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Sonochemical Formation of Methyl Hydroperoxide in Polar Aprotic Solvents and Its Effect on Single-Walled Carbon Nanotube Dispersion Stability

Michael W. Forney and Jordan C. Poler*

Department of Chemistry, University of North Carolina at Charlotte, 9201 University City Boulevard, Charlotte, North Carolina 28223-001

Received October 7, 2009; E-mail: jcpoler@uncc.edu

Abstract: Ultrasonication is a common method for dispersing nanoparticles and colloids. We have found that, under certain conditions, unintended sonochemical reactions can be initiated by the incident ultrasonic energy, yielding unwanted byproducts. In this work, we determined that methyl hydroperoxide can be produced by an autoxidation chain reaction when ultrasonicating polar aprotic solvents containing methyl groups. Methyl radicals were detected during ultrasonication by their interaction with lucigenin, which emits sonochemiluminescence. A colorimetric triiodide test was used to confirm the presence of a hydroperoxide. The concentration of methyl hydroperoxide as a function of the ultrasonication time was measured by titration with NaOH. When above the critical coagulation concentration, this sonochemical byproduct collapses the electrical double layer, disrupting the dispersion stability and lowering the dispersion limits. This is significant when developing ultrasonication processes for dispersion of nanoparticles and colloids. There are no other examples of sonochemically initiated solvent autoxidation destabilizing single-walled carbon nanotube dispersions reported in the literature.

Introduction

Nanomaterials, such as quantum dots, nanoparticles, nanowires, and nanotubes, exhibit technologically useful and fundamentally interesting physical, chemical, electronic, optical, and catalytic properties.[1] Most of these nanomaterials must be suspended or dispersed into a liquid phase during some stage of their processing or study. Typical methods incorporate some type of energy input into the system to disperse powdered nanomaterials, commonly by ultrasonication. In this paper, we will focus on the effects of sonochemically generated methyl hydroperoxide on single-walled carbon nanotubes[2] (SWNTs), but the results of this study are relevant to dispersing any nanparticles or colloids with ultrasonic energy.

SWNTs have captured the interest of many nanomaterials researchers due to some of their phenomenal properties, including 1D electron transport, excellent thermal conductivity, and the highest axial tensile strength reported.[3−5] Significant research effort has been directed toward using SWNTs as transistors,[6−8] reinforcement in composites,[9−11] high aspect ratio AFM tips,[12] nanoscale radios,[13] transparent flexible loudspeakers,[14] components for directed self-assembly of nanoscale structures,[15−18] and many other applications. Unless SWNTs are grown directly in their desired location, they must be dispersed into a liquid from the powder form in which they were produced. As mentioned above, the most common method for dispersing nanotubes is by ultrasonication, though other methods such as dilution[19,20] have been developed. Typical ultrasonication protocols use bath or tip ultrasonicators to transmit ultrasonic energy into a sample which disperses bundled

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SWNTs. Ultrasonic waves produced in a liquid provide sufficient energy to debundle SWNTs, overcoming attractive interparticle van der Waals forces such as dispersion and $\pi-\pi$ stacking interactions.

Depending on one's research objectives, SWNTs can be dispersed into organic solvents or water. Due to the hydrophobic nature of SWNTs, aqueous dispersions require surfactants to mediate the interface between SWNTs and water. Alternatively, SWNTs can be modified by acid functionalization or functionalized with stabilizing ligands.[21−24] To maintain pristine electronic and optical properties of SWNTs, organic solvents are necessary so that the SWNT properties are undisturbed by surfactants or functionalization. Furthermore, pristine SWNTs can interact with appropriately sized macromolecules that specifically bind to SWNTs of specific chirality (diameter), leading to directed self-assembly.[15,18]

Sample preparation and solvent choice are quite important when handling nanomaterials. A wide variety of organic solvents are used to disperse pristine SWNTs,[25−28] though amide solvents tend to be among the most successful.[19,27,28] *N*,*N*-Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidinone (NMP) are two of the most frequently used organic solvents for dispersing SWNTs; the experimental results in this paper focus on DMF. In addition to DMF and NMP, we also report on two other polar aprotic solvents: *N*,*N*-dimethylacetamide (DMA) and acetonitrile (MeCN).

We have observed that two parameters during ultrasonication can significantly affect the SWNT dispersion stability in these polar aprotic solvents: (1) oxygen concentration in the dispersant and (2) sample temperature during ultrasonication. Increasing the oxygen concentration during ice bath (IB) cooled ultrasonication (∼20 °C) reduces the dispersion stability, and decreasing the oxygen concentration enhances the dispersion stability. "Hot" ultrasonication (∼110 °C) yields stable dispersions, regardless of the oxygen concentration. It has been determined that the source of dispersion instability is a sonochemically generated byproduct, methyl hydroperoxide.

Results and Discussion

Anomalous dispersion instability was first observed when attempting to maximize the number of individually dispersed SWNTs in DMF by tip ultrasonicating samples for 2 h while keeping the sample cool with an IB. Visible aggregates formed within seconds or minutes, and the dispersion collapsed overnight. In contrast, dispersions formed by tip ultrasonicating for 30 min without an ice bath (hot) can be stable for months with no visible aggregation, as shown in Figure 1. Figure 2 displays the effect of various ultrasonication conditions on the SWNT dispersion stability. The source of the observed dispersion instability was not obvious and required demonstrating that several reasonable possibilities were not occurring. In this paper

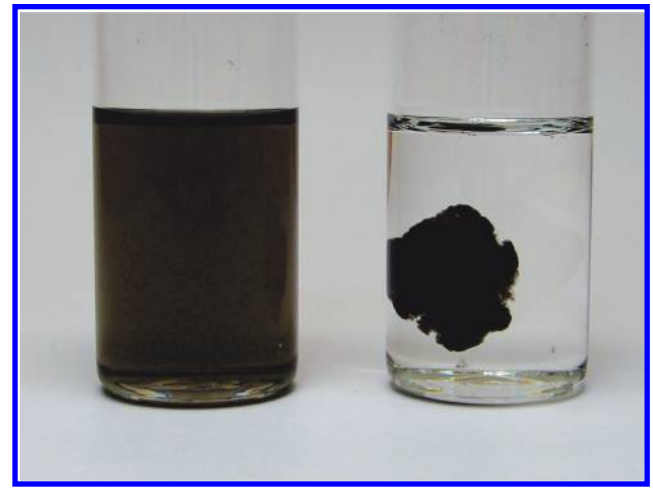

Figure 1. The dispersion on the left was ultrasonicated for 2 h without being cooled by an ice bath. The sample on the right was ultrasonicated for 2 h with an oxygen sparge and kept at ∼20 °C by an ice bath.

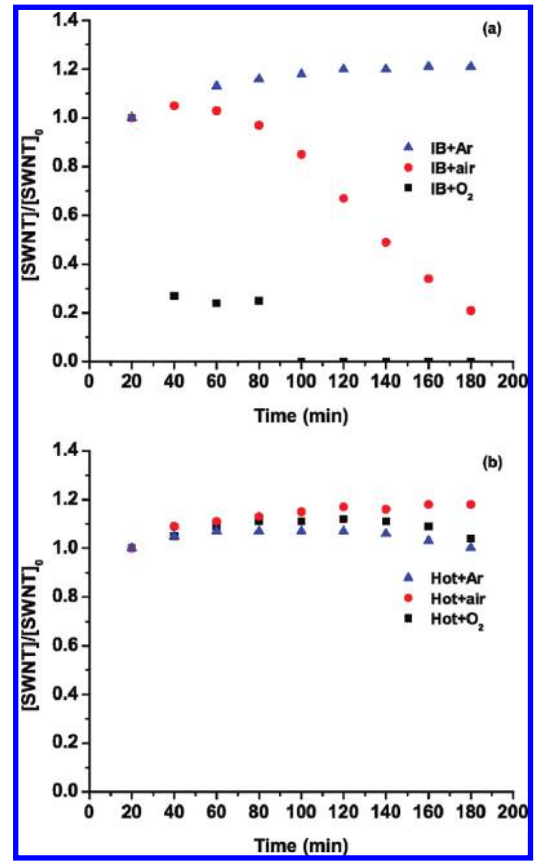

Figure 2. Concentration of SWNT dispersions plotted as a function of the ultrasonication time (normalized to the concentration at 20 min, $[SWNT]_0$). In (b), the samples are heated to ∼110 °C and are all stable, whereas in (a), the samples are cooled in an ice bath. When deaerated with Ar, the dispersions remain stable. Under ambient conditions, the dispersions quickly become unstable as the ultrasonication time increases. When O_2 is bubbled through the sample, virtually no SWNTs can be dispersed. The concentrations for IB + O_2 in (a) at 20 min are very small, ∼0.6 mg/L, compared with typical concentrations of ∼15 mg/L.

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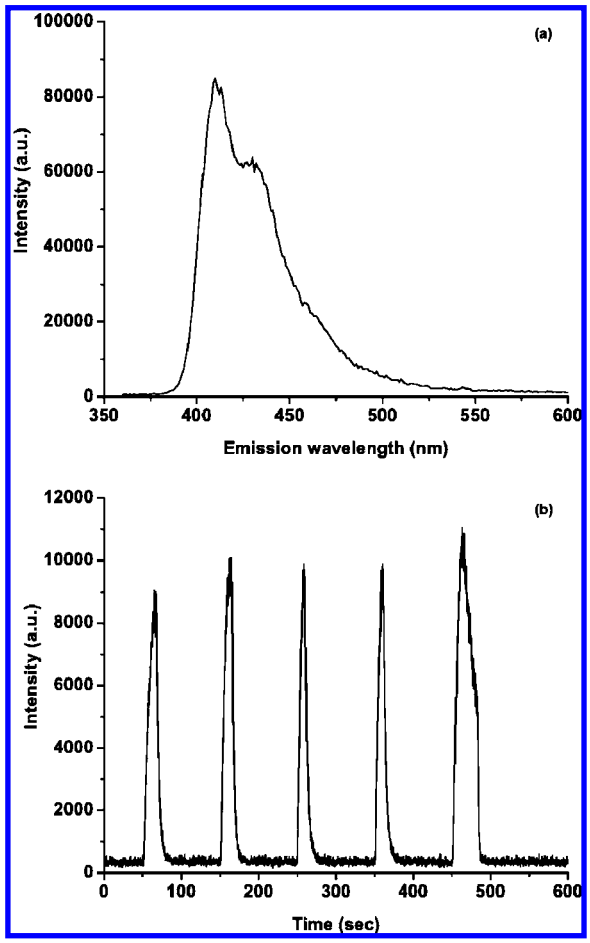

Figure 3. Sonochemiluminescence emission from lucigenin in DMF. Shown in (a) is the emission profile of lucigenin during ultrasonication. In (b), the sonochemiluminescence intensity at the emission peak (410 nm) is monitored as a function of time. The ultrasonicator was turned on for 10−15 s at 50, 150, 250, and 350 s. At 450 s, the ultrasonicator was turned on for 1 min to see at what intensity the sonochemiluminescence would saturate.

we address the source of dispersion instability, methyl hydroperoxide, and the mechanism by which it is formed.

It is known that radicals are produced during ultrasonication of DMF.[29−31] Moreover, cross-linking of bundled SWNTs can result from UV-induced free radical formation.[32] Therefore, it was hypothesized that the lower temperature may be extending radical lifetimes to the point where they are cross-linking SWNTs during ultrasonication. We were able to detect radical production by ultrasonication of DMF through the sonochemiluminescence of lucigenin as reported by Wang et al.[31] The lucigenin emission spectrum we observed was similar to theirs (see Figure 3a). As shown in Figure 3b, we monitored the luminescence emission peak (410 nm) while turning the ultrasonicator on and off. No luminescence was observed when the ultrasonicator was off, but strong luminescence appeared as soon as the ultrasonicator was turned on. Our observations are consistent with those of Wang et al.,[31] such that the sonochemiluminescence is due to the reaction of lucigenin with free radicals produced during ultrasonication. As indicated by Misik et al.,[33] methyl radicals should be more reactive than the corresponding nitrogen-centered radicals, and we expect them to dominate any radical reactions that occur during ultrasonication.

Wang et al.[31] used various natural flavonoids to suppress sonochemiluminescence of lucigenin by scavenging the free radicals generated by ultrasonication. We successfully used morin, one of the more efficient radical-scavenging flavonoids, to quench the sonochemiluminescence and to stop the rapid aggregation observed after low-temperature ultrasonication. Interestingly, we found that morin also acts as a surfactant capable of dispersing SWNTs into water. Consequently, the enhanced dispersion stability may have been due to morin's surfactant ability, free radical scavenging, or a combination of the two.

If SWNTs were cross-linked through radical initiation, they would exhibit modified electronic, optical, and vibrational properties due to disruption of their otherwise uniform sp^2-bonded structure. Raman spectra of SWNTs ultrasonicated under various ultrasonication protocols were extensively studied. The D/G^+ band ratio and the width of the G′ overtone band were compared in the Raman spectra. Point defects due to cross-linking should cause an increase in the defect (D) band and a relative decrease in the G^+ band. There was no observed change in the D/G^+ ratio upon ultrasonication. The width of the G′ band can be an indicator of the aggregation state of dispersed SWNTs.[34] While there was a correlation between dispersion stability and the G′ bandwidth, this provided little insight into the cause of dispersion instability. We could not distinguish between SWNTs from stable and unstable dispersions by Raman or UV−vis−NIR spectroscopy. It is clear from our data that ultrasonication under these conditions does not damage the SWNTs.

We also compared SWNTs from stable and unstable dispersions with scanning electron microscopy (SEM). When deposited onto a substrate, one would expect a significantly more "crossed" network of tubes if the SWNTs were cross-linking due to free radical initiation. There was no obvious morphological difference between stably dispersed SWNTs and SWNTs from unstable dispersions.

Further experimentation led to the observation that aggregated SWNTs from an unstable dispersion could be centrifuged out and stably redispersed into fresh DMF. Also, DMF could be "pretreated" by a 2 h ultrasonication while being cooled by an ice bath, and it would be rendered unusable for making dispersions. Adding SWNTs to pretreated DMF and ultrasonicating under a good protocol (i.e., 30 min at high temperature) still resulted in an unstable dispersion. From these experiments and the Raman and SEM results, we concluded that SWNTs are not significantly damaged or cross-linked during ultrasonication, but rather, the DMF is modified in a way that renders it incapable of dispersing SWNTs.

Fresh DMF was compared to DMF that had been IB or hot ultrasonicated for 2 h using several analytical methods. UV−vis and Raman spectroscopy showed no discernible difference between ultrasonicated and fresh DMF. NMR spectra showed an additional singlet for ultrasonicated DMF, due to small amounts of water absorbed during ultrasonication. FTIR spectra were, again, almost identical for ultrasonicated and fresh DMF.

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The only change was an increase in OH stretches, which we attributed to the absorbed water. There was no clear difference in the absorbed water concentration between IB and hot ultrasonicated samples.

The water concentration can affect the dispersion limit of SWNTs in DMF, so we tested whether it might also be affecting the dispersion stability. DMF's hygroscopic nature causes water to be absorbed during processing of uncovered samples, though ultrasonicated samples typically contain less that 0.5% water, as measured by NMR. To ensure that absorbed water was not significantly affecting SWNT dispersibility, a large stock dispersion was prepared by ultrasonicating for 30 min without an ice bath. Samples were drawn from the stock dispersion, and DI water was added to yield eight water concentrations ranging from 0.02% to 15% in DMF. The dispersion stability was monitored for five days at each of these water concentrations. Samples were centrifuged to remove aggregated SWNTs, and the SWNT concentration of the supernatant was measured by UV−vis−NIR spectroscopy.[26] The dispersion stability was unaffected on that time scale. However, the SWNT dispersion limit was reduced by up to 13% for higher water concentrations, but all of the samples showed stable SWNT concentrations at a given water concentration. Since much higher water concentrations (15% compared to 0.5%) only seem to affect the dispersion limit, but not the dispersion stability, absorbed water is not the cause of dispersion instability.

There were no detectable changes in the SWNTs or DMF using standard analytical techniques. However, it was found that if a sample is deaerated with argon before and during IB ultrasonication, stable dispersions are formed. Conversely, if oxygen is bubbled through a sample during IB ultrasonication, dispersions become entirely unstable, even during ultrasonications as short as 20 min. We also observed that IB ultrasonicated DMF exhibited an increase in conductivity and turned acidic, as determined by the indicator bromothymol blue (BTB).[35] The conductivities observed corresponded to ion concentrations on the order of 10^{-4} M, when compared to a conductivity calibration curve for NaBr in DMF, which is sufficiently high to collapse the electrical double layer that normally stabilizes dispersed SWNTs. For comparison, the critical coagulation concentration of NaBr is 6.8×10^{-5} M for SWNT dispersions in DMF.[17] It is well-known[36] that DLVO theory can be used to model the aggregation of SWNT dispersions; thus, the observed SWNT aggregation can be explained by classic DLVO theory.[37,38]

A variety of solvents often used to disperse SWNTs were tested to see whether they exhibited similar properties after being IB ultrasonicated for 2 h. NMP and DMA dispersions also become unstable under those ultrasonication conditions. Dispersions in chloroform, *o*-dichlorobenzene, and THF were unaffected. Comparing the general properties of the solvents tested, DMF, DMA, and NMP are all polar aprotic solvents with methyl substituents. Acetonitrile, which does not disperse SWNTs, but is a polar aprotic solvent with a methyl group, also showed the characteristic increase in conductivity and acidity after IB ultrasonication.

The observed commonalities among these solvents, especially the methyl groups, support our hypothesis that highly reactive methyl radicals are the cause of dispersion instability. However, the methyl radicals are not affecting the SWNTs directly, but are modifying the solvent in a way that increases the ionic strength and acidity, which collapses the electrical double layer of dispersed SWNTs due to the increased amount of electrolyte in solution.[17,36] Well-known radical chemistry[39,40] details the formation of alkyl hydroperoxides by the autoxidation mechanism:

$$^{\bullet}R + O_2 \rightarrow {}^{\bullet}RO_2$$

$$^{\bullet}RO_2 + SH \rightarrow RO_2H + {}^{\bullet}S$$

Substituting a methyl radical for $^{\bullet}R$, as found in ultrasonicated DMF, NMP, DMA, and MeCN, the autoxidation mechanism specific to our study is

$$^{\bullet}CH_3 + O_2 \xrightarrow{1} {}^{\bullet}CH_3O_2$$

$$^{\bullet}CH_3O_2 + SH \xrightarrow{2} CH_3OOH + {}^{\bullet}S$$

where SH represents some solvent species. When $^{\bullet}S$ is the methyl radical, this chain reaction should result in an exponential accumulation of methyl hydroperoxide. Our GC−MS data do not confirm a significant accumulation of methane, and the accumulation of methyl hydroperoxide increases as a weak power law function, as shown in Figure 6. While other radicals form during ultrasonication and could form additional alky hydroperoxides, the formation of methyl hydroperoxide is the dominant reaction pathway for the solvents DMF, DMA, NMP, and acetonitrile. Solvents which do not contain a methyl group do not form any detectable alkyl hydroperoxide. The presence of water in our system is not included in this mechanism. Hydrogen abstraction from water would lead to the formation of HO_2, a weak base which dissociates into H^+ and superoxide, O_2^-. Using chemical and spectroscopic studies, we were unable to detect the presence of superoxide.

In the sonochemically initiated autoxidation reaction outlined above, the product that accumulates is methyl hydroperoxide (CH_3OOH). There are no other examples of sonochemically initiated solvent autoxidation destabilizing SWNT dispersions reported in the literature. The most similar example[41] of sonochemical hydroperoxide production uses sonochemistry to convert alkyl halides into alkyl hydroperoxides by "reductive oxygenation". The sample conditions in this work are similar to ours, since they also cool their samples and aerate them to enhance the reaction.

Methyl hydroperoxide is acidic, which causes ultrasonicated polar aprotic solvents with methyl groups to show an increase in both acidity and conductivity. Although methyl hydroperoxide is a weak acid in water, on the basis of the conductivity measurements mentioned above and [CH_3OOH] measurements described below, it dissociates well in these polar aprotic solvents. It is this dissociation into ions that causes dispersions to aggregate once the critical coagulation concentration (CCC) has been reached. The accumulation of methyl hydroperoxide is a slow process, which is why dispersion collapse is not observed for short IB ultrasonications (unless O_2 is bubbled

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through). The rate-limiting step in radical-initiated autoxidation reactions is typically H abstraction,[29,30,40] but it is apparent from our results that the concentration of dissolved oxygen ultimately limits the rate of methyl hydroperoxide production. It is obvious from the two-step autoxidation mechanism that methyl hydroperoxide will not be produced if oxygen is not present, which is why deaerated solvents remain pH neutral and deaerated dispersions remain stable and pH neutral.

Recall that dispersions from hot ultrasonications are stable and dispersions from IB ultrasonications are sensitive to the presence of oxygen, as shown in Figure 2. Two hypotheses were considered to explain the temperature dependence; either O_2 solubility could be significantly reduced for high-temperature ultrasonication or other radical reaction pathways become preferable to the H abstraction step in the mechanism above. Oxygen solubility versus temperature was measured with GC−MS. Samples were prepared by bubbling O_2 through a septum into DMF for 2 h to ensure O_2 saturation. O_2 solubility was measured at three temperatures: 0, 20, and 110 °C. The samples were then injected into a GC−MS system, and the area under the oxygen peak was integrated. The relative concentrations of O_2 at 0 and 110 °C were roughly 70% and 10% higher than that at 20 °C, respectively. Consistent with Henry's law constants,[42] the lowest O_2 solubility was at room temperature. O_2 solubility does not explain the observed temperature dependence.

There are many radical reaction pathways that can lead to terminal rather than chain reactions. The three primary terminal pathways are[40]

$$2(^{\bullet}RO_2) \xrightarrow{3} O_2 + ROOR$$

$$^{\bullet}RO_2 + {}^{\bullet}R \xrightarrow{4} ROOR$$

$$2(^{\bullet}R) \xrightarrow{5} RR$$

where step 3 dominates at high $O_{2(g)}$ partial pressures and step 5 dominates for the $Ar_{(g)}$-sparged samples. Low-temperature IB ultrasonication of acetonitrile yields an acidic, high-conductivity solution. However, when the acetonitrile is held at 50 °C or higher, the solution stays pH neutral and there is no conductivity increase. Moreover, there is a strong peroxide peak (∼200 nm) that does accumulate for all high-temperature ultrasonications. At low temperature, the rate of methyl hydroperoxide formation is first-order in $O_{2(g)}$ partial pressure in the solvent, yet at high temperature the rate is not as high due to competing chain termination reactions Though difficult to prove, these terminal reaction pathways may dominate over the slow H abstraction step at high temperatures. Consequently, no excess of methyl hydroperoxide can accumulate, solvents stay pH neutral, and dispersions are stable.

For IB + Ar ultrasonicated samples, ethane was detected by GC−MS, further confirming that the active radical species is the methyl radical. When samples did contain O_2 (IB + air or IB + O_2), ethane was not detected. This supports our claim that methyl radicals are consumed in the first step of the autoxidation mechanism. We were unable to determine which terminal pathway is dominates during hot ultrasonications, but the terminal pathways proposed above are appropriate for an autoxidation reaction. Nevertheless, the autoxidation mechanism, leading to methyl hydroperoxide production, explains all previous observations about SWNT dispersion stability and the properties of IB ultrasonicated polar aprotic solvents.

We detected methyl hydroperoxide using standard methods such as the oxidation of iodide ions to triiodide.[43] The general reaction scheme is outlined as follows:

$$ROOH + 2H^+ + 2I^- \rightarrow ROH + H_2O + I_2$$

$$I^- + I_2 \leftrightarrow I_3^-$$

where we used a large excess of I^- to push the equilibrium to the right in the second step. Triiodide has strong optical absorption peaks at 290 and 365 nm.[43] After ultrasonication of an IB + O_2 sample for 2 h, triiodide was detected with a concentration on the order of 10^{-4} M (as determined by the absorption peak at 365 nm), showing that methyl hydroperoxide is formed due to sonochemically initiated autoxidation of methyl radicals.

We used several spectroscopic methods to look for methyl hydroperoxide. NMR, although quite sensitive, was unable to detect the low concentration of methyl hydroperoxide. A concentration on the order of 10^{-4} M is less than 10 ppm, with respect to DMF (or other solvent), which we are unable to easily detect. The methyl hydroperoxide concentration is also too low to see in an IR spectrum. We were able to detect methyl hydroperoxide by UV−vis−NIR, as it is known[44] that peroxides have an optical absorption below 200 nm. This absorption had not been observed in DMF, due to its UV cutoff at 270 nm, but a strong optical absorption was observed in IB + O_2 ultrasonicated acetonitrile, since this solvent has a lower UV cutoff at 190 nm. The intensity of this absorption scaled with the ultrasonication time. This absorption is not a result of H_2O_2 formation, because it is present in IB ultrasonicated samples that were kept dry during ultrasonication with $MgSO_4$, so we attribute the absorption to methyl hydroperoxide.

Methyl hydroperoxide concentrations were quantitatively determined by titrating with NaOH, using BTB as the indicator. The final methyl hydroperoxide concentration was determined under six ultrasonication conditions in DMF. Three samples were IB ultrasonicated, and three were hot ultrasonicated. Figure 4 shows sample temperatures during a 2.5 h ultrasonication. IB samples reach a final temperature of about 20 °C and hot samples reach about 110 °C, both within about 1/2 h. For each temperature condition, one sample was deaerated with argon (Ar), one was bubbled with oxygen (O_2), and the third was left under atmospheric conditions (air). All ultrasonications were 2 h long. The results, shown in Figure 5, correlate well with the observed dispersion stabilities. Whenever the methyl hydroperoxide concentration exceeded the CCC for a $Z_+ = 1$ salt in DMF, the dispersions were unstable. This occurred when oxygen was present and the samples were IB ultrasonicated.

For the two cases in which SWNT dispersions are rendered unstable (IB + O_2 and IB + air), the concentration of methyl hydroperoxide was monitored as a function of the ultrasonication time (Figure 6). In both cases, the methyl hydroperoxide concentration accurately predicts the SWNT dispersion stability

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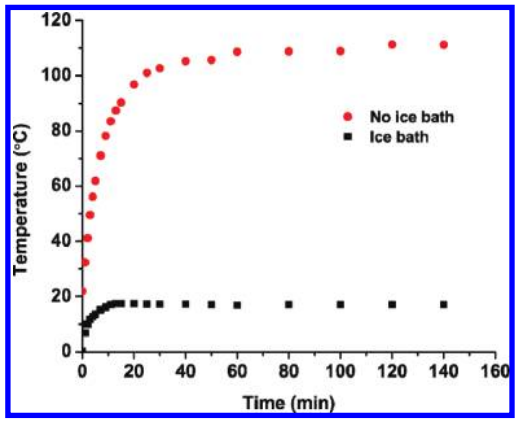

Figure 4. Temperature profile of samples during ultrasonication with and without an ice bath. Without an ice bath, the temperature stabilizes at ~110 °C. With an ice bath, it stabilizes at ~20 °C.

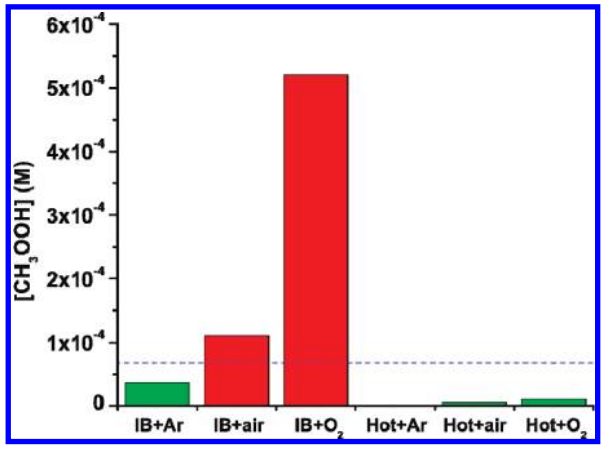

Figure 5. Typical methyl hydroperoxide concentrations in pure DMF after 2 h of ultrasonication under various ultrasonication conditions. Shown in red are the two cases where stable dispersions cannot be formed, IB + air and IB + O_2. Under these conditions, the approximate methyl hydroperoxide concentration is greater than the CCC for NaBr (6.8×10^{-5} M), which is shown as a blue dashed line, demonstrating that the dispersions are unstable due to collapse of the electrical double layer.

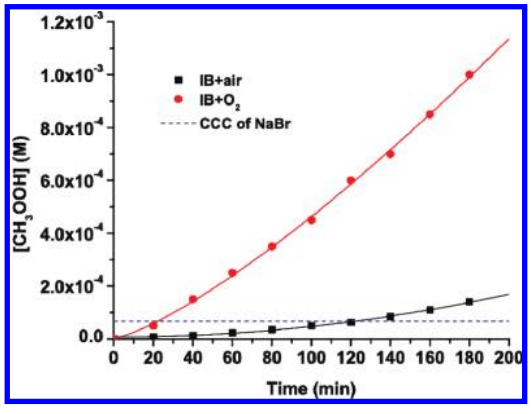

Figure 6. Concentration of methyl hydroperoxide in pure DMF as a function of the ultrasonication time, when ultrasonicated in an ice bath. If O_2 is bubbled through the sample, the CCC is reached after ~20 min of ultrasonication. If no gas is bubbled through, it takes ~120 min to reach the CCC.

when compared with the CCC for monovalent symmetric salt (6.8×10^{-5} M). Samples that were IB ultrasonicated and had O_2 bubbled through them are not stable after just 20 min, where the methyl hydroperoxide concentration is equal to the CCC for a +1 coagulant. Without O_2 bubbling, it takes approximately 120 min of ultrasonication to reach that CCC. As shown in Figure 6, the concentration of methyl hydroperoxide increases according to a weak power law dependence.

Many research groups use bath ultrasonication rather than tip ultrasonication to disperse SWNTs, so we also checked whether methyl hydroperoxide is produced during bath ultrasonication. The power generated by bath ultrasonication is much lower, so we expect less of an effect than with tip ultrasonication. An O_2-saturated sample was bath sonicated for 5 h and kept at 0 °C with a loose ice slurry, ensuring proper power transfer from the bath to the sample. Afterward, the methyl hydroperoxide concentration was determined by titration to be 5.8×10^{-5} M, which is close to the expected CCC. Therefore, there is enough power in a bath sonicator to produce similar reactions and thereby unintentionally destabilize a dispersion. More common bath ultrasonication protocols for dispersing SWNTs or other nanoparticles into small volumes do not use an ice bath or call for O_2 saturating the samples. Accordingly, we bath sonicated samples for 24 h and allowed them to warm to ~35 °C. No change in acidity was detected, such that bath ultrasonication under mild and standard conditions does not induce the formation of methyl hydroperoxide in any appreciable quantity. As we scale these processes to larger volumes, higher power and possibly cooling will be required. The results presented here suggest that an O_2-free solution will enable a higher dispersion limit and a more stable dispersion.

We varied the ultrasonication temperature and oxygen concentration to demonstrate the stability of SWNT dispersions as a function of the ultrasonication time (Figure 2). The same six ultrasonication conditions used for the titration experiments were also used to study the SWNT dispersion stability. At high temperatures, dispersions are stable regardless of whether argon, oxygen, or no gas is bubbled through the sample. Dispersion instability occurs when the samples are cooled with an ice bath during high-power tip ultrasonication. As can be seen in Figure 2, samples left under atmospheric conditions show progressively less stability as the ultrasonication time increases. Samples that have argon bubbled through them are stable regardless of the ultrasonication time because the autoxidation mechanism cannot occur. When oxygen is bubbled through the sample, the oxygen concentration (and consequently methyl hydroperoxide) is increased to the point where the dispersions are not even stable after just 20 min (the concentration of SWNTs falls to zero) of ultrasonication, precisely as predicted by the methyl hydroperoxide concentration as a function of time study (Figure 6).

Conclusions

SWNTs and other nanoparticles have high surface energies and are prone to aggregation due to collapse of the electrical double layer, as described by DLVO theory. Sonochemical reactions that could lead to acidic or other electrolytic species must be avoided to maximize the dispersion limit and stability. It is apparent from the results of this study that it is extremely important to monitor the experimental conditions when using ultrasonication to disperse nanomaterials into organic liquids, especially the methyl-containing polar aprotic solvents. We have found that, given the right conditions, ultrasonically generated methyl radicals can initiate an autoxidation reaction, leading to the production of methyl hydroperoxide and consequent destabilization of SWNT dispersions. However, elimination of oxygen from the samples prevents this reaction from occurring, and high-temperature ultrasonication allows terminal reaction

pathways to dominate. Whenever dispersing nanoparticles, it is advisable to deaerate the samples to eliminate potential sonochemical reactions involving absorbed oxygen, which could result in undesirable byproducts. As we show here, the polar aprotic solvent family is particularly susceptible to forming methyl hydroperoxide. We show that methyl hydroperoxide production by sonochemically initiated solvent autoxidation leads to the destabilization of SWNT dispersions.

This result is general across the polar aprotic solvents we studied and is particularly salient for DMF and NMP, as they are two of the best and most frequently used organic dispersants for SWNT dispersions. We have noted discrepancies in dispersion limits reported in the literature[25,26,28] for these solvents and believe that the formation of methyl hydroperoxide may be an important source of these discrepancies. Recent reports have even claimed that NMP can dissolve small SWNTs in a true thermodynamically stable fashion.[20] We have shown that SWNTs are not stable in NMP when the ionic strength exceeds the CCC. This low concentration of ions does not significantly change the dielectric constant of the dispersants, yet is does collapse the electrical double layer around the tubes. Therefore, SWNTs in DMF, DMA, and NMP behave as a kinetically stable dispersion and do not appear to be a thermodynamically stable solution. More work is needed in this field to determine the true dispersion limits of SWNTs in these and other solvents by ensuring that no sonochemical byproducts affect the dispersion limits. Further, it is important to clarify whether nanomaterials, such as SWNTs, are forming solutions or dispersions and how we distinguish between the two.

Experimental Section

N,*N*-Dimethylformamide (Fisher, Spectranalyzed), *N*-methyl-2-pyrrolidinone (OmniSolv, Spectrophotometry & Gas Chromatography), *N*,*N*-dimethylacetamide (Alfa Aesar, 99%), and acetonitrile (Burdick & Jackson, HPLC, anhydrous) were used as purchased. Deionized water was also Millipore filtered to 16 MΩ cm (referred to as "DI water"). Dispersions and pure solvents were ultrasonicated with a reflected power of 10 W rms (yielding an average power density of 0.4−0.5 W/cm^3, depending on the sample size).

Fluorescence measurements were taken with a HORIBA Jobin Yvon Fluorolog 2. The tip ultrasonicator was positioned over the fluorometer, with the tip inserted into a sample cuvette containing DMF and 100 μM lucigenin (Alexis Biochemicals). All emission was due to sonochemiluminescence, as there was no optical excitation of the solution. A Cary 5000 UV−vis−NIR spectrometer was used to measure the optical absorption for concentrations of SWNTs and triiodide. IR spectra were taken with a Nexus 870 FT-IR E.S.P. NMR spectra, for determination of water concentrations in DMF, were taken with a JEOL ECX-300.

A Thermo Finnigan Trace GC−MS instrument with Xcalibur software was used to measure oxygen concentrations in DMF. Relative oxygen concentrations were determined by integrating the peak area for $m/z = 31.5-32.5$. As a control study, Ar was used to deaerate a sample, and no O_2 peak was observed by GC−MS. GC−MS was also used to detect the formation of ethane during low-temperature ultrasonication of deaerated DMF samples.

IB ultrasonications were temperature regulated by submerging the sample vial in an ice bath during ultrasonication, which ensured that the average sample temperature was approximately 20 °C. Hot ultrasonications were not temperature regulated and reached an equilibrium temperature of approximately 110 °C.

Most samples were prepared with a Fisher Scientific Sonic Dismembrator 60 (1/8 in. tip ultrasonicator). Dispersions were made by adding ∼0.5 mg of HiPCO SWNTs (Grade P CNT, now Unidym) to the dispersants and ultrasonicated under various conditions. We monitored the dispersion stability as a function of the ultrasonication time by removing 1 mL aliquots every 20 min. After ultrasonication, the aliquots were allowed to sit undisturbed for two days so that any undispersed SWNTs would aggregate. Each aliquot was then centrifuged at 1000*g* for 10 min in a Fisher Scientific Micro7 tabletop centrifuge to sediment any aggregated SWNTs. A 100 μL volume of the supernatant was immediately transferred to a cuvette to measure the SWNT concentration on the basis of the optical absorption.[26]

The presence of methyl hydroperoxide was detected by oxidizing iodide ions to triiodide. We measured the concentration of triiodide produced by adding KI to a 2 h IB + O_2 ultrasonicated DMF sample. KI was dissolved in the sample to give an I^- concentration of 10^{-2} M (ensuring that the I^- concentration would be far in excess of the anticipated and measured I_3^- concentration of $\sim 10^{-4}$ M). The methyl hydroperoxide concentration as a function of the ultrasonication time was measured by titration, using a NaOH titrant and bromothymol blue (BTB) as the indicator. The end point was reached when the solution was the same shade of green as a reference sample, which had the same concentration of BTB in fresh DMF. When measuring the concentration as a function of the ultrasonication time, 1 mL aliquots were removed every 20 min during ultrasonication of a sample and tested. Generation of methyl hydroperoxide was independent of the SWNT concentration.

Oxygen-rich samples were prepared by bubbling pure oxygen through the samples for a minimum of 15 min before ultrasonication. Deaerated samples were prepared by bubbling pure argon through the samples for a minimum of 15 min. In both cases, the gas flow rate was kept low to prevent unnecessary solvent evaporation during ultrasonication. This was especially important at high temperatures, because excessive gas flow was observed to cause atomization of the solvent, leading to rapid solvent loss.

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Supporting Information Available: Additional and related background on colloid aggregation. This information is available free of charge via the Internet at http://pubs.acs.org.

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