

Fluorescent Carbon Nanotubes in Cross-Linked Micelles

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As illuminated in 1991,^{1,2} carbon nanotubes possess unique electronic and mechanical properties that have received much attention.³ The breakthrough finding that semiconducting single-walled carbon nanotubes (SWNTs) fluoresce⁴ has generated intense interest in their optical properties as well. For example, the fact that semiconducting SWNTs have a size-tunable energy gap (E_g) spanning a wide wavelength range from the visible to the infrared spectral regions⁵ and are highly robust emitters⁶ allows for potential applications in nanometer-scale optoelectronics,^{7,8} biotechnology,^{9–11} and quantum optics.^{12,13}

Typically, as-synthesized nanotubes form tightly bundled ropes with a mixture of metallic and semiconducting SWNTs.^{14,15} The electronic properties of these ropes are different from that of individual SWNTs: bundling broadens SWNT energy levels and red-shifts their overall band gap energy.¹⁶ Bundling of nanotubes also results in intertube energy transfer that completely quenches their fluorescence.^{4,17} However, dispersing and isolating nanotubes in surfactant micellar structures allows them to fluoresce.⁴ These suspen-

sions have some limitations because they are highly sensitive to environmental conditions, such as surfactant concentration, and the presence of salts in the solution.¹⁸ For example, drying or cooling the SWNT suspension causes aggregation and forces the majority of suspended nanotubes to rebundle into ropes. In addition to general problems with stability, for aqueous suspensions it is very difficult to observe fluorescence from SWNTs with diameters larger than 1.2 nm due to strong absorption by water in the near- and mid-infrared.⁴

One potential solution to the relative instability of nanotube dispersions is to cross-link the surfactant surrounding the nanotube. Cross-linking the micellar head groups encases the SWNT in a robust hydrophobic cage, which should produce a stable suspension in a variety of environmental conditions. For example, it has been reported that polystyrene-*b*-poly(acrylic acid) (PS-PAA) micelles can be cross-linked to encase SWNTs,¹⁹ and significant resistance to flocculation was recently reported for SWNT suspensions in cross-linked PEG-terminated block copolymers (PEG-eggs), which are stable for months.²⁰ However, fluorescence from PS-PAA films shows inhomogeneous broadening and PEG-egg surfactants require complicated synthesis techniques.

We report a procedure for producing isolated SWNTs inside cross-linked micelles of Sarkosyl, a surfactant for which we have found considerable advantages with respect to typical surfactants used to solubilize nanotubes. Significantly, upon cross-linking the Sarkosyl, SWNTs remained largely isolated from one another even when the suspension was dried into densely packed nanotube films.

Purified HiPco SWNTs were used for all studies. Suspensions in Sarkosyl were obtained by adding 0.05 wt % of nanotubes to a 2 wt % aqueous Sarkosyl solution. One hour of homogenization was followed by 15 min of probe sonication (~40 W). Suspended ropes were separated from isolated nanotubes by ultracentrifugation at $108\,000 \times g$ for 4 h; the supernatant was ultracentrifuged for an additional 1.5 h at the same speed. The supernatant, containing individual Sarkosyl-wrapped SWNTs, was reserved and used in the cross-linking experiments. For comparison, SWNTs were also suspended in sodium dodecyl sulfate (SDS) and PS-PAA in D₂O using similar methods.^{4,19}

Sarkosyl-wrapped nanotubes were cross-linked using a method similar to that reported for cross-linking PS-PAA and PEG-egg SWNT suspensions.^{19,20} However, in our method we used *N*-hydroxysulfosuccinimide (sulfo-NHS) in addition to 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC) to activate the carboxylic acid groups (Figure 1). In a typical experiment, 1 mL of Sarkosyl SWNT suspension was added to 2 mL of deionized water. Immediately added to this solution were 500 μ L of 0.14 M

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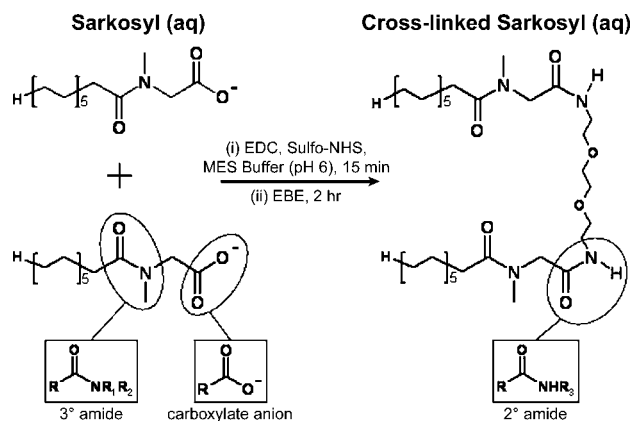


Figure 1. Scheme for cross-linking micellar head groups in aqueous Sarkosyl suspensions of SWNTs. Sarkosyl carboxylate anion functional groups are replaced with bridging secondary amides.

EDC and 500 μL of 0.32 M sulfo-NHS solution in 0.5 M 2-(4-morpholino)ethanesulfonic acid buffer (MES, pH \sim 6). The solution was stirred gently for 15 min before adding 12 μL of 2,2'-(ethylenedioxy)bis(ethylamine) (EBE). The solution was left undisturbed for 2 h, with stirring, to allow the cross-linking reaction to complete. It is important to note that Sarkosyl had to be associated with the SWNTs prior to cross-linking; preformed cross-linked Sarkosyl micelles did not suspend SWNTs. The PS-PAA SWNT suspensions were created following the procedure in ref 19. For solid films, the suspensions were precipitated by centrifugation, collected onto a microscope slide, and dried overnight.

FTIR and fluorescence spectroscopies were used to verify the success of the cross-linking reaction. Fluorescence spectra were collected with a Ge detector and an Acton Research Corporation 300i spectrometer with excitation at 633 nm. FTIR spectra were acquired using a Shimadzu FTIR-8400S spectrometer and showed the appearance of the expected amide modes (C–N and N–H) upon cross-linking. FTIR data are discussed in detail in the Supporting Information.

Carbon nanotube structures can be characterized by two integers (n,m) that define both the nanotube diameter and chirality.³ These parameters define the optical properties of a particular nanotube, as SWNTs emit at discrete energies characteristic of a specific nanotube (n,m) structure (Figure 2).^{4,5} In particular, the narrow spectral widths of these fluorescence peaks indicate the presence of a significant number of isolated nanotubes.^{4,5} Also apparent in Figure 2 is that the fluorescence spectrum for nanotubes solubilized in SDS is quite similar to that in Sarkosyl, except for an overall red-shift (for Sarkosyl) of 73 cm^{-1} , again indicating the presence of isolated nanotubes. This energy shift of the fluorescence peaks, differing in magnitude and sign for a given surfactant, has been explained as a chemical perturbation of the electronic states of the SWNT due to the strong hydrophobic interaction between the nanotube and the surfactant.²¹ Upon cross-linking, we observed an average \sim 60% decrease in fluorescence intensity and no significant spectral shift (Figure S1, Supporting Information). Of particular importance is that the fluorescence spectrum from

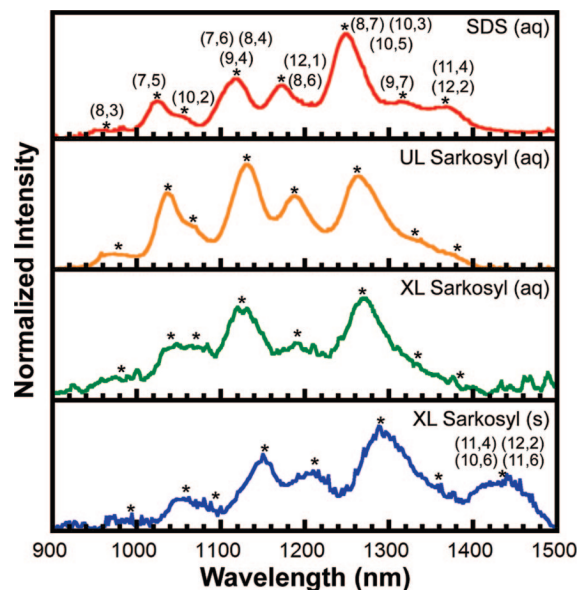


Figure 2. Band gap fluorescence from SWNTs dispersed in SDS, unlinked (UL) Sarkosyl, cross-linked (XL) Sarkosyl, and a solid dried film of XL Sarkosyl. The SWNT (n,m) structures associated with each peak are labeled.⁵ All spectra are normalized to the SDS peak at \sim 1250 nm.

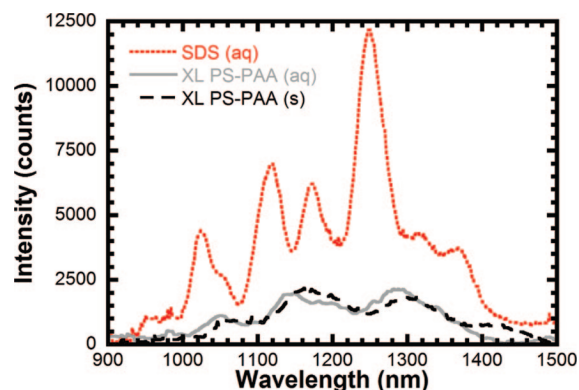


Figure 3. Band gap fluorescence from SWNTs dispersed in suspensions of SDS (dotted red) and XL PS-PAA (solid gray) and a solid film of XL PS-PAA (dashed black). The spectrum of the solid film was normalized to the XL PS-PAA suspension for clarity.

a sample of SWNTs dispersed in a cross-linked Sarkosyl solid film is similar to the unlinked solution spectrum in terms of spectral line width, with an additional red-shift of 190 cm^{-1} (Figure 2).

Fluorescence spectra from SWNTs dispersed in PS-PAA (Figure 3) are red-shifted by 183 cm^{-1} relative to spectra from SWNTs in SDS, as expected. However, in contrast to the case of dispersing nanotubes in Sarkosyl, the fluorescence intensity for SWNTs dispersed in PS-PAA is weaker than for SWNTs in SDS by about a factor of 4, and there is significant spectral broadening of each line (Figure 3). For example, spectral bands resulting from (7,6) and (8,6) nanotubes are indistinguishable for aqueous samples of SWNTs dispersed in PS-PAA (broad single peak at 1140 nm), as shown in Figure 3. However, the peaks at 1150 and 1210 nm, respectively, can be well resolved for cross-linked solid films of SWNTs in Sarkosyl (Figure 2). Also shown in Figure 3 is the fluorescence spectrum from a dense stain of SWNTs dispersed in cross-linked PS-PAA surfactant. For this solid sample, the fluorescence spectrum is similar to the

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solution PS-PAA spectrum, with corresponding spectral bands further red-shifted by 60 cm^{-1} .

Typically, nanotubes undergo significant rebundling upon being cast into solid films (e.g., from simply drying the suspension), which causes a significant decrease in the overall fluorescence quantum yield¹⁶ and a red-shift in the fluorescence energy due to nanotube–nanotube electronic coupling.⁴ To mitigate this effect partially, the concentration of nanotubes in solution can be diluted to such an extent that upon the formation of a solid film, the low density of nanotubes prevents significant aggregation. However, the drawback of this approach is that the fluorescence intensity from such a sample is relatively weak, and the relative percentage of isolated nanotubes is small.

In contrast, several features of the solid films made from cross-linked Sarkosyl SWNT samples are noteworthy. It is of particular significance that the width of the narrow features in the solid sample fluorescence spectrum are comparable to that of nanotubes dispersed in an SDS solution, which suggests the absence of significant nanotube rebundling (Figure 2).⁴ Furthermore, the relative magnitude of the SWNT fluorescence from the solid sample suggests that cross-linking successfully maintains micelles that are completely intact, again resulting in a high density of isolated nanotubes (Figure S1, Supporting Information). Thus, in principle, thin films of nanotubes that have relatively high fluorescence intensities can now be fabricated. The fluorescence quantum yield for Sarkosyl suspensions is $\sim 0.05\%$, estimated to be a factor of 10 brighter than the dried cross-linked films. However, direct comparison of an aqueous suspension with the cross-linked solid film is compounded by differences in both the sample density and the excitation volume. In addition, we observed that the solid cross-linked Sarkosyl samples had the attractive property that they could be redissolved in water, resulting in the complete recovery of all aspects of the solution-phase fluorescence spectrum. Finally, in the solid film, we note the presence of a relatively strong fluorescence band centered at 1450 nm, corresponding to fluorescence from (10,6), (11,6), (11,4), and (12,2) nanotubes. This band is completely absent in the aqueous samples, likely due to hole-doping associated with SWNT sidewall protonation in the liquid Sarkosyl suspensions.^{22,23}

It is interesting to note that upon casting into solid films, the fluorescence peaks for the PS-PAA and the Sarkosyl

samples red-shift on the order of 100 cm^{-1} . The origins of this additional shift are likely a combination of changes in the local chemical interactions of the nanotube with the surfactant and changes in the local dielectric screening of the exciton.²⁴ In aqueous dispersions, the exact nature of the local dielectric environment is difficult to model due to uncertainties in the exact orientation of the surfactant molecules with respect to the nanotube, as well as what fraction of the electron–hole interaction is taking place through the surrounding water. In principle, cross-linked nanotube films encase isolated nanotubes in a relatively homogeneous surfactant layer, which may be more amenable to calculations of the important dielectric screening effect.

In conclusion, we have used intramicellar cross-linking to encase SWNTs in a robust Sarkosyl cage, allowing for the observation of fluorescence from SWNTs even in dense solid samples. This discovery also allows for studies of SWNT fluorescence in wavelength regions where typical solvents (e.g., water) absorb strongly. As was recently demonstrated,²⁰ infrared fluorescence imaging applications that would benefit from this cross-linking procedure include those for which nanotubes are in poor conditions for micellar suspensions, such as the highly saline environment present inside cells.

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Supporting Information Available: Additional characterization data (Fluorescence, FTIR, Raman, and AFM; PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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