High Weight Fraction Surfactant Solubilization of Single-Wall Carbon Nanotubes in Water

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ABSTRACT

We report a simple process to solubilize high weight fraction single-wall carbon nanotubes in water by the nonspecific physical adsorption of sodium dodecylbenzene sulfonate. The diameter distribution of nanotubes in the dispersion, measured by atomic force microscopy, showed that even at 20 mg/mL ~63 ± 5% of single-wall carbon nanotube bundles exfoliated into single tubes. A measure of the length distribution of the nanotubes showed that our dispersion technique reduced nanotube fragmentation.

Most applications employing the unique electronic, thermal, optical, and mechanical properties of individual single-wall carbon nanotubes (SWNTs)[1−13] will require the large-scale manipulation of stable suspensions at high weight fraction. Tube solubilization provides access to solution-phase separation methodologies[14−17] and facilitates chemical derivatization,[18] controlled dispersion and deposition,[19,20] microfluidics, fabrication of nanotube-based fibers[21,22] and composites,[23,24] and optical diagnostics.[25] Furthermore, high volume fraction suspensions will bring nanotube science into better contact with fundamental research on self-assembly in complex fluids.[26−28] Unfortunately, nanotubes aggregate easily and are difficult to suspend as a result of substantial van der Waals attractions between tubes.[29]

Thus far, some progress has been made toward the solubilization of SWNTs in both organic and aqueous media. Dissolution in organic solvents has been reported with bare SWNT fragments (e.g., 100−300 nm in length)[30,31] and with chemically modified SWNTs.[18,32,33] Dissolution in water, which is important because of potential biomedical applications and biophysical processing schemes, has been facilitated by surfactants and polymers[14,15,34−36] (with sodium dodecyl sulfate, SDS, the most widely used surfactant), by polymer wrapping,[37,38] and by chemical modification.[33,39−41] In most of these studies, however, the extent to which the suspended material exist as single tubes or small bundles of tubes has not been reported. Furthermore, tube aggregation in solution has not been well quantified.

In this paper, we report the creation of high weight fraction suspensions of surfactant-stabilized SWNTs in water with large fraction of single tubes. A single-step solubilization scheme was developed in which nanotubes were mixed with surfactants in low-power, high-frequency sonicators for long time periods; the scheme enhanced the disaggregation of bundles with dramatically reduced tube breakage. We have also discovered that a commercially available surfactant—sodium dodecylbenzene sulfonate (NaDDBS) consisting of a benzene ring moiety, a charged group, and an alkyl chain—enhances the stability of SWNTs in water by a factor on the order of 10 to 100 compared to that of other commonly employed surfactants and polymers. The fraction of single tubes at the highest concentration (20 mg/mL) was measured by atomic force microscopy (AFM) to be greater than 63%. New and quantitative insight about nanotube solubilization is derived from comparisons of single tube yield, measured by AFM, as a function of surfactant type, concentration, and sonication procedure.

Our nanotubes were obtained in purified form from Tubes@Rice (laser-oven SWNTs, batch P081600[42]) and Carbon Nanotechnologies Inc. (HiPCO SWNTs, batch 79[43]). The purified laser-oven nanotubes were >90 wt % SWNTs, and the HiPCO samples were 99 wt % SWNTs (0.5 wt % Fe catalyst). Typically, we mixed the base material with surfactant and sonicated the suspension in a low-power, high-frequency (12 W, 55 kHz) bath sonicator for ~16 to 24 h.

To evaluate competing stabilization characteristics, we explored the dispersing power of a range of surfactants: NaDDBS ($C_{12}H_{25}C_6H_4SO_3Na$), sodium octylbenzene sulfonate (NaOBS; $C_8H_{17}C_6H_4SO_3Na$), sodium butylbenzene sulfonate (NaBBS; $C_4H_9C_6H_4SO_3Na$), sodium benzoate ($C_6H_5CO_2Na$), sodium dodecyl sulfate (SDS; $CH_3(CH_2)_{11}$-OSO_3Na), Triton X-100 (TX100; $C_8H_{17}C_6H_4(OCH_2CH_2)_n$-

OH; $n \approx 10$), dodecyltrimethylammonium bromide (DTAB; $CH_3(CH_2)_{11}N(CH_3)_3Br$), dextrin, and poly(styrene)−poly-(ethylene oxide) (PS−PEO) diblock copolymer.

The first step toward solubilization was to find suitable concentration ratios of nanotube to surfactant. To this end, we mixed 0.01 mg/mL nanotube dispersions with various surfactant concentrations and sonicated the suspension for 24 h. A ratio was deemed suitable when the nanotubes dispersed and did not reaggregate after sonication. The optimum surfactant-dependent ratio of nanotube to surfactant varied from 1:5 to 1:10 by weight. The optimum ratio for NaDDBS was 1:10. For nanotube dispersions greater than 0.1 mg/mL, the input surfactant concentration usually exceeded critical micelle concentrations (CMCs); we did not, however, observe evidence of surfactant micelles or other phases. Presumably, most surfactant in suspension adsorbed onto the nanotube surfaces.[44,45]

The NaDDBS−nanotube dispersions, and one close relative, were by far the most stable; dispersed nanotube concentrations in NaDDBS ranged from 0.1 to 20 mg/mL. The resulting suspensions remained dispersed for at least 3 months; neither sedimentation nor aggregation of nanotube bundles was observed in these samples. By contrast, we were unable to prepare stable nanotube suspensions with the other additives at concentrations greater than 0.5 mg/mL. With the exception of NaOBS, a close relative of NaDDBS, reliable disaggregated dispersions in the other surfactants required nanotube concentrations of ~0.1 mg/mL.

Figure 1a exhibits vials of the nanotube dispersions in NaDDBS at 20 mg/mL after 2 months and in SDS at 0.5 mg/mL and in TX100 at 0.8 mg/mL, both after 5 days. We readily observe that the NaDDBS−nanotube dispersion is homogeneous, whereas SDS−nanotube and TX100−nanotube dispersions contain coagulated bundles of tubes at the bottom of their respective vials. Quantitative information about the distribution of the diameter and length of the dispersed nanotubes was derived directly by AFM. An example of an AFM image used for the analysis is shown in Figure 1b.

To obtain the AFM images and distributions, we deposited surfactant-stabilized nanotubes onto a silicon wafer. The tube surface density was sufficient for analysis when the nanotube suspension weight fractions were ≤1.0 mg/mL; suspensions with greater weight fractions (e.g., 20.0 or 10 mg/mL) were rapidly diluted to 1.0 mg/mL or 0.1 mg/mL and then spread over the silicon wafer for the AFM measurements. The AFM image quality was improved substantially by baking the resultant wafers at 180 °C in air for ~4 h; apparently, baking removes much of the surfactant from the wafer and tubes. AFM images were taken in tapping mode using a Nanoscope III Multimode (Digital Instruments Inc., Santa Barbara, CA). Digital Instrument-supplied software was used to derive the length and the diameter of every accessible nanotube. Tube diameters were derived from our height measurements, which had a resolution of 0.1 nm. Tube lengths were determined within our lateral resolution of 20−50 nm; it was difficult to characterize tubes accurately whose lengths were less than 50 nm, so their contributions are not reflected in the measured distributions.
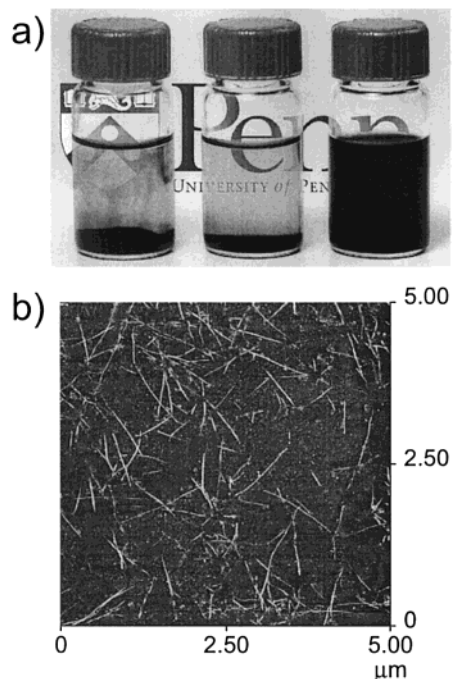

Figure 1. (a) Vials (6 mL) containing aqueous dispersions of (left to right) SDS−HiPCO at 0.5 mg/mL, TX100−HiPCO at 0.8 mg/mL, and NaDDBS−HiPCO of SWNTs at 20 mg/mL. SDS−HiPCO and TX100−HiPCO samples were imaged after sitting for 5 days whereas NaDDBS−HiPCO samples were imaged after 2 months of sitting at room temperature. NaDDBS−HiPCO suspensions appeared homogeneous whereas SDS−HiPCO and TX100−HiPCO suspensions had coagulated nanotubes in the body and at the bottom of the vials. (b) Tapping-mode AFM image of TX100-stabilized laser-oven-produced single-walled carbon nanotubes on a silicon surface. The nanotube suspension was prepared at 0.1 mg/mL by the bath sonicator.

A summary of the AFM observations is given in Figure 2. We examined ~300 tubes for each distribution plot. The shaded regions define single tubes; we assumed 1.3 and 1.5 nm as the upper bounds for a single tube diameter of HiPCO[46] and of laser-oven[43] nanotubes, respectively. The first four distributions are for NaDDBS−HiPCO dispersions. From Figure 2a, we see that a NaDDBS−HiPCO dispersion prepared at 0.1 mg/mL was ~74 ± 5% single tubes. This yield changed modestly as a function of increasing nanotube weight fraction; see Figure 2b and c. Furthermore, we measured the distribution from the 10 mg/mL suspension after allowing it to sit for 1 month; the single-tube fraction did not change appreciably (~54 ± 5%; Figure 2d). By contrast, HiPCO stabilized in SDS and TX100 at a concentration of just 0.1 mg/mL had SWNT yields of only ~16 ± 2% (Figure 2e) and ~36 ± 3% (Figure 2f), respectively.

The mean length (L_{mean}) of single tubes for the four NaDDBS−HiPCO distributions was ~165 nm with a standard deviation between 75 and 95 nm. The number of longer tubes (i.e., ≥300 nm) was observed to decrease slightly in the samples that were diluted to 1 mg/mL (distributions not shown). SWNT length distributions for SDS−HiPCO ($L_{mean} = 105$ nm ± 78 nm) and for TX100-HiPCO ($L_{mean} = 112$ nm ± 54 nm) were shifted a bit lower; generally, we did not find many long SWNTs using SDS or TX100.
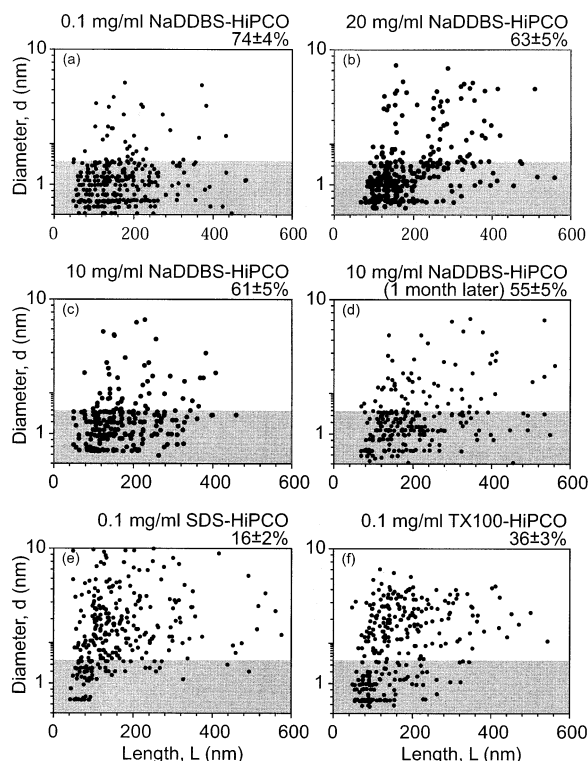
Figure 2. Length and diameter distribution of HiPCO tubes obtained from AFM images after dispersion by the bath sonicator and stabilization by three different surfactants. When the original suspension concentration was greater than 0.1 mg/mL, the dispersions were rapidly diluted to 0.1 mg/mL and then spread over a silicon wafer for the AFM distribution measurements. Note: the contributions of tubes whose lengths were less than 50 nm are not reflected in these distributions because the lateral resolution of our measurements made it difficult for us to detect them unambiguously. (a) The fraction of single tubes in a NaDDBS−HiPCO solution prepared at 0.1 mg/mL was ∼74 ± 5%. (b) We obtained ∼63 ± 5% single tubes when we prepared NaDDBS−HiPCO solution at 20 mg/mL. (c) A NaDDBS−HiPCO solution prepared at 10 mg/mL had ∼61 ± 5% single tubes. (d) The distribution did not change appreciably when we looked at the sample after a month (∼55 ± 5% single tubes). When we prepared 0.1 mg/mL HiPCO solution with SDS or TritonX-100 surfactant, the fractions of single tubes were (e) 16 ± 2% and (f) 36 ± 3%, respectively.

We now return to the solubilizing capabilities of the various surfactants. Any successful method must reckon with the substantial van der Waals attractions of bare tubes.[29]
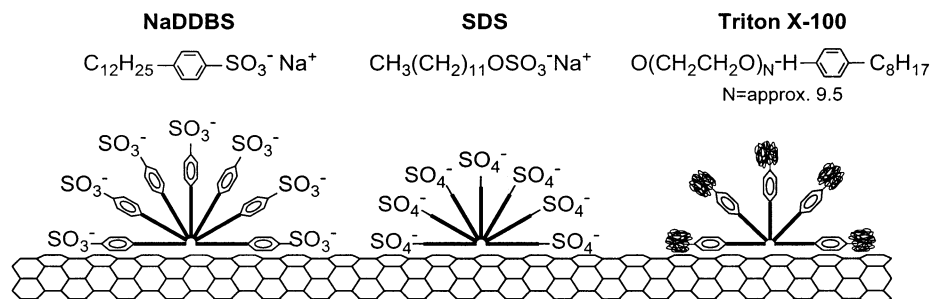
Speculation as to how our surfactants might adsorb onto the nanotubes is suggested in Figure 3; we believe the tubes are stabilized by hemimicelles[44,45,47] that sheath the surface. Molecular dynamics simulations are underway at the University of Pennsylvania to test these speculations. The superior dispersing capability of NaDDBS compared to that of SDS (dispersing capability ≤0.1 mg/mL) or TX100 (≤0.5 mg/mL) can be explained in terms of graphite−surfactant interactions, alkyl chain length, headgroup size, and charge as pertains *particularly* to those molecules that lie along the surface, parallel to the tube central axis. We suspect SDS has a weaker interaction with the nanotube surface compared to that of NaDDBS and TX100 because it does not have a benzene ring. Indeed π-like stacking of the benzene rings onto the surface of graphite is believed to increase the binding and surface coverage of surfactant molecules to graphite significantly.[47] Dextrin (<0.05 mg/mL) and DTAB (<0.1 mg/mL) also did not disperse nanotubes well because we believe that they do not have ring moieties.

The alkyl chain part of adjoining surfactant molecules probably lies flat on the graphitic tube surface.[44,45,47] Most of our surfactants had alkyl chains with lengths on the order of 2 nm. Thus, when adsorbing onto a small-diameter nanotube surface, it is probably energetically favorable for the chains to lie along the length of the nanotubes rather than to bend around the circumference. This chain interaction distinguishes TX100 (8-carbon alkyl chain) from NaDDBS and SDS (both have a 12-carbon alkyl chain). Longer chain lengths improve surfactant energetics, given similar rings and headgroups. For example, sodium benzoate (no alkyl chain, ≤0.01 mg/mL) and NaBBS (4-carbon alkyl chain, <0.1 mg/mL) have the same ring and headgroup size as NaDDBS but performed relatively poorly because of substantially shorter alkyl chain lengths. However, NaOBS (8-carbon alkyl chain, ≤8 mg/mL) performed quite well. Sodium hexadecylbenzene sulfonate had a longer alkyl chain (16 carbons) but did not dissolve in water at high concentration (≥5 wt %) at room temperature.

The different responses of NaDDBS and TX100 arise from different headgroups and chain lengths. The headgroup of TX100 (PEO chains) is polar and larger than that of NaDDBS (SO_3^-); its large size may lower its packing density compared to that of NaDDBS. Furthermore, the

Figure 3. Schematic representation of how surfactants may adsorb onto the nanotube surface. Tube stabilization depends on the surfactant molecules that lie on the tube surface parallel to the cylindrical axis. We speculate that the alkyl chain groups of a surfactant molecule adsorb flat along the length of the tube instead of the diameter. We believe NaDDBS and TX100 disperse the tubes better than SDS because of their benzene rings. NaDDBS disperses better than TX100 because of its headgroup and slightly longer alkyl chain (see text). The spacing between the benzene rings on the surfactants and the tube surface is large enough to accommodate the SO_3^- charged groups.
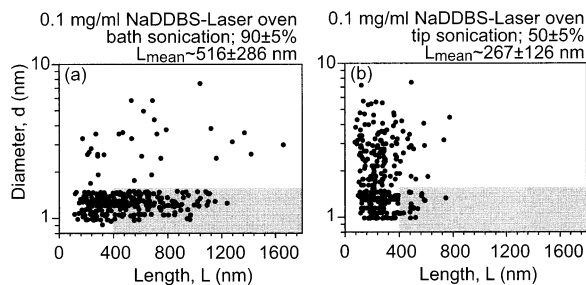
Figure 4. Length and diameter distribution of a 0.1 mg/mL laser-oven single-walled nanotube suspension dispersed by tip and bath sonicators and stabilized by NaDDBS. (a) The low-power bath sonication scheme made high-yield single tubes (90 ± 5%) and left many single tubes with lengths larger than 400 nm. L_{mean} was ~516 ± 286 nm. (b) The tip-sonication technique gave a significantly lower yield (50 ± 5%) and also fragmented the tubes. We observed only a few nanotubes with lengths longer than 400 nm; L_{mean} was ~267 ± 126 nm.

electrostatic repulsion of SO_3^- leads to the charge stabilization of tubes via screened Coulomb interactions that, by analogy with colloidal particle stabilization, may be significant for solubilization in water compared to the more steric repulsion of the TX100 headgroup. Generally, added salt (NaCl) of greater than 25 mM induced aggregation in the NaDDBS samples. PS−PEO diblocks, which had long PEO chains as headgroup, did not stabilize nanotubes well (≤0.1 mg/mL).

Last, we investigated the relative efficacy of different sonication techniques on the dispersion of nanotubes. Tube breakage is a critical parameter; SWNTs with large lengths (e.g., >500 nm) are often preferred because, for example, they introduce greater anisotropies into the properties of composites.[48] The standard approach is to disperse nanotubes using a high-power tip sonicator ($^1/_8$ in., 6 W, 22.5 kHz) for a short time (~1 h). For comparison, we prepared 0.1 mg/mL HiPCO tubes and laser-oven tubes in NaDDBS, SDS, and TX100 and measured the length and diameter distributions. The essential observations are summarized in Figure 4 for 0.1 mg/mL laser-oven tubes in NaDDBS. The nanotube dispersion prepared by bath sonication had a very high yield of single tubes (~90 ± 5%), a significant fraction of which were long single tubes with lengths longer than 400 nm (L_{mean} = 516 nm ± 286 nm); see Figure 4a. Similar samples prepared by tip sonication (Figure 4b) had lower SWNT yields (~50 ± 4%) and L_{mean} = 267 ± 126 nm. These effects were not as pronounced in HiPCO samples because the nanotubes were already rather short.

To summarize, we have demonstrated a simple scheme to solubilize high weight fraction single-wall carbon nanotubes in water. Suspension concentrations were improved by a factor of 10−100 with respect to commonly used surfactants, and the new sonication technique also dramatically reduced tube fragmentation. Preliminary transport measurements on these tubes suggest that our treatment does not alter the SWNT electronic properties. Single tubes prepared at high concentration by these means can now be used for the creation of novel composite materials, for the self-assembly of tubes in suspension, and for use as sensors in water.

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