Supporting Information for JA076700M

Interfacial Trapping of Single-Walled Carbon Nanotubes

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Experimental Details:
Nanotube suspensions were prepared with a given initial mass (typically 6 mg) of raw SWNTs (Rice HPR 145.1) and mixed with 200 mL of an aqueous Gum Arabic (Sigma-Aldrich) surfactant solution (1 wt. %) to form an initial concentration of 0.03 mg/mL. High-shear homogenization (IKA T-25 Ultra-Turrax) for 1 hr and ultrasonication (Misonix S3000) for 10 min were used to aid dispersion. Control samples were ultracentrifuged at 26,000 rpm (Beckman Coulter Optima L-90 K) to remove nanotube bundles. Toluene (Acros, 99%) was added to other aqueous SWNT suspensions and the mixture was shaken vigorously for 30 s to increase interfacial area and remove SWNT bundles from the suspension. Note that other organic solvents immiscible with water can also be used. These solvents may have slightly different responses due to changes in the interfacial tension. All chemicals were used as received.

Absorbance and fluorescence spectra were recorded using an Applied NanoFluorescence Nanospectrolyzer with excitation from 662 and 784 nm diode lasers. The aqueous phase was carefully removed after interfacial trapping to prevent further emulsification. Optical images were collected by a Nikon ECLIPSE TE2000-E optical microscope. Emulsions with and without SWNTs were collected by removing the interphase that forms during mixing and dropping it on microscope slides.

Toluene/Water Emulsions:
Figure S1a and S1b are optical micrographs of emulsions stabilized with Gum Arabic and Gum Arabic-coated SWNTs, respectively. A large emulsion size distribution is seen for both systems as seen in Figure S2. The Gum Arabic stabilized emulsions have an average size of 75 ± 6 μm while the SWNT solution has an average size of 91 ± 5 μm. In addition to having a larger average size, it appears that the SWNT stabilized emulsions also have a bimodal size distribution. Finally, the emulsions in Figure S1b appear to have some particulate at the interface.
Figure S1. Toluene/water emulsions stabilized by (a) Gum Arabic and (b) Gum Arabic-suspended SWNTs.

Figure S2. Diameter distribution of emulsions stabilized by (a) Gum Arabic and (b) Gum Arabic-suspended SWNTs. The average diameter of the emulsions are $75 \pm 6 \mu m$ and $91 \pm 5 \mu m$, respectively.

**Fraction of individual SWNTs in suspension:**
The relative intensity of the van Hove peaks in the absorbance spectra and their width are related to the fraction of individual SWNTs in solution and dispersion quality. Tan and Resasco showed that the resonance ratio could be used to characterize the fraction of
individual SWNTs in solution. This ratio is calculated by comparing the area for the resonant band with the non-resonant band (carbonaceous impurities and π-plasmon). An example is shown in Figure S3 for interfacial trapping. The resonance ratios were calculated for the peaks near 660 and 740 nm. Table S1 shows the calculated values for the resonance ratio for different dispersion samples. As can be seen in the table, the interfacial trapping method shows improved dispersion characteristics and improved fractions of individually suspended SWNTs. Ultracentrifugation yields the best dispersion characteristics and estimated quantum yields but suffer from very low SWNT yields. Further research on interfacial trapping should yield better SWNT dispersion characteristics with high yields.

![Absorption Spectrum](image)

Figure S3. Absorption spectrum of SWNTs in the range of the S_{22} interband transitions. The spectra is split into the resonant band and the non-resonant background associated with carbonaceous impurities and π-plasmon. The integrated area of each is then used to calculate the resonance ratio which is directly related to the fraction of individual SWNTs in the suspension.

Table S1: Comparison of the resonance ratio for different samples.

<table>
<thead>
<tr>
<th>Dispersion History</th>
<th>Peak near 660 nm</th>
<th>Peak near 740 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.0334</td>
<td>0.0244</td>
</tr>
<tr>
<td>Interfacial Traps</td>
<td>0.0463</td>
<td>0.0378</td>
</tr>
<tr>
<td>Ultracentrifugation</td>
<td>0.0625</td>
<td>0.0545</td>
</tr>
</tbody>
</table>
Absorbance and Fluorescence Spectra at lower concentrations:

To further prove that the enhancement of the fluorescence seen in Figure 3 is due to the removal of bundles, SWNT suspensions with lower concentration are prepared (0.005 mg/mL). After interfacial trapping, the fluorescence spectra has only slight decreases in intensity as seen in Figure S4a. However, the absorbance in Figure S4b has decreased significantly. The slight decrease in fluorescence intensity could be due to the removal of individual SWNTs during interfacial trapping. Therefore, the obvious decrease in absorbance can only be attributed to the removal of bundles or other carbonaceous impurities from the aqueous phase. This data further suggests that SWNT bundles are selectively removed from the aqueous phase using interfacial trapping. Note that ultracentrifugation at this low concentration yielded no measurable absorbance or fluorescence.

Figure S4. (a) Fluorescence and (b) absorbance spectra of SWNTs at a concentration of 0.005 mg/mL. For the fluorescence spectra in (a), the upper and lower panel are excited at 662 and 784 nm, respectively.

References


