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Quantitative comparison of ultracentrifuged and diluted single walled nanotube dispersions; differences in dispersion quality

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We have carried out a quantitative comparison of the dispersion quality for ultracentrifuged and diluted surfactant-stabilised single walled nanotube dispersions. We have characterised these dispersions at a set concentration of $\sim 30 \mu\text{g.mL}^{-1}$ by absorption and photoluminescence spectroscopy as well as by statistical atomic force microscopy. Both the ultracentrifuged and the diluted samples contained significant quantities of bundles as well as individual nanotubes. The ultracentrifuged sample contained ~ 4 times more individualised SWNTs than the diluted sample with partial concentrations of individual nanotubes of 4.8 and $1.1 \mu\text{g.mL}^{-1}$ respectively.

Introduction

In recent years, a significant amount of research has been carried out in the area of dispersion and exfoliation of single walled nanotubes (SWNTs) in the liquid phase. In general, pristine nanotubes can be dispersed in a small number of special solvents(1-5) or in a wider range of solvents, but particularly water, with the aid of third phase dispersants such as polymers(6,7), surfactants(8-11) or biomolecules like DNA(12-20). Alternatively, nanotubes can be dispersed in super-acids(21) or by covalent functionalisation(22,23).

However, the most common technique is to disperse SWNTs in water with the aid of surfactants or DNA. Ultrasonication is generally used to promote exfoliation followed by vigorous ultracentrifugation (UCF) to remove most of the bundles(10,11,19,24,25). This produces a dispersion that is significantly enriched in individual nanotubes, but at the cost of typically more than 80% of the starting nanotube mass(10). While this has been a very successful method, it is also a very inefficient one, especially given the high cost of high-quality nanotubes. An alternative to ultracentrifugation is to control the population of individual nanotubes in a dispersion by controlling nanotube concentration(1,2,4,8,12,16,26,27). This relies on the observation that nanotubes tend to debundle as the concentration is lowered. This technique is less wasteful and allows the researcher greater control over the properties of the final sample, however, highly exfoliated samples often only exist at low concentrations which limits potential applications.

Thus, each technique has distinct advantages and disadvantages. A comparative study of these two processes would be beneficial in order to directly compare the sizes of the objects (small bundles and individual nanotubes) in the dispersions generated by each technique. This would provide answers to questions such as 1) does ultracentrifugation remove all bundles from the dispersion and, if not, what is the distribution of bundle diameters, and 2) at a given concentration, are there differences in the diameter distribution of samples prepared by each method? In this work, we have produced dispersions by both ultracentrifugation and dilution of the same starting SWNT dispersion. This gave two dispersions with almost identical nanotube concentrations. We have used absorption and photoluminescence spectroscopy as well as statistical atomic force microscopy (AFM) analysis to elucidate the differences in dispersion quality between ultracentrifuged and diluted dispersions. In addition, we have investigated the effect of varying the initial surfactant and nanotube concentrations on the final sample quality.

Experimental Procedure

A solution of SDBS (Sigma Aldrich) was prepared at a concentration of $2 \text{ mg}\cdot\text{mL}^{-1}$ in D_2O (Sigma Aldrich) and left stirring overnight. This surfactant-concentration is well above the critical micelle concentration (CMC) of SDBS ($\text{CMC}_{\text{SDBS}} = 0.73 \text{ mg}\cdot\text{mL}^{-1}$ (28)). While exfoliated nanotubes have been observed in dispersions with surfactant-concentrations well below the CMC(29,30), $2 \text{ mg}\cdot\text{mL}^{-1}$ was shown to be the minimum SDBS-concentration necessary to obtain high fractions of dispersed nanotubes(27). Purified HiPCO SWNTs (www.cnanotech.com, Lot number PO342) were dispersed in the SDBS solution at a concentration of $1 \text{ mg}\cdot\text{mL}^{-1}$ as described elsewhere(27). Briefly, the dispersion was sonicated for 5 min with a high power sonic tip (Vibra Cell CVX; 750 W, 38%, 20 kHz), followed by 1 hr in a Branson 1510 sonic bath (frequency 42 kHz, rated power output 80 W), followed by a further 5 min under the sonic tip. Ice-water cooling was used throughout to prevent heating in the sample. The dispersion was left to stand for 24 hrs to equilibrate. It should be noted that, throughout this paper, the word concentration refers to the nanotube concentration unless otherwise stated.

Mild centrifugation (90 min at 5,500 rpm ($\sim 3,000g$)) was employed to remove any large micrometer-sized aggregates not dispersed during sonication(4,8,16,27). The supernatant was carefully decanted, giving a dispersion that contained both individual nanotubes and bundles with a wide range of diameters(8). The concentration of this dispersion was measured by UV-vis-IR absorption spectroscopy to be $0.24 \text{ mg}\cdot\text{mL}^{-1}$. This dispersion was used as a stock sample for all further dispersions.

A portion of the stock sample was ultracentrifuged at 122,000g for 4 hrs using a Beckman-Coulter Optima L-100 XP Ultracentrifuge. Again, the supernatant was carefully decanted, giving a second sample which was rich in individual SWNTs. The concentration of this supernatant was measured by UV-vis-IR to be 0.03 mg.mL^{-1} . A third sample was prepared by diluting the stock sample to match the concentration of the ultracentrifuged sample. This dispersion was diluted with the SDBS solution in order to keep the surfactant-concentration well above the CMC, as is required to produce stable samples(8,31). The sample was sonicated with the sonic tip for 5 minutes in ice-water and left to equilibrate for 24 hrs.

UV-vis-NIR absorption spectra were recorded for all samples using a Varian Cary 6000i. The concentration of each sample was calculated from the absorbance at 660 nm, using an extinction coefficient of $3389 \text{ mL.mg}^{-1}.\text{m}^{-1}$ as measured by Bergin et. al. for similar SDBS-SWNT dispersions(8). NIR-PL line spectra were recorded using an Edinburgh Instruments FLS920 fluorescence spectrometer with a Hamamatsu R5509 NIR photomultiplier tube in order to probe the individual semiconducting nanotubes. The samples were excited at a wavelength of 650 nm, and emission was detected over a wavelength range of 900-1400 nm. A $2 \text{ mm} \times 2 \text{ mm}$ quartz cuvette was used for all measurements. This small cuvette is matched to the geometry of the spectrometer and reduces the reabsorption and inner filter effects which are seen in high concentration samples(8,32).

AFM analysis was carried out in order to determine the sizes of nanotube/bundle in the samples. AFM samples were prepared by soaking silanised silicon substrates(33) in the dispersions overnight. The samples were then immersed in Millipore water for 20 min to remove excess SDBS and dried under vacuum at room temperature. All samples were imaged using a multimode Nanoscope III atomic force microscope in tapping mode. POINTPROBE silicon cantilevers with typical tip diameters of $\sim 50 \text{ nm}$ were used throughout. Diameter and length distributions were obtained for each sample by measuring the height and length of 150 different nanotubes randomly selected from different points on the silicon substrate.

Results and Discussion

Absorption spectra for the stock sample (after mild centrifugation); the ultracentrifuged sample; and the diluted sample are shown together in the inset of Figure 1. The concentration of the stock sample was 0.24 mg.mL^{-1} , illustrating that 76 wt% of the starting dispersion was lost during the initial mild centrifugation. The concentration of the ultracentrifuged (UCF) sample was 0.03 mg.mL^{-1} , equating to a loss of 87.5% nanotubes by weight relative to the stock sample. Including the initial mild centrifugation, the UCF sample lost 97% of its mass compared to the original starting dispersion. The

concentration of the diluted sample (DLT) was found to be 0.028 mg.mL^{-1} , close to the target value of 0.03 mg.mL^{-1} . The absorption spectra for the DLT sample and the UCF sample are shown together in Figure 1. It is clear that, although both samples are of similar concentration, the UCF sample exhibits much sharper, better defined absorption peaks. It has been found that, when comparing similar samples, sharper peaks often indicate a better dispersion with a greater number of individual nanotubes(10,34,35). Thus, the absorption spectra suggest that the UCF sample may contain a greater number of individual nanotubes.

Figure 2 shows PL line spectra for all three samples. Individual semiconducting SWNTs emit in the NIR, while the presence of metallic nanotubes leads to quenching in bundles. Thus, to a first approximation, only individual semiconducting nanotubes fluoresce(10). At low concentrations, the PL emission can be considered to be proportional to the partial concentration of individual nanotubes in the dispersion (total mass of individuals per volume). However, it is important to note that at higher concentrations, inner-filter and reabsorption effects lead to a significant reduction in intensity(32). In this case, the concentrations of the UCF and DLT samples are low enough that inner-filter and reabsorption effects are negligible. The abundance of individual nanotubes in each sample can thus be investigated by comparing the samples' PL intensities. It was found that the UCF sample displayed approximately 3 times more intense PL, suggesting the presence of ~ 3 times more individual nanotubes than the DLT sample. Interestingly, both samples have the same spectral shape (see Figure 2 inset), so it can be inferred that both ultracentrifugation and dilution give similar individualised populations of each (n,m) tube type. This suggests that for all chiralities, the UCF sample contains approximately 3 times more individual nanotubes than the DLT sample. The PL from the stock dispersion was the least intense of all samples. However, this can be attributed to inner-filter and reabsorption effects due to the high sample concentration(32) and thus, the PL intensity is not proportional to the mass of individual nanotubes in the dispersion.

AFM analysis was carried out to compare nanotube/bundle sizes in all samples. Diameter distributions and typical AFM images are shown in Figure 3 for all three samples. The stock dispersion had a broad distribution of bundle diameters ranging up to $D \sim 10 \text{ nm}$, but with small numbers of bundles with diameters as large as 45 nm . The diameters and distribution widths are much smaller for the two less concentrated samples than for the stock sample, regardless of whether the concentration was reduced by removing nanotubes (ultracentrifugation) or adding surfactant solution (dilution). In each case, the majority of objects have diameters below 3 nm . It has been suggested that ultracentrifugation removes all bundles from the dispersion, leaving a dispersion that contains only individual SWNTs(10,19,32,36). However, previous studies on DNA-SWNT dispersions have shown that small bundles remained in solution even after vigorous ultracentrifugation(16). Here it was found

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that a small, but significant population of small bundles remained in the dispersion after ultracentrifugation. In fact, a significant number of bundles had diameters of up to 4 nm, with a few bundles having diameters as great as 10 nm.

A range of parameters can be calculated from bundle diameter distributions, allowing one to quantitatively compare different dispersants and different processing techniques(4,8,12,16,27). All parameters for the UCF and DLT samples are shown together in Table 1, allowing easy comparison. It was found that in all cases the UCF sample was superior to the DLT sample. The measurements/calculations for these parameters are shown elsewhere(4,8,16).

The mean diameter was found to be $\langle D \rangle = 4.8 \pm 0.5$ nm in stock sample, reducing to just $\langle D \rangle = 1.5 \pm 0.1$ nm in the UCF sample, as compared to $\langle D \rangle = 2.4 \pm 0.3$ nm in the DLT sample. Mean lengths were calculated and found to be $\langle L \rangle = 420.3 \pm 21.8$ nm and $\langle L \rangle = 315.0 \pm 22.8$ nm for UCF and DLT samples respectively. The shorter lengths observed in the DLT dispersion can be attributed to increased sonication-induced nanotube breakage in the sample due to the extra 5 min tip sonication during sample preparation. It was not possible to calculate length distributions for the stock sample, due to overlapping of the nanotubes/bundles. We can calculate the population of individual SWNTs by counting the number of objects observed with $D < 1.4$ nm. The fraction of individual nanotubes (N_i/N_T) was calculated, ranging from just 27% in the stock sample, to 72% in the UCF sample, and 51% in the DLT sample. Hence, as predicted by the PL and absorbance data, the ultracentrifuged sample contained a greater population of individual nanotubes.

While it is known that a large fraction of individual nanotubes can be obtained by reducing the sample concentration(8,27), the low concentrations involved are often impractical for many applications. Thus it is useful to have a measurement that accounts for both the concentration and the debundling in the system. One such measurement is the total number of objects per unit volume solution (N_T/V), which would be maximised if large numbers of individual nanotubes and very small bundles could be obtained at high concentrations. Measured values of $N_T/V = 16.3 \mu\text{m}^{-3}$ and $N_T/V = 4.8 \mu\text{m}^{-3}$ were observed for the UCF and DLT samples respectively. The latter value is typical of values previously reported for diluted SDBS-SWNT dispersions of similar concentrations(8,27). However, the former value is much higher than previously observed for diluted surfactant dispersions, where maximal values were found to be between 5.4 and $7.5 \mu\text{m}^{-3}$ depending on surfactant type(27). Another useful quantity to evaluate is the number of individual nanotubes per unit volume (N_i/V). Again, the UCF sample was found to be superior with a value of $N_i/V = 11.7 \mu\text{m}^{-3}$ as opposed to $N_i/V = 2.5 \mu\text{m}^{-3}$ in the DLT sample.

Two other useful parameters are the mass-fraction of individual nanotubes (M_i/M_T) and the partial-concentration of individual nanotubes (M_i/V) (4,16), which allow for the fact that most of the nanotube mass can be contained in a just few bundles. Again the UCF sample was found to be superior to the DLT sample with a mass-fraction $M_i/M_T = 0.16 \pm 0.03$ as opposed to $M_i/M_T = 0.04 \pm 0.01$ and a partial-concentration $M_i/V = (4.8 \pm 0.9) \times 10^{-3} \text{ mg.mL}^{-1}$ as opposed to $M_i/V = (1.1 \pm 0.3) \times 10^{-3} \text{ mg.mL}^{-1}$. These latter figures mean that there are 4.3 ± 2 times more individual SWNTs in the UCF sample than the DLT sample. As mentioned previously, the PL intensity is proportional to the partial-concentration of individual nanotubes in the dispersion. It was found that the PL from the UCF sample was approximately three times greater than the DLT sample. Thus, the difference in PL intensity can be fully explained by the difference in the partial-concentrations of individual nanotubes in the two samples within error. We note that this also means that the PL intensity is a good proxy for M_i/V .

Both samples discussed above had surfactant- and nanotube concentrations of 2 mg.mL^{-1} and $\sim 0.03 \text{ mg.mL}^{-1}$ respectively. We were unable to fully analyse samples with higher surfactant-concentrations, due to the formation of large-scale surfactant networks on the AFM substrates which prevented statistical analysis. However, the results discussed above show that the partial-concentration of individual nanotubes is well-reflected by the sample's PL intensity. This allows us to use spectroscopy for the analysis of samples as a function of surfactant- and nanotube concentrations.

Two new stock samples were prepared at a concentration of 1 mg.mL^{-1} with surfactant-concentrations of 5 mg.mL^{-1} and 2 mg.mL^{-1} respectively. The nanotube concentrations after mild centrifugation were found to be 0.5 mg.mL^{-1} (5:1) and 0.32 mg.mL^{-1} (2:1), showing that is 5 mg.mL^{-1} is a more effective surfactant-concentration for dispersing nanotubes. Two separate dilution series, with concentrations ranging from the 'stock' concentration down to 0.003 mg.mL^{-1} , were prepared by diluting the stock samples with their respective surfactant solutions. All dilutions were tip sonicated for 5 min and left to equilibrate for 24 hrs. As before, the samples were ultracentrifuged and the supernatant decanted off. The fraction of nanotubes remaining after ultracentrifugation was calculated from the absorbance and are shown in Figure 4A. In the 5:1 series, the fraction remaining was reasonably independent of the initial nanotube concentration with $(17.1 \pm 1.3) \%$ remaining. In the 2:1 series, the fraction remaining increased as the nanotube concentration decreased, ranging from 10.6 % to 29 % in the most and least concentrated samples respectively. A third 5:1 concentration series was prepared by diluting the 5 mg.mL^{-1} stock sample to match the concentrations of the 5:1 UCF series (after UCF). This allowed us to compare ultracentrifugation and dilution over a wider nanotube concentration range.

The partial-concentration of individual nanotubes (M_i/V) is well-represented by the PL intensity. Thus, assuming that the quantum efficiency is independent of surfactant concentration, we can easily compare M_i/V for each series. The intensities of the 1120 nm peak are shown in Figure 4B. Within each series, M_i/V decreases as the SWNT concentration decreases as observed previously for diluted samples(27). It is clear that the 5:1 UCF series outperformed both the 5:1 DLT series and the 2:1 UCF series at all concentrations. In fact, the 5:1 UCF series was between 2.2 and 7.5 times greater than the 5:1 DLT series. Interestingly, the 5:1 DLT series is of similar magnitude to the 2:1 UCF series. In order to compare the mass-fraction (M_i/M_T) in each series, we divided the PL intensity at 1120 nm ($\propto M_i/V$)(4) by the absorbance at 1120 nm ($\propto M_T/V$) to obtain a value that is proportional to M_i/M_T . In all samples, the data increased with decreasing SWNT concentration, again as observed on dilution.(27) As before, the 5:1 UCF series outperformed both the 2:1 UCF series and the 5:1 DLT series at all concentrations. The 2:1 UCF series was of similar magnitude to the 5:1 UCF series at low concentrations but dropped off at higher concentrations. In contrast, the 5:1 DLT series displayed low M_i/M_T at all concentrations studied. This work clearly shows that higher dispersion quality, as measured by the population of individual SWNTs, is achieved for ultracentrifuged samples compared to diluted samples. However, we note that the surfactant content plays a critical role as observed previously(27).

Conclusion

In conclusion, we found that all UCF samples contained a much greater fraction of individual nanotubes than the samples prepared by dilution. At a 2:1 ratio and a concentration of 0.03 mg.mL^{-1} , the UCF sample had more than three times more objects per unit volume (N_T/V) and more than four and half times more individual nanotubes per unit volume (N_i/V) as calculated by AFM. The PL from the UCF sample was a factor of three times more intense and sharper, better defined absorption peaks were observed. However, it should be noted that the ultracentrifugation does not remove all nanotube bundles from the dispersion, with 84% of the nanotube mass still contained in small bundles. In addition, 97% of the nanotube mass initially dispersed was lost during the two centrifugation steps. By comparison, samples prepared by dilution still contained a reasonably high fraction of individual nanotubes (51%) but with less waste, with 76% (by mass) lost during the initial mild centrifugation step. In addition, preparing samples by dilution allows the researcher much greater control over the final qualities of the dispersion.

We found that the mass fraction and the partial-concentration of individuals in the ultracentrifuged samples are dependent on the surfactant- and nanotube concentrations in the stock sample. We found that increasing the surfactant-concentration to 5 mg.mL^{-1} produced superior

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samples, while the partial-concentration of individuals was greatest when the initial nanotube concentration was maximised. However, the mass-fraction of individuals was maximised when an initial nanotube concentration of 0.01 mg.mL^{-1} was used. Thus, to maximise M_i/V , it is best to start with a high nanotube concentration, whereas to maximise M_i/M_T an initial nanotube concentration of 0.01 mg.mL^{-1} is best.

Ultracentrifugation and dilution have applications in different areas. Ultracentrifugation is clearly the best option for maximising the fraction of individual nanotubes in the dispersion. However, for many applications (e.g. composite formation) it is often sufficient to prepare samples that contain very large numbers of small bundles. Thus, for these purposes, dilution is clearly a less wasteful and more cost effective option.

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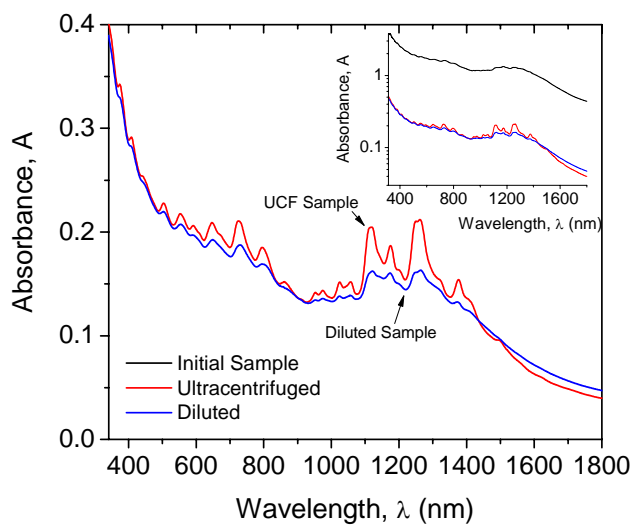


Figure 1: Absorbance spectra for the ultracentrifuged dispersion (red) and the diluted dispersion (blue) are shown above. The absorbance peaks are sharper in the ultracentrifuged sample. The inset is plotted on a log scale and includes the original dispersion (black) for comparison.

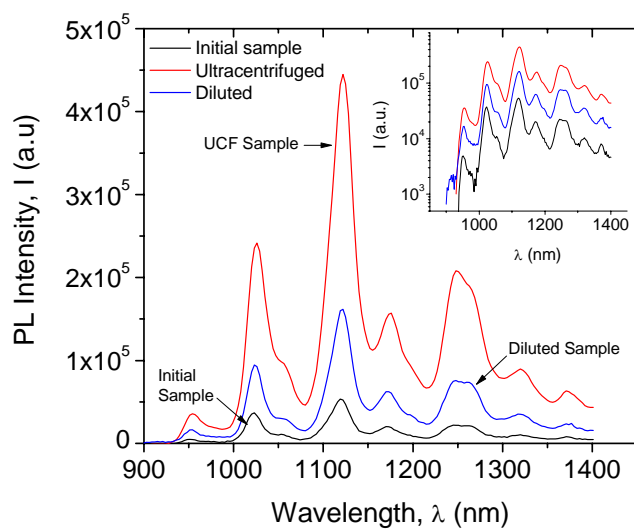
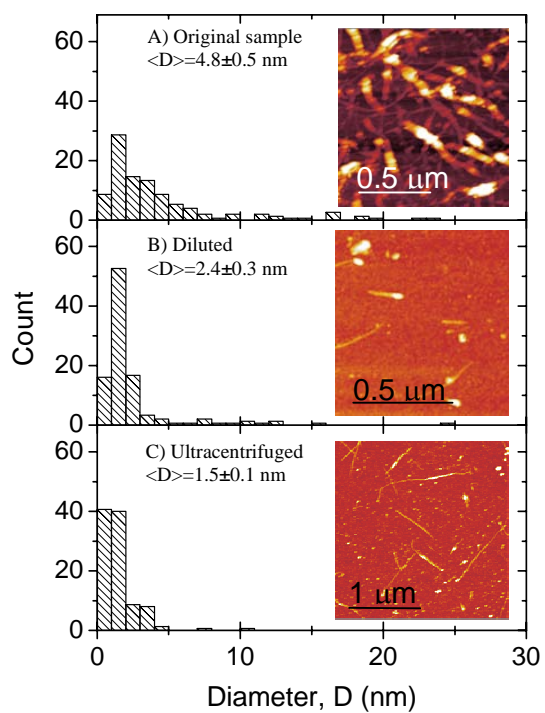


Figure 2: Photoluminescence spectra for all three dispersions. Due to inner filter and reabsorption effects, the stock dispersion has the lowest PL intensity. Inset: The same data on a log plot showing that all three curves have the same spectral profile.

**Figure 3**

Histograms of bundle diameters, plus a typical AFM image for all three dispersions are shown above.

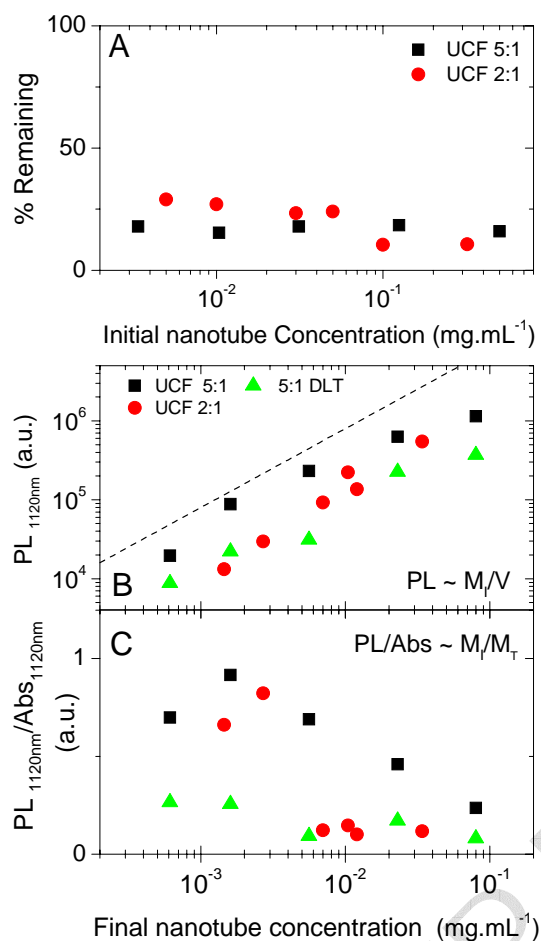


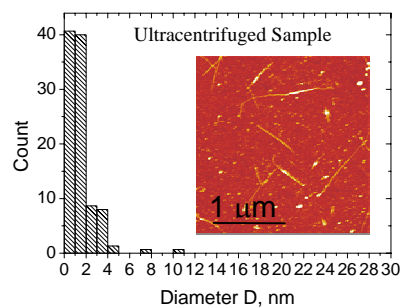
Figure 4: Spectroscopic data for nanotube dispersions after UCF as a function of both initial and final nanotube concentrations and for surfactant:nanotube ratios of 5:1 and 2:1. A) Percentage of nanotubes remaining after UCF as a function of initial nanotube concentration. B) PL intensity which we expect to be proportional to the mass of individual SWNTs per dispersion volume as a function of final nanotube concentration. The dashed line illustrates linearity. C) The ratio of PL intensity to absorbance (both at 1120 nm) as a function of final nanotube concentration. We expect this quantity to be proportional to the mass fraction of individual SWNTs.

	UCF Sample	Diluted Sample
C_{NT}	0.03 mg mL ⁻¹	0.028 mg mL ⁻¹
$\langle D \rangle$	1.48 ± 0.10 nm	2.44 ± 0.26 nm
D_{rms}	1.9 ± 0.2 nm	4.0 ± 0.6 nm
$\langle L \rangle$	420.3 ± 21.8 nm	315.0 ± 22.8 nm
N_i/N_T	0.72	0.51
M_i/M_T	0.16 ± 0.03	0.04 ± 0.01
M_i/V	(4.8 ± 0.9) × 10 ⁻³ mg mL ⁻¹	(1.1 ± 0.3) × 10 ⁻³ mg mL ⁻¹
N_{tot}/V	16.3 μm ⁻³	4.8 μm ⁻³
N_i/V	11.7 μm ⁻³	2.5 μm ⁻³

Table 1

Comparison of statistical parameters for UCF and diluted samples.

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We quantitatively compare dispersion quality and levels of nanotube exfoliation for nanotube dispersions prepared by both dilution and ultracentrifugation.

Graphical Abstract

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