

Dispersion of Single-Walled Carbon Nanotubes of Narrow Diameter Distribution

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The dispersibility and bundle defoliation of single-walled carbon nanotubes (SWNTs) of small diameter (<1 nm) have been evaluated on CoMoCAT samples with narrow distribution of diameters. As previously observed by photoluminescence and Raman spectroscopy, the CoMoCAT sample exhibits a uniquely narrow distribution of (n,m) structures that remains unchanged after different dispersion conditions. This narrow distribution allowed us to develop a method for quantifying the dispersability of the samples from their optical absorption spectra in terms of two ratios: the “resonance ratio” and the “normalized width.” The former is defined as the quotient of the resonant band area and its nonresonant background. The latter is defined as the ratio of the width of the band at half-height to the peak height on a spectrum that has been normalized at 900 nm, making this an intensive property, rather than varying with the path length. In this study of the CoMoCAT sample, we have used the S22 transition corresponding to the (6,5) nanotube to do these calculations, which is the most abundant species. These two ratios provide a quantitative tool to compare different dispersion parameters (time of sonication, degree of centrifugation, etc.) on the same type of sample. From this comparison, an optimal procedure that maximizes the spectral features was selected; this procedure allowed us to contrast various surfactants at different pH values and concentrations. Several surfactants were as good or even better than the one we have used in previous studies, dodecylbenesulfonic acid sodium salt (NaDDBS). Despite differences in their dispersion abilities, none of the surfactants investigated generated new features in the absorption spectra nor changed the distribution of nanotube types, which confirms that the high selectivity of the CoMoCAT sample is in the original sample rather than caused by selective suspension of specific (n,m) nanotubes.

Introduction

Single-walled carbon nanotubes (SWNT)^{1,2} are 1-D nanomaterials with unusual properties and attractive potential applications.^{3,4} Different methods, including arc discharge,⁵ laser ablation,⁶ and chemical vapor deposition,⁷ have been used to produce SWNT. Most of these methods yield nanotube products with a wide distribution of diameters and chiralities (helicities). Therefore, in most experimental investigations dealing with SWNT, it is not possible to study the properties of one specific nanotube type but rather an average of a very large number of them. The recently developed CoMoCAT method,⁸ (CO disproportionation on bimetallic Co–Mo catalysts supported on silica) produces SWNT of very narrow diameter and chirality distributions.^{9–12} Depending on the specific reaction conditions (temperature, pressure), the CoMoCAT material can be composed of a very small number of nanotubes, with one of them dominating. In particular, synthesis at 750 °C and 80 psig results in an SWNT material in which the dominant species is the (6,5) semiconducting type. Stable suspensions of this material in surfactant solutions provide a unique opportunity to study the optical absorption properties of one specific species, with little overlapping.

To get stable and homogeneous dispersions of nanotubes, various approaches including covalent and noncovalent stabilization of SWNT have been studied and reported in the literature. Although each of them has some specific advantages,

the noncovalent approach has been of particular interest since by this method the structure and properties of nanotubes are preserved. In the last several years, the noncovalent stabilization by surfactants or polymers has been widely used in the preparation of aqueous solutions with higher concentration or with higher fractions of individually dispersed SWNTs than those produced by other methods.^{13–15} Among the various surfactants investigated, sodium dodecyl sulfate (SDS)¹⁶ and sodium dodecylbenzene sulfonate (NaDDBS)¹⁷ are the most commonly used. Despite the relatively large number of studies on surfactant–SWNT interactions,^{18–20} further investigation on this approach is still important to gain a better understanding of the effects that play a role in the dispersion procedure as well as to determine the most suitable surfactants for a specific nanotube type.

In a typical dispersion procedure, after the surfactant has been adsorbed on the nanotube surface by hydrophobic or π – π interactions, ultrasonication for minutes or hours may help surfactants debundling (or exfoliating) nanotubes by Coulombic or hydrophilic interactions and so overcoming the van der Waals forces among individual nanotubes. Since an individual nanotube covered by surfactant molecules has a density similar to that of water,²¹ centrifugation at 20 000–170 000g for long periods of time has thought to be needed to separate carbonaceous impurities and large SWNT bundles from clean SWNT. Small-size bundles may be separated by an optional second sonication step, which can further increase the fraction of individual nanotubes in the suspension.²² Various surfactants/polymers have been compared with respect to their ability to suspend

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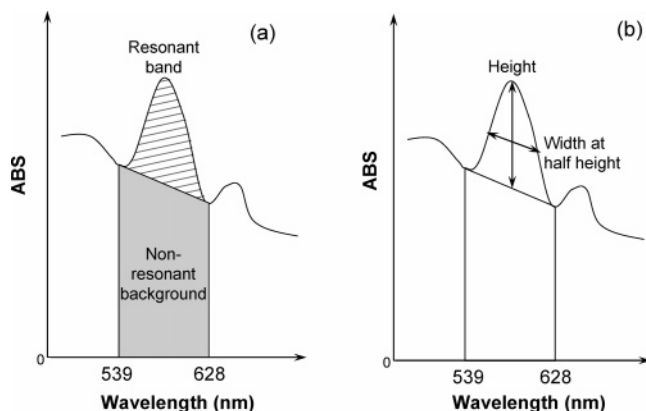


Figure 1. Estimation of (a) resonance ratio = (area of resonant band)/(area of nonresonant background); (b) normalized width = (width of resonant band)/(height of resonant band).

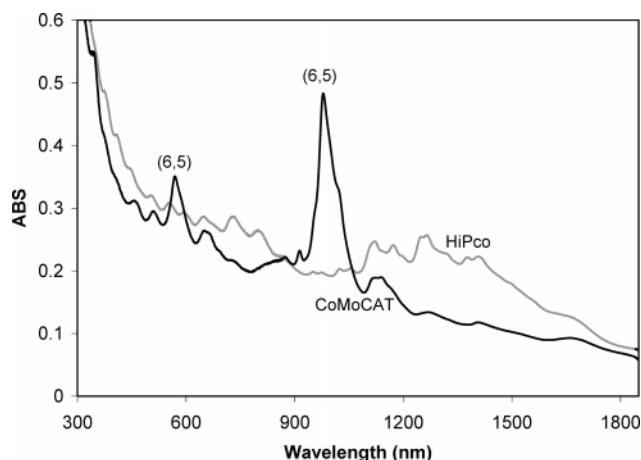


Figure 2. Optical absorption spectra of nanotubes produced by HiPco and CoMoCAT methods in D₂O after 2 h sonication with NaDDBS (1 g/L) and 1 h centrifugation at $\sim 27\,000g$.

SWNT by following this procedure.¹⁴ Among the ionic surfactants, NaDDBS has been found to yield the best resolved spectral features while nonionic surfactants, with high molecular weight, are able to suspend larger quantities of SWNT. That is, surfactants with higher suspendibility do not necessarily result in sharper spectral features. At the same time, for a given nanotube sample, that is, without taking purity into account, better resolved spectral features indicate a higher fraction of individual nanotubes in the suspension. The sharpness of the spectral features relative to the background can be quantified by two parameters. The first one, that we call “resonance ratio,” is the ratio of the resonant band area to its nonresonant background, as illustrated in Figure 1a. A very similar method has been developed by Haddon et al.²³ The second parameter, that we call here “normalized width,” is the ratio of the width of the band at half-height to the peak height on a spectrum that has been normalized at 900 nm, as shown in Figure 1b. This normalization makes this ratio an intensive property that does not vary with the path length. We have used these two ratios to quantify the effect of different factors in the dispersion procedure, as applied to SWNT prepared by the CoMoCAT process.

The absorption spectrum of dispersed CoMoCAT nanotubes is remarkable. In Figure 2, a comparison is made with a suspension of HiPco nanotubes suspended in NaDDBS solution by exactly the same dispersion procedure as that used for the CoMoCAT sample. Clearly, the CoMoCAT nanotubes have

much more pronounced spectral features at 567 and 978 nm, corresponding to the E11 and E22 transitions of the (6,5) nanotube, previously identified as the most abundant semiconducting nanotube in this sample.¹² Similar results on CoMoCAT sample have been already shown with DNA dispersions.²⁴

In this contribution, we have investigated the spectral features of CoMoCAT nanotube suspensions following the same optimized dispersion procedure on various surfactants (anionic, cationic, and nonionic) including both novel and previously reported surfactants. We have made a quantitative comparison on the basis of the normalized width and resonance ratio described above. We have found that some surfactants are better than or comparable to the previously reported preferred surfactant, NaDDBS.¹⁷ In addition, we have evaluated the impact of varying pH and nanotube concentration in the suspensions.

Materials and Methods

Purified CoMoCAT single-wall carbon nanotubes (batch WW2) were provided by South West Nanotechnologies, while purified HiPco single-wall carbon nanotubes (batch P0279) were purchased from Carbon Nanotechnologies, Inc.

The following surfactants were used in this work: dodecylbenzenesulfonic acid sodium salt (NaDDBS, from TCI America); sodium cholate, sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium *p*-toluenesulfonate (CTAT), hexadecyltrimethylammonium bromide (CTAB), and polyoxyethylene (10) octylphenol (Triton X-100) (from Sigma-Aldrich); poly(ethylene oxide) (20) sorbitan mono-oleate (Tween 80, from ACROS organics); alkylidiphenyloxide disulfonate salts (Dowfax 8390 or *n*-hexadecyl diphenyloxide disodium disulfonate, Dowfax 2A1 or disodium dodecylphenoxybenzene disulfonate, from Dow Chemical Company); and sodium diisopropylnaphthalene sulfonate (Aerosol OS, from CYTEC Industries, Inc). Anionic gemini surfactants, Ceralution F (sodium 2-(1-carboxylatoethoxy)-1-methyl-2-oxoethyl laurate and C12/C14-fatty acid-ethylendiamidethersulfate), from SASOL North America Inc. Surfynol CT131/324 are a blend of anionic and nonionic gemini surfactants, in which anionic has more content than nonionic, from Air products and Chemicals, Inc. All nanotubes and surfactants were used as received without further purification. All solutions were prepared with UHP water purified through a Barnstead Nanopure II system (measured resistivity = 18.1 mega-ohm-cm) or heavy water (D₂O, from ACROS organics).

To prepare the nanotube suspensions, 5 mg SWNT was added to 25 mL surfactant solution in a 25 × 95 mm vial. The dispersion was then ultrasonicated for a specified period of time with a horn sonic dismembrator (Model 500, Fisher Scientific) running at 35% power output. The resulting suspension was centrifuged in an automatic centrifuge (Sorvall SS-3, Du pont Instruments) at preset speed for times ranging from 30 min to several hours. In each run, the upper 50% of the resulting supernatant, a stable solution with well-dispersed individual nanotubes, was taken out for characterization. A UV-vis spectrophotometer (UV-2101PC, Shimadzu) with 2-mm or 10-mm light path cuvettes was used to investigate the wavelength range 300–900 nm while a Bruker Equinox 55 FTNIR was used for the NIR range, 850–1900 nm. To calculate the resonance ratios and normalized widths obtained with the different surfactants, all suspension samples were first diluted to approximately the same absorbance intensity at a wavelength of 900 nm before acquiring the spectra.

Results and Discussion

It is well-known that the procedure used to disperse nanotubes has a significant impact on the SWNT concentration, stability,

and fraction of individual tubes in the final suspension. It is also accepted that it is not easy to replicate the same procedure used in dispersing nanotubes among different laboratories because of the many factors involved in this process that many times are not reported. In addition to the more commonly reported operating conditions, such as surfactant and nanotube concentration, sonication and centrifugation times, other parameters such as the total amount of liquid, the shape and size of the vial, the depth of the probe under the solution during sonication, the procedure used to avoid overheating the sample during sonication, and the different G-forces used during centrifugation can be critical in determining the degree of dispersion. As a result, although there are abundant dispersion results in the literature,^{14,21} each lab has developed their own conditions and many times a direct comparison is not possible. Another complication in making valid comparisons is the method used to evaluate the state of dispersion. For example, atomic force microscopy (AFM) is a widely used method to monitor suspended nanotubes by imaging them after deposition on a substrate by different techniques.¹³ However, AFM is not a direct method and it is not readily accessible in many labs. In addition, AFM can only probe a few nanotubes at a time which may not be fully representative of the whole sample. By contrast, optical absorption of SWNT suspensions in the UV–vis–NIR region carries the information of all the nanotubes present in the sample. In addition, the spectral features are reproducible for each kind of nanotube and they can be easily compared to published spectra,^{22,25} which makes it possible to obtain an (n,m) -identification of the suspended nanotubes in the sample.²⁶ Moreover, under the same conditions, the intensity of the resonant peaks compared to the background can provide an indication of the fraction of suspended nanotubes. Therefore, both the resonance ratio and the normalized width, as defined in Figure 1, can be used to quantify the quality of the suspension. These ratios can be used either for comparing dispersion procedures and surfactants with a given nanotube sample or for comparing different nanotube samples with a given dispersion procedure.

First, we used this protocol to evaluate different dispersion procedures using the CoMoCAT sample and NaDDBS as a surfactant. This comparison is illustrated in Figure 3a, which shows the as-obtained UV–vis spectra at different sonication times, without any dilution or normalization. As expected, longer sonication times increased the intensity of the resonant peaks, but at the same time increased the nonresonant background, as previously observed with dimethylformamide (DMF).²⁷ Also, all the peaks increased simultaneously during the sonication process. As shown in Figure 3b, the area fraction of (6,5) band relative to all bands keeps nearly constant. This is an important result that shows that all the nanotube types are dispersed to the same extent; that is, there is no preferential suspension on any specific nanotube type. If this were the case, one or more peaks would have increased faster than the others. This is a confirmation that the standard CoMoCAT sample is indeed very rich in (6,5) nanotube, and this enrichment is not the result of selective suspension of any kind. The resonance ratios obtained from the spectra in Figure 3a are calculated and plotted in Figure 4a. It is observed that most of the increase in resonance ratio occurs during the first hour of sonication. This result may indicate that during the first hour of sonication, a large degree of debundling (exfoliation) takes place. Sonication for much longer times may have a negative effect because of nanotube damaging. We observed that sonication for very long times (i.e., 3 days) resulted in a continuous increase in background, while

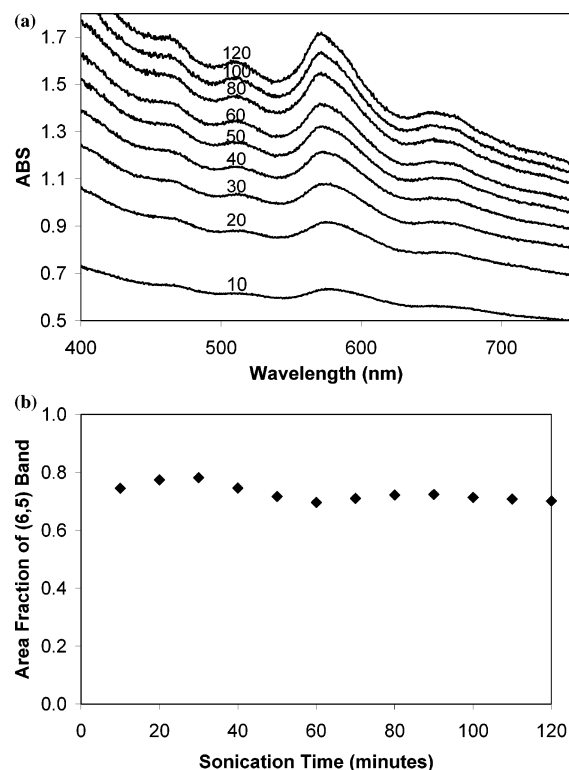


Figure 3. (a) UV–vis spectra of NaDDBS (1 g/L) dispersed SWNT (0.2 mg/mL) from CoMoCAT methods at different sonication time (minutes) without any dilution. (b) The area fraction of (6,5) resonant band (~ 567 nm) relative to all bands between 436 and 709 nm as a function of sonication time.

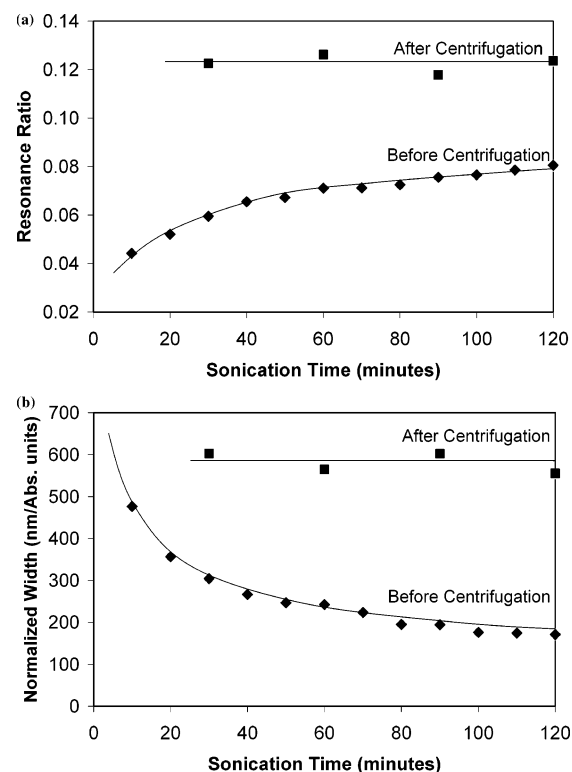


Figure 4. (a) Before and after centrifugation resonance ratio as a function of sonication time. (b) Before and after centrifugation normalized width as a function of sonication time.

the resonance peak intensity remained almost constant. Assuming that there are enough nanotubes to disperse in the system, the increased background after long sonication time can be

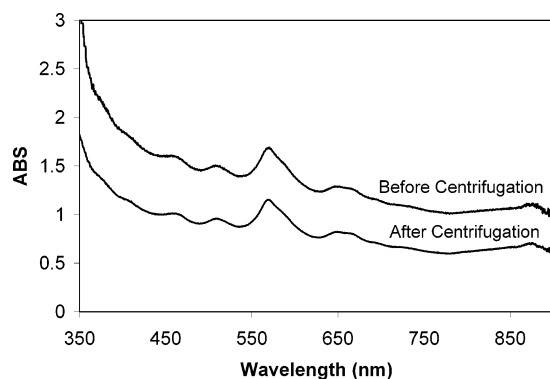


Figure 5. UV-vis spectra of CoMoCAT SWNT (0.2 mg/mL) dispersed in NaDDBS with 2 h sonication, before and after 1 h centrifugation at $\sim 27\,000g$.

ascribed to an increase in the damage or even in the disassembling of nanotubes. As a result, the resonance ratio decreases at very long sonication times. In Figure 4b, the ratio of half-peak width to peak height is seen to decrease with increasing sonication time; that is, the absorption band becomes sharper and more intense as the number of suspended individual nanotubes increases. In this case, 2-h sonication appeared as the optimum treatment and it was used in all subsequent experiments.

Centrifugation greatly enhances the resonance ratio because it removes from suspension several undesirable species (graphite, catalyst residues) as well as large SWNT bundles. This enhancement is reflected in an improvement of the spectrum quality, as illustrated in Figure 5. It is seen that after centrifugation the background decreases significantly, while only a small decrease is observed in the intensity of the resonance peaks. Therefore, those nanotubes that may remain in the sediment of the centrifugation ($27\,000g$) contribute little to the spectral features and perhaps are in the form of large bundles. As seen in Figure 4a, even when because of different sonication the original suspensions had different resonance ratios, the subsequent centrifugation increased the resonance ratio to about the same value. These high resonance ratios were also observed after diluting more concentrated samples obtained with longer sonication times. That is, on centrifuged samples with the same surfactant concentration, the only effect of sonication time is to increase the yield of suspended nanotubes but not the resonance ratio. It is clear that bundles above a certain size are removed during centrifugation. After a minimum sonication time, longer times may only increase the number of small bundles in suspension but not the distribution of bundles left in suspension after the centrifugation. Of course, when the centrifugation conditions are changed, the final suspension can also change. As seen in Figure 6, both longer centrifugation times (Figure 6a) and higher g forces (Figure 6b) cause a more efficient removal of bundled nanotubes, narrowing the distribution in the final suspension. The greatest effect is observed during the initial hour of centrifugation. That is, as shown in Figure 6a, 12 extra hours of centrifugation (from 1 to 13 h) only increased the resonance ratio by 15%. At the same time, increasing the relative centrifugal force (RCF) from $3000g$ to $47\,800g$ with 1 h of centrifugation causes an increase in resonance ratio of 26% (see Figure 6b). So, increasing RCF seems to be more efficient than increasing centrifugation time. In previous reports, centrifugation conditions as severe as $122\,000g$ for 4 h have been found necessary to prepare individual dispersed nanotubes.²¹ In the following comparison of various surfactants, we have used 1 h centrifugation at an

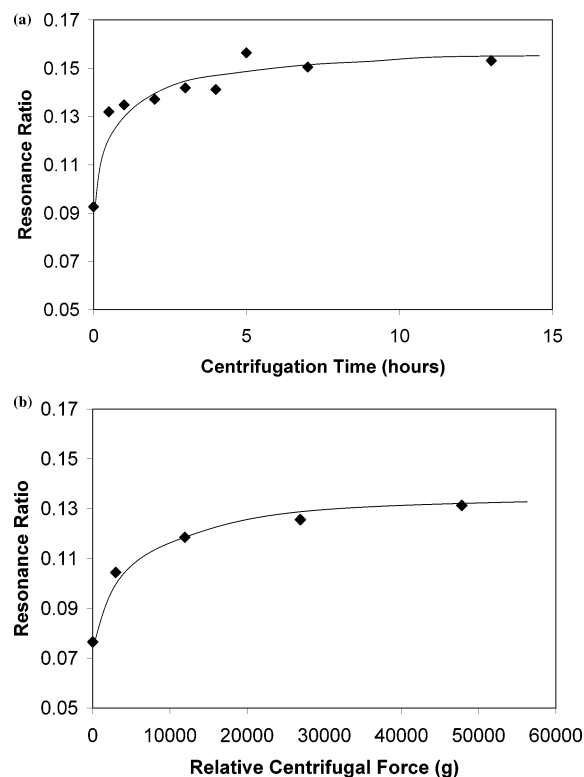


Figure 6. Resonance ratio as a function of centrifugation time (centrifugal force = $27\,000g$). (b) Resonance ratio as a function of centrifugation force (centrifugation time = 1 h).

RCF of $27\,000g$, which in most cases is sufficient to achieve high dispersions.

After determining the optimal dispersion procedure, several commercial surfactants were tested to compare their relative debundling ability using the same amount of SWNT, 0.2 mg/mL (see Table 1). As shown below, a minimum initial concentration of surfactant is needed to maximize the resonance ratio, but we did not use the same concentration for all surfactants because each one has a different critical micelle concentration (CMC), and when enough surfactant is present the final concentration of free monomer is that of the CMC. Because of a significant reduction in free monomer concentration caused by the surfactant adsorption on the nanotube surface, the concentration that matters is the final concentration, which is always less than or equal to the CMC. In a previous study,¹⁷ we determined the adsorption isotherms (amount adsorbed as a function of final concentrations) for the case of the NaDDBS surfactant. In that case, we were able to establish the relationship between initial concentrations of surfactant and SWNT that resulted in maximum nanotube suspension. However, it is not practically possible to do the same detailed analysis for each surfactant. Measuring the concentration of free monomer in the presence of nanotubes is not a trivial task. High-pressure filtration with ultrafine filters is necessary to separate the adsorbent-adsorbate phase from the free monomer. Therefore, in this study, each surfactant was used at the initial concentration recommended by the vendor for typical industrial application or at that recommended in published reports.^{13,14,18,28,29}

In addition to the NaDDBS which we reported before, we have found several other surfactants that are as good as, or even better, than NaDDBS for this application. The results are summarized in Table 1. The surfactants that showed the best performance are Na cholate, Surfynol CT324, Aerosol OS, and Dowfax 2A1. Dowfax is an anionic alkyldiphenyloxide disul-

TABLE 1: Resonance Ratio of SWNT Suspension for Different Surfactants and 0.2 mg/mL Purified CoMoCAT Nanotube after Same Dispersing Procedure

surfactant	pH	type	ring structures	surfactant concentration (g/L)	resonance ratio
Sodium Cholate	natural	anionic	yes	20	0.147
Surfynol CT324	natural	anionic/nonionic		15	0.144
Aerosol OS	natural	anionic	yes	10	0.142
Dowfax 2A1	natural	anionic	yes	10	0.139
NaDDBS	natural	anionic	yes	5	0.132
NaDDBS	natural	anionic	yes	10	0.131
Dowfax 8390	natural	anionic	yes	10	0.129
NaDDBS	(pH = 13)	anionic	yes	1	0.126
NaDDBS	natural	anionic	yes	1	0.125
Surfynol CT131	natural	anionic/nonionic		15	0.123
CTAB	natural	cationic	no	1	0.119
Triton X-100	natural	nonionic	yes	5	0.112
Ceralution F	natural	anionic	no	15	0.106
Tween80	natural	nonionic	no	5	0.1
CTAT	(pH = 2)	cationic	no	1	0.097
Surfonic L24-7	natural	nonionic	no	0.2	0.093
SDS	natural	anionic	no	10	0.084
CTAT	natural	cationic	no	1	0.078
CTAT+NaDDBS	natural	cationic/anionic	yes	1	0.072

fonate surfactant, which means that it has a dibenzene group and twice the charge as that of NaDDBS. The benzene ring in the surfactant has been proposed to be one of the main reasons for high nanotube dispersing ability.¹³ At the same time, a higher charge in the headgroups strengthens the electrostatic repulsion among surfactant-covered nanotubes; this repulsion has the added effect of inhibiting the reattachment of nanotubes, making the suspension more stable.

As shown in Table 1, a surfactant from the same family, the Dowfax 8390 (with a longer hydrophobic tail, C16) is not as good as the Dowfax 2A1 (with a shorter tail C12). According to the so-called “unzipping” mechanism,¹⁹ the surfactant has to get into the small spaces between the bundle and the individual tubes to compete with the adsorption and exfoliate the tubes. Then, surfactants with too long or too large hydrophobic groups have difficulties in penetrating in the intertube region and, thus, have a lower electrostatic charge after adsorption, which eventually reduces the debundling efficiency of a given surfactant.

Since the presence of phenyl groups enhances the surfactant–nanotube interaction, one may predict that a surfactant with a naphthalene group (two fused rings) in its hydrophobic group should also be effective in this application. This is in fact verified for the case of Aerosol OS, which is even better than the Dowfax surfactants, showing that naphthalene is even more effective than benzene (NaDDBS) or double-benzene structures (Dowfax). We also show here that not only aromatic groups but also naphthenic (saturated rings) groups provide good surfactant–nanotube interaction. These naphthenic structures are present in the molecule of sodium cholate, which contains three six-member rings and one five-member ring in the hydrophobic tail and it is anionic; sodium cholate exhibited the highest resonance ratio, 0.147. This superior dispersing ability is in good agreement with previous work by Hertel et al.,³⁰ who reported spectroscopic data of suspended single- and double-wall carbon nanotubes.

The use of mixtures of surfactants is effective in many applications because of synergistic effects that improve surfactant packing on surfaces and modifications of repulsive/attractive forces.³¹ We have investigated the use of surfactant mixtures in the dispersion of SWNT. For that purpose, we have used Surfynol CT324, which is a commercial blend of anionic and nonionic surfactants. In this mixture, the content of the anionic

one is higher than that of the nonionic, gemini (two tails) surfactant. Excellent performance has been observed with this mixture resulting in a resonance ratio of 0.144. The other similar mixed surfactant, Surfynol CT131, exhibited a performance similar to that of NaDDBS.

However, the use of surfactant mixtures does not necessarily guarantee an effective dispersing ability. For example, we tested a mixture of NaDDBS with CTAT with the presumption that the mixture promotes the formation of wormlike micelles,³² with an appropriate geometry for stabilization of nanotubes. Unfortunately, the mixture was ineffective in suspending individual nanotubes, as illustrated by the low resonance ratio of 0.072 obtained with the mixture 90% CTAT plus 10% NaDDBS, even lower than that obtained with CTAT by itself. The reason for this failure may be that the two surfactants have opposite charges, and when both molecules adsorb onto the nanotube surface, Coulombic interactions between isolated tubes decrease and, thus, less individual nanotubes may remain in the final suspension. In summary, nonionic surfactants are not as effective as ionic surfactants, even with aromatic groups in the hydrophobic tail. For the ionic surfactant, the efficiency can be increased by either modification of the hydrophobic tail, especially incorporating ring groups, or using the synergistic action of surfactant mixtures.

As expected, there is a clear correlation between the resonance ratio and the normalized width. As illustrated in Figure 7, an effective surfactant, which results in a large fraction of individual SWNT in suspension, has both a high resonance ratio and a low spectral width while the opposite trend is seen with ineffective surfactants. For example, SDS and TritonX100, which have been previously used by many researchers, do not appear as particularly effective for our SWNT material.

It is well-known that the pH of the solution has a significant impact on the adsorption of ionic surfactants. In this study, we have compared the interaction of some of the most effective surfactants at different pH values. It is seen in Table 1 that the resonance ratio for NaDDBS (anionic) at pH = 13 is hardly improved when compared to that at natural pH, but for the cationic surfactant CTAT, which may form wormlike micelles,³³ decreasing the pH to 2 causes a 24% increase in the resonance ratio. We can explain this behavior in terms of the charge on the nanotube surface, directly related to the pH of the solution and to the point of zero charge (PZC) of the nanotubes. In an

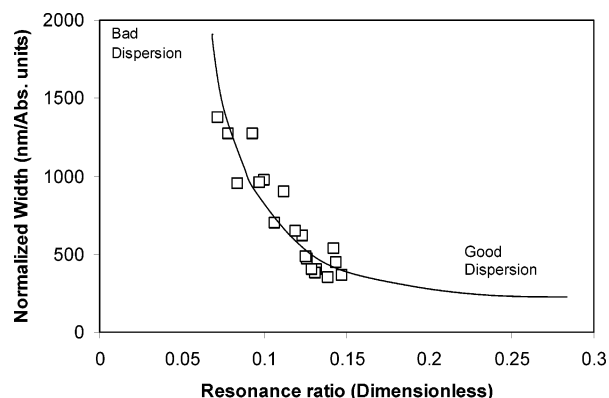


Figure 7. Combined resonance ratio and normalized width of UV-vis spectra of SWNT dispersed over different surfactants. The most effective surfactants exhibit a low width ratio and high resonance ratio.

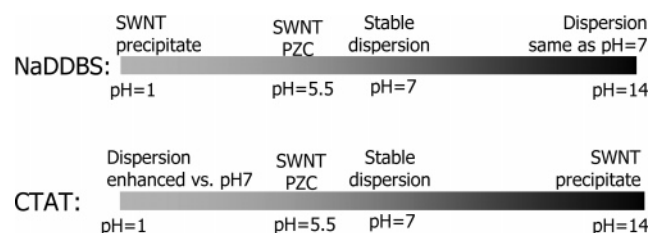


Figure 8. The impact of pH on the ionic surfactant dispersed SWNT from CoMoCAT methods.

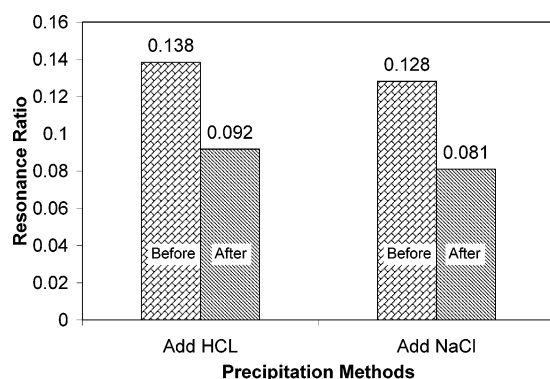


Figure 9. Resonance ratios obtained before and after precipitation of SWNT sample suspended in NaDDBS solution (starting with natural pH, 0.2 mg SWNT/mL, 1.0 g surfactant/liter). Original suspension was centrifuged (1 h, 27 000g), but no further centrifugation was done after addition of HCl or NaCl.

earlier study of our group, the PZC of nanotubes was around 5.5.¹⁷ As a result, lowering the pH to 2 changed the surface charge of the nanotubes from negative to positive and thus greatly enhanced the adsorption of cationic surfactant. However, this would not happen for an anionic surfactant such as NaDDBS (Figure 8). For each surfactant, changing the pH in the wrong direction (i.e., lowering pH for NaDDBS or increasing pH for CTAT) will cause nanotubes to precipitate from suspension. In our experiments, we observed floccules being formed in suspension in about 10 min after changing the pH. By checking the concentration of free surfactant in the suspension, it was determined that most of the adsorbed surfactant has left the nanotube surface and was back in solution. Similar results have been previously obtained by a researcher working with polystyrene latex surfaces, on which the adsorption of SDS was observed to decrease with increasing the surface charge density.³⁴

As shown in Figure 9, the resonance ratio of NaDDBS-suspended samples significantly dropped after either changing

pH by addition of HCl or changing the ionic strength by addition of NaCl. In both cases, the reduction in resonance ratio was about the same ($\sim 35\%$). This drop can be ascribed to rebundling of nanotubes caused by either destabilization of the surfactant-nanotube interaction (at lower pH) or reduced repulsion among surfactant-covered individual tubes (increased ionic strength of the medium). Both effects will have the same result of loss of individual nanotubes and rebundling.

Increasing the concentration of surfactant may have a positive impact on the resonance ratio, but after a certain minimum concentration, the effect is not important. For example, as shown in Table 1, a 5% improvement was observed when the initial concentration of NaDDBS increased from 1 g/L to 5 g/L, but it did not further increase at 10 g/L.

Conclusion

Using the resonance ratio and the normalized width for the most intense band in the UV-vis spectra (6,5) of nanotube suspension, we have investigated the dispersion procedure and have compared the ability of different surfactants to disperse CoMoCAT nanotubes, a sample with much narrower distribution of nanotube types than any other nanotube sample. The resonance ratio is related to the fraction of individual nanotubes in final suspension. We attempted to maximize this ratio by tuning the dispersion parameters, which include sonication time, centrifugation time, and the relative centrifugal force. It was found that all of these factors play a significant role. After developing a standard procedure, resonance ratios were calculated for several surfactants. All surfactants examined were able to suspend nanotubes and form homogeneous stable suspensions. They all had similar optical absorption spectra but with different intensity and resonance ratios. Several surfactants with high debundling ability were identified. It appears that both the presence of ring structures in the hydrophobic tail as well as the charge of the hydrophilic head play important roles in the dispersion process. Depending on the point of zero charge of the pristine SWNT and the specific charge of surfactant, changing the pH may either enhance the dispersibility or cause the precipitation of nanotubes.

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