The Role of Surfactant Adsorption during Ultrasonication in the Dispersion of Single-Walled Carbon Nanotubes


Center for Nanoscale Science and Technology, Rice University, Houston, Texas, USA

The ionic surfactant-assisted dispersion of single-walled carbon nanotubes in aqueous solution has been studied by Raman and fluorescent spectroscopy during ultrasonic processing. During the process, an equilibrium is established between free individuals and aggregates or bundles that limits the concentration of the former that is possible. This equilibrium is a function of free sodium dodecyl sulfate concentration. At surfactant concentrations below this value, fluorescence is shifted to a lower energy due to an increase in micropolarity from water association at the nanotube surface. The mechanism of dispersion is postulated as the formation of gaps or spaces at the bundle ends in the high shear environment of the ultrasonicated solution. Surfactant adsorption and diffusion then propagate this space along the bundle length, thereby separating the individual nanotube. The former is found to be controlling, with the use of a derived kinetic model for the dispersion process and extraction of the characteristic rate of nanotube isolation.

Keywords: Single-Walled Carbon Nanotubes, Surfactant Adsorption, Raman Spectroscopy, Fluorescent Spectroscopy, Ultrasonic Process.

1. INTRODUCTION

The solution phase dispersion of carbon nanotubes is important for the development of bulk processing techniques and makes possible the exploration of established reaction chemistries. The problem is not straightforward, however; carbon nanotubes invariably exist after synthesis as aligned aggregates or bundles that are tightly bound by an estimated 500 eV/μm of tube length.1,2 Although ultrasonication of carbon nanotubes in organic solvents3–5 and aqueous surfactant solutions2,6,7 is widely used, the mechanism of this dispersion and the factors that optimize its efficiency are poorly understood. Many researchers have screened various surfactants6,7 and polymer adsorbates2 to modify the hydrophobic surface of carbon nanotubes to permit water solubilization. Few techniques exist for monitoring dispersion in the solution phase, and past work has ignored the aggregation tenancy of nanotubes and has instead relied upon the solution mass density of carbon or optical density as a measure of solubility and dispersion.2,5,6,8

The discovery of nanotube fluorescence7 makes possible a more precise method of detecting individual nanotube dispersion and separation from a bundle.

A nanotube in an aligned bundle does not emit because of energy transfer to neighboring tubes, particularly those that are metallic, that then allow nonirradiative depopulation of the excited state. In this paper, the dispersion process is monitored by examining transient fluorescent emission and Raman scattering at 785-nm excitation as a function of ultrasonic processing in sodium dodecyl sulfate.

2. EXPERIMENTAL DETAILS

The dispersion process was monitored with a flow-through apparatus where high-shear homogenization, ultrasonication, and Raman and fluorescence spectroscopies were performed continuously on a 1-liter carbon nanotube/water slurry (not previously sonicated) at 200 mg carbon/liter recycled from a central reservoir. Solution was pumped at a flow rate of 420 ml/min from a sealed, N2-blanketed flask with a diaphragm pump (Cole-Palmer) into a flow-through high-shear homogenizer (Cole-Palmer.) This solution was then fed to a flow-through ultrasonication unit (Sonic and Materials, Inc., Newtown, CT) with temperature regulation at 32 °C through a cooling jacket on the device itself. The intensity of the unit was calibrated by measuring the temperature

Received: 11 October 2002. Revised/Accepted: 31 January 2003.
for all portions of the transient response is \(1/(0.75 \text{ h})\), and, hence, the initial activation via sonication must instead be rate limiting. The overall process rate reflects the probability that the collapse of a microbubble during the ultrasonic processing actually initiates the unzipping of the individual from the bundle and is therefore intensity dependent. The latter process, once initiated, proceeds relatively quickly.

4. CONCLUSIONS

During ultrasonic processing of carbon nanotubes in aqueous solution with SDS, an equilibrium is established between free individuals and aggregates or bundles that limits the concentration of the former that is possible. This equilibrium is a function of free SDS concentration. For surfactant concentrations below the CMC, fluorescent emission is shifted to lower energy as the surface coverage falls below saturation. The micropolarity increase due to water association at the nanotube surface accounts for the broadening and shifting of the spectrum in this way. The mechanism of dispersion is postulated as consisting of the formation of gaps or spaces at the bundle ends in the high-shear environment of the ultrasonicated solution. Surfactant adsorption and diffusion then propagate these spaces along the bundle length, ultimately separating the individual nanotube. The former step is reasoned to be rate determining, using the results of a derived kinetic model for the dispersion process and extracting the characteristic rate of nanotube isolation.

Acknowledgments: Financial support was provided by the National Science Foundation (NSF) Focused Research Group on Fullerene Nanotube Chemistry (DMR-0073046), the NSF Center for Biological and Environmental Nanotechnology (EEC-0118007), and the Robert A. Welch Foundation (C-0689). Support from NASA (NCC9-77) for the development of the HiPco method is also gratefully acknowledged.

References and Notes

aggregates. This solution was then diluted by the addition of deionized water and transferred to a cuvette. Raman and fluorescence spectra were generated as a function of solution SDS concentration. No change in the peak positions of the fluorescence is observed at concentrations above the critical micelle concentration (CMC) of SDS in water at 298 K (8.1 mM). Below this concentration, peaks shift to lower energy (Fig. 5), and the addition of SDS to reconstitutes reverses this shift. These changes were metastable over a period of hours. Equilibration of the samples overnight resulted in irreversible roping and hence elimination of fluorescence.

When normalized with respect to the maximum shift observed in a solution of carbon nanotubes in 1% wt SDS/H₂O, this ratio traces a Langmuir adsorption isotherm for SDS on the carbon surface:

\[
\frac{\Delta E}{\Delta E_{\text{max}}} = \frac{K_{\text{SDS}} C_{\text{SDS}}}{K_{\text{SDS}} C_{\text{SDS}} + 1}
\]  

Here \(\Delta E\) is the shifted peak position relative to that in a 1% SDS/H₂O solution, and \(\Delta E_{\text{max}}\) is the maximum shift observed (by extrapolation to zero concentration). The trend is overlaid in Figure 6. The adsorption equilibrium constant, \(K_{\text{adj}}\), is 0.98 liter/mol and similar to SDS adsorption from solution on graphitic surfaces. Adsorption of the surfactant necessarily excludes water from the nanotube surface. This decrease in micropolarity with decreasing water association on the chromophore surface shifts the absorption and emission spectrum to higher energy and increases the fluorescence intensity through the elimination of nonradiative energy transfer processes. The rapid reversibility of the shift with SDS concentration indicates that the adsorbed phase on the nanotube surface is in dynamic equilibrium with the bulk, and hence surfactant removal below the \(C_{\text{SDS}} = \text{CMC}\) threshold is expected to ultimately destabilize suspended nanotubes. This was observed after overnight equilibration of samples prepared at 34 mM SDS and then diluted to below 8.1 mM.

![Figure 5. Fluorescence spectra with increasing dilution of surfactant.](image)

![Figure 6. Peak centers in energy scaled by the maximum observable shift for four fluorescent features. The smooth curve is the trend, assuming that the shift is directly proportional to surfactant surface coverage and that the latter demonstrates a simple Langmuir monolayer adsorption equilibrium (Eq. (1)).](image)

3.3. Insights from Modeling the Transient Dispersion Process

The concentration of fluorescent individuals appears to come to a stable equilibrium at a particular surfactant concentration. This implies that the separation of the nanotube from the bundle is reversible, leading to a dynamic equilibrium that is a function of both carbon and surfactant concentration. Modeling this process, we write

\[
\frac{dC_1}{dt} = k_z C_b C_{\text{SDS}} - \frac{k_z}{K_{\text{eq}}} C_1
\]  

where \(C_1\) and \(C_b\) are the concentrations of individual (I) and bundled (b) nanotubes in solution, and the SDS monomer concentration in the bulk is \(C_{\text{SDS}}\). The constant \(k_z\) is the bundle “unzippering” rate, and \(K_{\text{eq}}\) is the equilibrium constant between individual nanotubes and bundles. By definition the total nanotube mass concentration \(C_T\) is constant:

\[
C_T = C_b(t) + C_1(t)
\]

Integration of Eqs. (2) and (3) yields

\[
C_1(t) = \frac{[K_{\text{eq}} C_T C_{\text{SDS}}(\gamma(t) - 1)] + C_1(0) C_{\text{SDS}} [1 + K_{\text{eq}} C_{\text{SDS}}]}{\gamma(t) [1 + K_{\text{eq}} C_{\text{SDS}}]}
\]

with

\[
\gamma(t) = e^{k_z [C_{\text{SDS}} + 1/K_{\text{eq}}] t}
\]

Equation (4) accurately models many aspects of nanotube dispersion in solution during sonication, including the observation that production of fluorescent nanotubes saturates for a given SDS concentration. This limiting concentration is given by

\[
C_{1,\text{max}} = \frac{K_{\text{eq}} C_{\text{SDS}}}{K_{\text{eq}} C_{\text{SDS}} + 1} C_T
\]
3.1. Increases in Resonance Enhancement with Debundling

When in aligned bundles, carbon nanotubes are known to undergo significant changes to their composite electronic structure, including the formation of a pseudo-gap for metallic nanotubes and an orthogonal electronic dispersion in the otherwise 1-D electronic structure. Experimentally, this electronic dispersion significantly broadens photon absorption, shifts it to lower energy, and reduces the overall intensity. When freed from bundles, isolated individuals demonstrate sharper, more intense absorption features corresponding to singularities in their 1-D electron density of states. Raman scattering can couple to and become resonantly enhanced with these transitions and increase in scattering intensity.

In Figure 1, this is why the tangential mode at 1593 cm\(^{-1}\) increases in intensity during the sonication process. At lower frequencies, the radial breathing modes undergo a unique reversal in relative intensities. The 266 cm\(^{-1}\) feature corresponds to the (10, 2) nanotube with a \(v_2 \rightarrow c_2\) optical transition at 734 nm. In a bundle, the interband transitions for this feature shift to lower energy and become partially resonant with the excitation laser at 785 nm. The 233 cm\(^{-1}\) feature belongs to the (11, 3) with a \(v_2 \rightarrow c_2\) at (792 nm). When isolated, this nanotube shows a considerable enhancement in Raman scattering. Similarly, the features at 225 cm\(^{-1}\) (10, 5) with \(v_2 \rightarrow c_2\) at 786 nm and 215 cm\(^{-1}\) (9, 7) at 790 nm also increase in intensity with increasing individual dispersion. The feature at 203 cm\(^{-1}\) (13, 3) has a transition at a lower wavelength (760 nm) and does not increase notably. The width of the resonance window in energy necessarily increases with aggregation as the absorption peaks broaden. The (13, 3) feature is both enhanced by the shifting of resonance and diminished by the broadening of the transition and remains unchanged.

Fluorescence becomes observable during the sonication experiment only with the addition of surfactant, indicating that the adsorbed phase plays a critical role in the debundling process. The mechanism of isolating individuals is explored in more detail below, but bundles are postulated not to fluoresce because of energy transfer to neighboring nanotubes in the bundle. Energy transfer to metallic nanotubes particularly quenches the emission by providing a nonradiative decay pathway.

3.2. Solvatochromic Shifts Observed with Surfactant Adsorption

The systematic shifting of fluorescent emission to higher energy follows the addition of surfactant during the sonication process. This behavior was found to occur as an effect that is separate from ultrasonic processing. To examine this process in more detail, sonicated solution was centrifuged at 30,000 rpm to remove large
rise of pure water fed to the device and performing an energy balance (230 W).

The outlet of the sonicator passed through a flow-through cuvette (Stermas), where Raman and fluorescent spectroscopies were performed at 1-min intervals with a Kaiser Raman process spectrometer (Ann Arbor, MI) at 785-nm excitation. The CCD camera of the spectrometer allows for detection out to 1050 nm, where it captures a portion of the nanotube fluorescence spectrum at 785-nm excitation. In this way, both Raman and fluorescent spectroscopies were captured in real time during processing. The observed intensity $I$ of a spectral feature was related to the concentration of emitting and scattering carbon nanotubes, $c$, with the use of a point-scattering model\textsuperscript{9,10} where

$$\ln \left( \frac{I}{I_0} \right) = \ln(Jc) - kc(\delta_1\varepsilon_1 + \delta_2\varepsilon_2)$$

Here, $I_0$ is the incident excitation intensity, $J$ is the scattering coefficient, $k$ is $\log(e) = 2.303$, and $\varepsilon_i$ and $\delta_i$ are the absorptivity and effective path lengths of the incident (1) and scattered (2) radiation. A calibration plot generated in the experimental setup yields $J = 60.6.9 \text{ L/mg}$ and $(\varepsilon_1\delta_1 + \varepsilon_2\delta_2) = 2.03 \text{ L/mg}$ and suggest that attenuation due to reabsorption and scattering were minor below 50 mg/liter of completely sonicated 1% sodium dodecyl sulfate (SDS) suspended nanotubes.

During the actual flow-through experiment, SDS (98% pure; Aldrich) was increasingly added to the solution reservoir. Dilution experiments were also conducted offline, and processed solution was subsequently diluted by the addition of deionized water to produce the desired SDS concentration. The nanotubes were synthesized by high-pressure CO disproportionation (HiPco) as described previously\textsuperscript{11} and were generated as reactor run 106.1 at Rice University. The nanotubes were used without further purification.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the Raman/fluorescence spectrum of the nanotube solution at the start of the experiment at 0 mM SDS concentration ($\times3$) and after 5 h of ultrasonic processing with progressive SDS addition terminating at 34 mM. Ultrasonic processing increases the Raman tangential mode at 1593 1/cm by a factor of 3.6 as individual nanotubes are dispersed but does not change the Raman shift of this peak.

During the process, the evolution of fluorescent emission is monitored as a function of time. Figure 1 labels the emission from the (6, 4), (9, 1), (8, 3), (6, 5), and (7, 5) nanotubes as indicated\textsuperscript{12}. Following the growth of these fluorescent features as a function of time, the intensity from the sample appears to rise and saturate after the addition of an aliquot of surfactant. Figure 2 shows the growth of the (8, 3) feature as an example. No emission is evident at the start of the experiment, where sonication proceeds in the absence of surfactant. After each addition of surfactant, the fluorescence intensity rises and stabilizes to a steady-state value over a period of about 20 min to 1 h, depending on the amount of added surfactant. An increased sonication time did not result in an increase in the Raman D-band, indicating that few defects if any were introduced by the processing. The effect of oxygen was explored by first degassing the reservoir for 2 h at 100 °C and then conducting the processing in a N$_2$ shelter gas and again in a stream of flowing O$_2$ at 1 atm. The change in purge gas had no apparent effect.

Also during the process, immediately after the addition of surfactant, the fluorescent features shift systematically to higher energy. Figure 3 shows the peak centers of the (8, 3) (a) and (7, 5) (b) nanotubes as a function of time. The shifts occur immediately after each addition, and, when compared on the energy scale, they do so by nearly the same magnitude (8 meV).

Raman peaks in the region from $\sim$200 to 400 cm$^{-1}$ arise from the scattering of distinct nanotubes with the frequency as an inverse function of the diameter of the