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Communication

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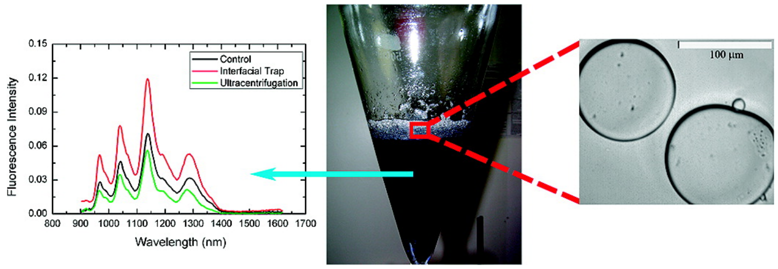

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Interfacial Trapping of Single-Walled Carbon Nanotube Bundles

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Single-walled carbon nanotubes (SWNTs) have excited researchers for several years because of their unique physical and chemical properties, which can be used in microelectronic, materials science, and biomedical applications.[1] However, many common solvents cannot offer sufficient solvation forces to suspend SWNTs yielding low degrees of solubility.[2] Surfactants or polymers are often used to stabilize SWNT suspensions.[3−5] The conventional method to disperse individual nanotubes in aqueous solutions is by high-shear homogenization and ultrasonication in various surfactant solutions. While individual nanotubes are coated with a surfactant, some SWNT bundles remain because of large van der Waals attractions.[6] The bundling of nanotubes perturbs the electronic structure quenching the fluorescence of SWNTs.[7,8] Ultracentrifugation is often used to remove nanotube bundles, but it is limited to analytical scales. Therefore, alternative routes are needed for large-scale removal of SWNT bundles.

The adsorption of particles at oil/water interfaces results in emulsion stabilization. These colloidal-stabilized emulsions were first characterized by Pickering in 1907.[9] These systems have recently gained renewed interest because of their ability to self-assemble nanorods at the interface,[10] to separate particles, such as ampicillin and phenylglycine crystal mixtures in water/alkanol systems,[11] and to prepare unique porous structures.[12] Recently, Wang, Hobbie, and co-workers[13] were the first to show SWNT-based stabilization of emulsions. Bare nanotubes were used as amphiphobic surfactants that stabilized toluene/water emulsions for months.[13] Later, DNA-wrapped SWNTs were shown to stabilize emulsions for the synthesis of colloidal particles.[14] Stabilized emulsions were also seen in length-based separations of functionalized SWNTs.[15] More recently, researchers have begun to use SWNT-based Pickering emulsions for other applications such as controlled release capsules[16] and lubricating additives.[12]

In this communication, we introduce a process to remove nanotube bundles from aqueous suspensions by liquid−liquid interfacial trapping at toluene−water interfaces. Not only is the approach simpler than ultracentrifugation, but the resulting suspensions also have higher fluorescence intensities indicative of a higher concentration of individually suspended nanotubes.

Figure 1a represents a typical example of the system after phase separation. As can be seen in the separatory funnel, a stable interphase is formed with a lower aqueous phase less than 1 min after mixing. Optical micrographs (Figures 1a and S1b) confirm emulsion stabilization by SWNTs with diameters of approximately 91 μm. These emulsions are slightly larger than those formed using only Gum Arabic and also appear to have different distributions of emulsion diameter (see Supporting Information). The movement of nanotubes to the interface can be expected from free energy changes induced by changes in wetting and interfacial area as shown in Figure 1c.[10,17,18] These energy changes have explained why larger particles are more stable at the interface.[19] Similarly, SWNT bundles are likely to be trapped at the toluene−water interface.

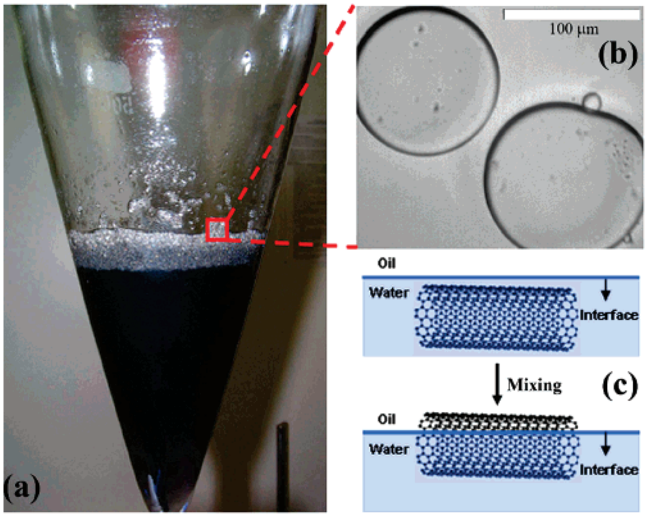

Figure 1. Interfacial trapping process for an initial SWNT mass concentration of 0.03 mg/mL. (a) A separatory funnel showing the interface between the oil and water phases. (b) Optical micrograph of toluene/water emulsions stabilized by SWNTs. (c) Illustration of the adsorption of SWNTs at the interface resulting in changes to the interfacial area and the wetting properties of the nanotube.

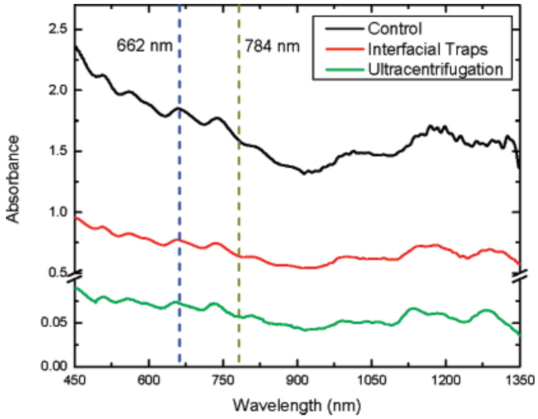

Figure 2. Absorbance spectra of Gum Arabic-suspended SWNTs from an initial mass concentration of 0.03 mg/mL of raw material. Dotted lines show the excitation wavelength used in the fluorescence experiments. The control spectrum (black line) is the sample after homogenization and sonication. This sample is then subjected to either ultracentrifugation (green line) or interfacial traps (red line). Note the break in the absorbance scale.

Vis−NIR absorbance spectra are shown in Figure 2. The solutions were allowed to settle for at least 60 min to ensure that steady state was achieved. The homogenized and sonicated sample (control) has high absorbance due to the concentration of both individual (as evidenced by the van Hove singularities) and bundled SWNTs. The absorbance of the suspension clearly decreased after interfacial trapping, demonstrating removal of nanotubes from the aqueous phase. In addition, the spectra blue shift and the spectral

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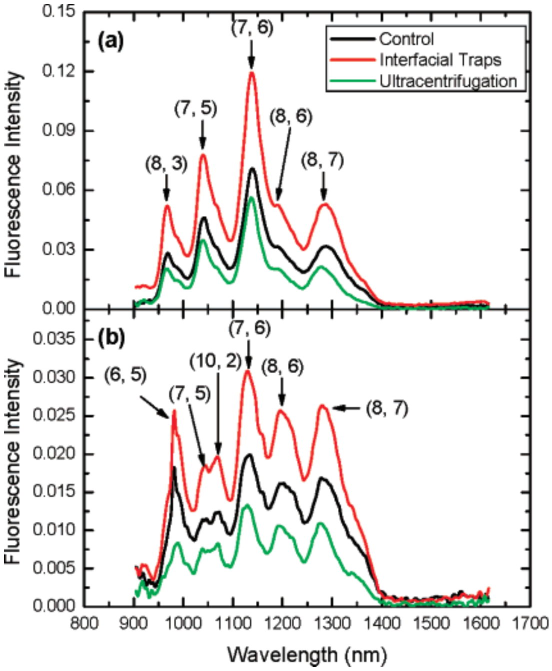

Figure 3. Fluorescence spectra of Gum Arabic-suspended SWNTs from an initial mass concentration of 0.03 mg/mL of raw material with (a) excitation at 662 nm, and (b) excitation at 784 nm. The control spectra are the samples after homogenization and sonication. This sample is then subjected to either ultracentrifugation or interfacial traps.

features are better resolved, indicating a higher fraction of individual SWNTs.[20] When the control suspension was ultracentrifuged, the absorbance of the aqueous phase is significantly lower, demonstrating nearly complete removal of nanotubes. The fraction of individual nanotubes in each sample can be estimated by comparing the resonant absorbance spectra to the absorbance of the nonresonant background[20] (see Supporting Information). This ratio shows that interfacial trapping increases the fraction of individual SWNTs in the sample when compared to the control sample.

Fluorescence spectra of the aqueous phase were recorded with excitation at 662 and 784 nm as shown in Figure 3a and 3b, respectively. For comparison, the spectra after homogenization and ultrasonication is shown (control) as well as the spectra using conventional ultracentrifugation rather than interfacial trapping. The spectra show that ultracentrifugation results in a substantial decrease in fluorescence intensity indicative of the removal of individual nanotubes. However, the fluorescence intensity after interfacial trapping has increased when compared with the control sample.

Fluorescence intensities are related to the concentration of individual nanotubes. In highly concentrated suspensions such as the control sample, the intensities are also affected by bundles. The intertube spacing in the control sample can be expected to be small because of the high volume fraction of both individual and bundled nanotubes. As mentioned previously, bundled nanotubes will not exhibit fluorescence, but it is also expected that the fluorescence intensity of individually suspended SWNTs will decay as the volume fraction increases because of energy-transfer self-quenching mechanisms.[21] Selective removal of SWNT bundles from the solution would allow more individual, semiconducting SWNTs to be excited and result in increased fluorescence intensities. At lower initial mass loadings, the effect of bundles on fluorescence is reduced. Figure S4a shows that the fluorescence at low concentrations has only a slight change after interfacial trapping, while the absorbance in Figure S4b has diminished significantly. The dependence of fluorescence changes on concentration and the reduced absorbance at low initial SWNT concentrations suggest that bundle removal is responsible for the changes in fluorescence seen in Figure 3.

In conclusion, a new liquid−liquid method is developed to remove SWNT bundles from an aqueous suspension. This new interfacial trapping technique offers a simple route to achieve large-scale production of aqueous SWNT suspensions. The significant decrease in absorbance intensity combined with increases in fluorescence intensity suggests that this method has selectively removed nanotube bundles from the aqueous suspension. Ultracentrifugation results in better dispersions, but interfacial trapping results in aqueous dispersions with higher fluorescence intensities and overall yields. However, further studies are expected to improve dispersion quality.

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Supporting Information Available: Experimental details, optical micrographs of emulsions stabilized by Gum Arabic and Gum Arabic-suspended SWNTs, diameter distributions of emulsions, the calculation of SWNT fractions, and fluorescence and absorbance spectra at lower initial mass concentrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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