

Individually Suspended Single-Walled Carbon Nanotubes in Various Surfactants

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ABSTRACT

Individual single-walled carbon nanotubes (SWNTs) have been suspended in aqueous media using various anionic, cationic, nonionic surfactants and polymers. The surfactants are compared with respect to their ability to suspend individual SWNTs and the quality of the absorption and fluorescence spectra. For the ionic surfactants, sodium dodecylbenzene sulfonate (SDBS) gives the most well resolved spectral features. For the nonionic systems, surfactants with higher molecular weight suspend more SWNT material and have more pronounced spectral features.

Single-walled carbon nanotubes (SWNTs) have been of great interest to researchers over the past decade because of their unique physical and chemical properties and potential applications.¹ To exploit these unique properties, many groups have suspended nanotubes in organic² and aqueous media.^{3–5} Recently, single-walled carbon nanotubes have been suspended in aqueous media as individuals surrounded by a sodium dodecyl sulfate (SDS) adsorbed phase.⁴ It was found that not only is the optical spectrum very structured but also that nanotubes fluoresce in the near-IR with a similar spectrum.⁴ Combined, both techniques elucidate the expected van Hove singularities from the density of states with minimal perturbation of the SWNTs.⁶ While SDS-suspended nanotubes have many applications, the use of other surfactant and polymer systems can greatly increase the applications of suspended nanotubes. For example, in the biomedical field poly(ethylene oxide) is the preferred solubilizing polymer,^{7–12} and in materials science it is best to have tailored surfactant and polymer systems for different applications.^{13–18} In this paper, we present SWNTs suspended in a wide range of surfactants and polymers with an analysis of yield and spectral features.

Various anionic, nonionic, and cationic surfactants and polymers (Table 1 and Supporting Information) were used to suspend as-produced HiPco¹⁹ SWNTs from Rice Univer-

sity (HPR 106.1). Starting with 300 mg/L SWNTs in 200 mL of aqueous surfactant or polymer (2 wt %), individually suspended nanotubes were produced following the procedure previously described⁴ that involves high-shear homogenization, ultrasonication, and ultracentrifugation. Since it is known that the absorption and fluorescence spectra of SDS-suspended nanotubes changes in acidic conditions,²⁰ all samples were studied at pH 10 (except sodium dodecylsulfonate (SDSA), which was studied at pH 6 because the system flocculates under basic conditions).

The absorption spectra of the suspended individuals were observed using a Shimadzu UV-3101PC UV–visible-NIR scanning spectrophotometer. Raman and a portion of the fluorescence spectra were measured using a Kaiser Optical Systems, Inc. Raman spectrometer with 785 nm laser excitation. Samples were also sent to the Technion-Israel Institute of Technology for cryogenic-transmission electron microscopy (cryo-TEM) imaging.

The cryo-TEM image of SDS suspended nanotubes before centrifugation (Figure 1a) shows that suspensions of nanotubes that have been sonicated contain metal catalyst and individual and bundled SWNTs. Interestingly, the metal catalyst associates with the larger SWNT bundles rather than the individuals and smaller SWNT bundles. This association undoubtedly adds density to the larger bundles making centrifugation more effective. Consequently, the resulting

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Table 1. Surfactant and Polymer Suspended Nanotubes Spectral Properties

surfactant/polymer ^a	molecular weight	mass percent conversion	(8,3) fluor. G-peak	(8,3) fluor. pos. relative to SDS (cm ⁻¹) ^b
anionic				
SDS	288.4	3.3 ± 0.5	3.6 ± 0.5	0 ± 10
SDBS	348.5	3.9	4.6	2
SDSA	272.4	6.0	4.5	-30
Sarkosyl	293.4	2.8	4.3	-117
TREM	428	4.0	3.0	-47
PSS-70	70,000	4.7	1.4	-214
cationic				
DTAB	308.4	5.6	2.3	-129
CTAB	364.5	5.1	2.3	-124
nonionic				
Brij 78	1,198	4.3	1.3	-203
Brij 700	4,670	6.4	2.5	-106
Tween 85 ^c	1,839	3.9	1.8	-79
Triton X-405 ^c	1,966	5.0	2.8	-119
PVP-1300 ^c	1,300,000	4.1	0.4	-211
EBE	4,970	6.4	3.6	-75
Pluronic P 103	4,950 (1,485) ^d	1.9	0.7	-68
Pluronic P 104	5,900 (2,360) ^d	3.0	0.8	-69
Pluronic P 105	6,500 (3,250) ^d	4.8	1.4	-70
Pluronic F 108	14,600 (11,680) ^d	8.7	1.2	-95
Pluronic F 98	13,000 (10,400) ^d	9.4	1.1	-97
Pluronic F 68	8,400 (6,720) ^d	5.8	1.2	-103
Pluronic F 127	12,600 (8,820) ^d	7.1	1.6	-84
Pluronic F 87	7,700 (5,390) ^d	8.8	1.5	-105
Pluronic F 77	6,600 (4,620) ^d	2.5	0.5	-208
Pluronic F 85	4,620 (2,310) ^d	0		

^a Sodium dodecyl sulfate (SDS – Aldrich); sodium dodecylbenzenesulfonate (SDBS – Aldrich); sodium dodecylsulfonate (SDSA – Aldrich); sodium *n*-lauroylsarcosinate (Sarkosyl – Aldrich); sodium alkyl allyl sulfosuccinate (TREM – Cognis Corporation); polystyrene sulfonate (PSS – Aldrich); dodecyltrimethylammonium bromide (DTAB – Aldrich); cetyltrimethylammonium bromide (CTAB – Aldrich); Brij (Aldrich); Tween (Aldrich); Triton X (Aldrich); poly(vinylpyrrolidone) (PVP – Aldrich); PEO-PBO-PEO triblock polymer (EBE – DOW); PEO-PPO-PEO triblock polymer (Pluronic – BASF) See Supporting Information for structures. ^b The position of the (8,3) fluorescence feature in SDS suspended nanotubes is at 10,505 cm⁻¹ or 952 nm. ^c Lower molecular weight Tween and Triton X surfactants and PVP and Pluronic polymers were tried, but none yielded nanotubes in the decant. ^d Number in parentheses is PEO molecular weight.

decanted material contains mostly individual nanotubes and the only metal catalyst found is at the end of nanotubes (Figure 1b, an SDS decant). We believe that the nanotubes are largely uniformly covered by the surfactant. The striation pattern seen by others when imaging dried surfactant/SWNT samples²¹ is not evident in the liquid state. SDS micelles are also imaged (arrows); some seem to decorate the individual nanotube (arrowheads). Cryo-TEM studies indicate that a large percentage of the nanotubes are present as individuals.

Their presence as individuals in a low perturbing adsorbed phase environment permits fluorescence and narrow absorption features. Figure 2a is a comparison of the absorption spectra, normalized at 632 nm, of nanotubes suspended by four different surfactants. SDS and SDBS give the bluest shifted nanotube spectra of all the surfactants and polymers tested. Cetyltrimethylammonium bromide (CTAB) and Brij 700 are also displayed to give an idea of the red shifting seen with other surfactants; an explanation for these observations is given below. Figure 2b compares the Raman and partial fluorescence spectrum, normalized to the G-peak,²² for the same four surfactants. Other than shifts in the fluorescence peak positions, the Raman spectral profile and line positions of the radial breathing modes (RBMs) and

G-peak are the same in all surfactants. In this study each surfactant and polymer was tested for its ability to suspend nanotubes and the spectral properties of those suspensions. Table 1 lists the results of the SWNT suspensions in the surfactants and polymers studied.

Mass percent conversion is a measure of the surfactant or polymer's ability to suspend nanotube material, that which is left in the decant compared to the original concentration. So for SDS the final concentration of SWNTs in the decant is 9.9 mg/L giving a 3.3% conversion. This mass percent conversion stays constant for varying initial concentrations up to 500 mg/L before beginning to fall off. For the ionic surfactants and polymers, the mass percent conversions are similar, but in the nonionic nanotube suspensions there is much variation. Within each individual nonionic surfactant or polymer series of suspended nanotubes (Brij, Tween, Triton X, and PVP), as the surfactant or polymer molecular weight increases, mass percent conversion increases in most cases from no conversion to an average nanotube suspendability of 5% mass conversion. The same trend of higher molecular weight polymers enhancing the suspendability of nanotubes is true for the Pluronic series. This is easily explained with steric stabilization by the adsorbed surfactant or polymer layer. As the PEO chains of the Pluronic

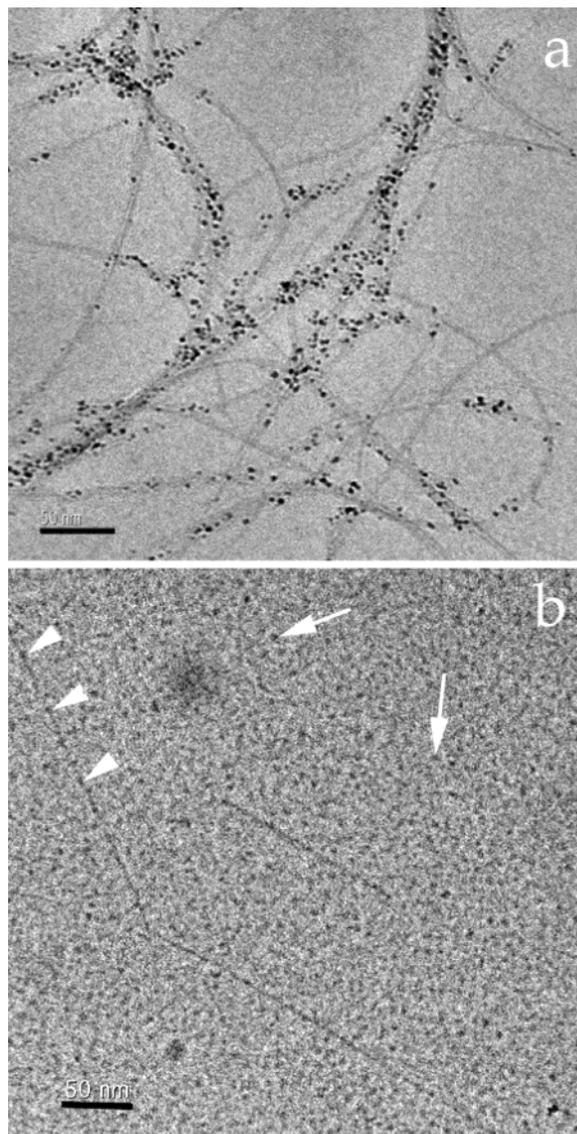


Figure 1. Cryo-TEM images of SDS suspended nanotubes (a) before and (b) after centrifugation.

polymers extend into the water, they impede nanotube aggregation;²³ this type of stabilization is not seen in the ionic surfactants because charge repulsion is the dominating factor impeding nanotube aggregation. Since the Pluronic series is stabilized by PEO, the mass percent conversion should be highly dependent on the PEO molecular weight and not as much on the PPO molecular weight; mass percent conversions for the Pluronic series are shown plotted in Figure 3. Spectral properties of the nanotube suspensions were also probed in two other ways. The (8,3) nanotube fluorescence peak to G-peak relative intensity ratio is given as a relative measure of the energy transfer of the excited state to the surroundings. The (8,3) fluorescence peak position shift relative to an SDS suspension provides a relative measure of the interaction of the excited state with its surroundings.

Figure 4 shows the correlation between the fluorescent yield and fluorescent peak position relative to SDS with respect to the hydrophobic portion of the surfactant or

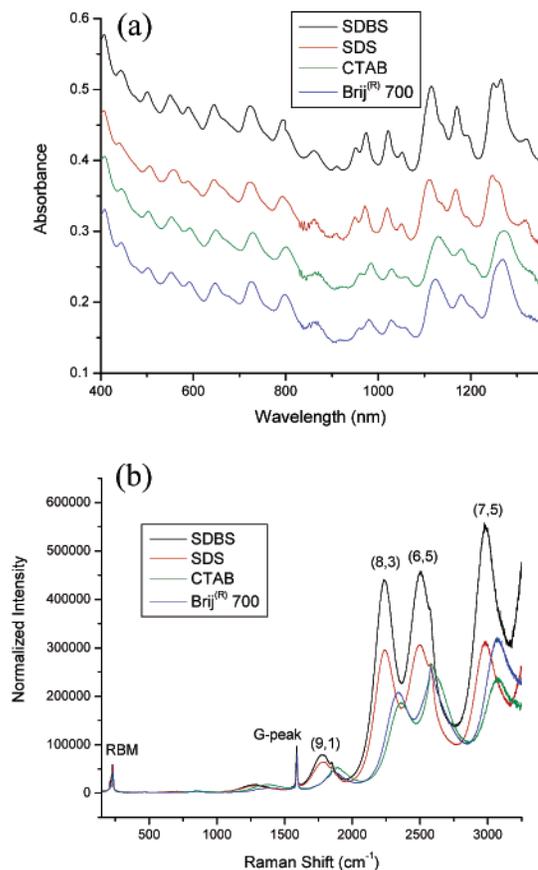


Figure 2. (a) Absorption spectra, (b) Raman and fluorescence spectra of nanotubes suspended in select surfactants.

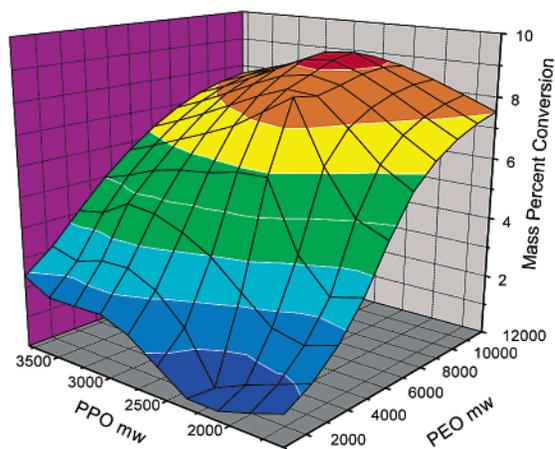


Figure 3. Surface contour plots of PEO and PPO molecular weight effects within the Pluronic series of polymers relative to mass percent conversion of individual nanotubes.

polymer. There appears to be a linear correlation between fluorescent yield and spectral shift for the surfactants with hydrocarbon tail groups and simple headgroups. This same linear behavior is seen in SDS suspended nanotubes when the SDS concentration is dropped below its critical micelle concentration (cmc),²⁴ which decreases the SDS coverage around the nanotube allowing water to reach the sidewall of the nanotube. These two results suggest that water at the nanotube surface decreases the fluorescent intensity and shifts the fluorescence peak. However, there are surfactants with

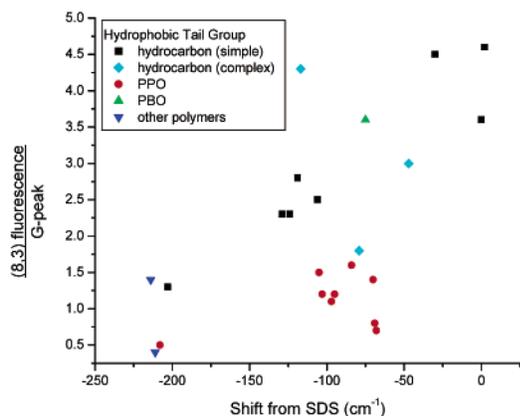


Figure 4. Plot to show the correlation between the (8,3) fluorescence peak position relative to SDS and (8,3) fluorescent yield relative to the G-peak with respect to the type hydrophobic tail group.

hydrocarbon tail groups, such as Sarkosyl, that do not fit the linear pattern. In this case, the fluorescent intensity is greater than expected relative to the observed spectral shift. Fluorescent yield appears also to be strongly affected by the hydrophobicity of the central polymer chain for nanotubes suspended in nonionic polymers as indicated by EBE relative to the Pluronic series.

A series of anionic, cationic, and nonionic surfactants and polymers have been tested for their ability to suspend individual single-walled nanotubes. A nonionic surfactant or polymer's ability to suspend nanotubes appears to be due mostly to the size of the hydrophilic group, with higher molecular weights suspending more nanotube material because of enhanced steric stabilization with longer polymeric groups. By tailoring a surfactant or polymer's head and tail groups one can tailor the suspendability of nanotubes and the spectral properties of those suspensions to fit specific applications. The ability to suspend nanotubes as individuals with various surfactants in water opens the door for material engineers, biomedical researchers, and others to incorporate individual nanotubes into a variety of water-based chemical environments.

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Supporting Information Available: Chemical structures of all surfactants and polymers used to suspend individual nanotubes are available free of charge via the Internet at <http://pubs.acs.org>.

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