eqn. 3)

where f = friction coefficient, $\eta =$ the viscosity of the bulk medium, L = the length of the particle, $Y = \ln(L/r_{an})$, and r_{an} is the anhydrous radius of the particle. Here, since both the DWCNTs and SWCNTs in the sample are approximately the same diameter, it was assumed that both types of particles have $r_{an} = 1.404$ nm which was calculated as the anhydrous radius of the RZU-B3TT DWCNT sample dispersed in 10 g/L DOC.

After calculating *s* for DWCNT-DOC and SWCNT-DOC particles of varying length, a weighted average (top 40 %) of the sedimentation coefficients was taken. This calculation was performed for DWCNT-DOC and SWCNT-DOC particles in solutions with ρ and η matching all those which were experimentally tested. The calculated DWNCT and SWCNT *s* values described above were then applied to deconvolute the experimentally measured *s* values (in each H₂O/D₂O solution condition) into contributions from both DWCNT and SWCNT populations. The results of this analysis are shown in Table S2 below.

Table S2 Deconvolution of experimentally measured *s*-values for the REDOX-3BT fraction in different density solutions into contributions from SWCNTs and DWCNTs.

Solution	DWCNT s _{avg} (Sv)	SWCNT s _{avg} (Sv)	Experimental s _{avg} (Sv)	Φυνοντ	φswcnt
0% D ₂ O	22.86	16.75	20.05	0.539	0.461
20% D ₂ O	21.18	15.36	18.60	0.557	0.443
40% D ₂ O	19.63	14.16	16.93	0.506	0.494
60% D ₂ O	18.21	13.07	15.99	0.569	0.431
80% D ₂ O	16.89	12.06	14.69	0.544	0.456
100% D ₂ O	15.69	11.13	13.54	0.528	0.472



Fig. S13 Comparison of experimental SW-DWCNT *s*-distributions with simulated SWCNT and DWCNT *s*-distributions in 40 % (a) and 100 % (b) D_2O solutions. Simulated DWCNT *s*-distributions are represented by purple lines. Simulated SWCNT *s*-distributions are represented by blue lines. *s*-distributions for REDOX-3BT sample extracted from experimental data are represented by the black curves. All s-distributions are normalized to 1 by the highest distribution intensity.

7.8 Estimating SWCNT/DWCNT Composition from *s*-distributions measured at higher iodixanol concentrations

Alternatively, one can also obtain an estimate of SWCNT and DWCNT composition in the REDOX-B3T sample by simply integrating the area under each SWCNT (A_{SWCNT}) and DWCNT (A_{DWCNT}) peak in the *s*-distributions measured at higher iodixanol concentrations (Fig. 6). Relative nanotube concentrations are then computed by dividing the area of each peak by the total area, $A_{total} = A_{SWCNT} + A_{SWCNT}$. The results of this analysis for measurements performed at all three different iodixanol concentrations can be found in Table S3. The average composition of SWCNTs and DWCNTs was calculated to be 45.2 % and 54.8 %, respectively, agreeing well with the values obtained from the densitometry data. It should be noted that many *s*-distributions contain long tails at higher Sv values which we attribute to small concentrations of aggregates in the sample. Contributions from these tails were excluded when computing the relative concentrations of SWCNTs and DWCNTs.

The same type of analysis can be applied to the RZU-3BTT sample to estimate the fraction of contaminating SWCNTs. The results of this analysis come out to be \approx 93% DWCNTs

and 7% SWCNTs. We note that this SWCNT concentration is likely an upper limit, as noise in the distribution (especially in the regions of the tails) might influence the integration procedure.

Table S3 SWCNT and DWCNT compositions calculated from *s*-distributions of the REDOX-3BT sample in solutions containing high concentrations of iodixanol.

Sample	φswcnt	Фрисит
6% iodixanol	0.44	0.56
9% iodixanol	0.455	0.545
12% iodixanol	0.461	0.539

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