

# Stable Sequestration of Single-Walled Carbon Nanotubes in Self-Assembled Aqueous Nanopores

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**S** Supporting Information

**ABSTRACT:** We demonstrate the ability to stably sequester individual single-walled carbon nanotubes (SWNTs) within self-contained nanometer-scale aqueous volumes arrayed in an organic continuum. Large areal densities of  $4 \times 10^9 \text{ cm}^{-2}$  are readily achieved. SWNTs are incorporated into a surfactant mesophase which forms 2.3 nm diameter water channels by lyotropic self-assembly. Near-infrared fluorescence spectroscopy demonstrates that the SWNTs exist as well-dispersed tubes that are stable over several months and through multiple cycles of heating and cooling. Absence of physical distortion of the mesophase suggests that the SWNTs are stabilized by adsorbed surfactants that do not extend considerably from the surface. Our findings have important implications for templated assembly of carbon nanotubes using soft mesophases and the development of functional nanocomposites.

Many properties of single-walled carbon nanotubes (SWNTs) are contingent upon their isolation and stabilization in surrounding media. Techniques used to disperse SWNT must be specifically tailored to the nature of the suspending media. Amphiphilic small molecules and macromolecular agents stabilize against SWNT aggregation in aqueous systems.<sup>1,2</sup> In super acids, sidewall protonation reduces the van der Waals interactions that drive SWNT aggregation.<sup>3,4</sup> With the exception of certain aromatic liquids, however, SWNT dispersion in oily or nonpolar media remains a considerable challenge.<sup>5–8</sup> In nonpolar solvents, physisorption of surfactants on the nanotubes is diminished as the hydrophobic surfactant tails no longer exhibit preferential affinity for the nanotube sidewalls. Instead, dispersion techniques rely on covalent attachment of functional moieties to the nanotube sidewall to promote stabilization. The existing covalent techniques, while effective, complicate sample preparation and significantly perturb the unique electronic and optical properties (e.g., photoluminescence) of SWNTs.<sup>9,10</sup>

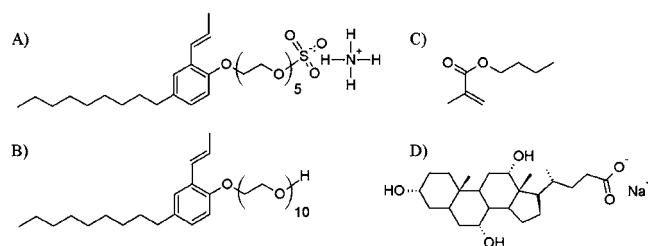
This work circumvents the difficulty of dispersing pristine SWNTs in nonpolar media by confining nanotubes to isolated aqueous pockets. Conceptually, SWNTs are confined and stabilized within self-contained aqueous volumes in a nonpolar continuum. This approach differs markedly from conventional methods both in its use of compartmentalized water for the SWNTs and the resulting ability to disperse nanotubes in nonpolar media without the need to functionalize tube sidewalls. Stable dispersion of pristine SWNTs in nonpolar

media, particularly in reactive meso-structured fluids, would significantly advance the prospects for the development of nanotube-based systems often envisioned for size- and chemo-selective transport.<sup>9–11</sup>

In this work, we present the first evidence of such stable sequestration of SWNTs in self-assembled nanometer-scale aqueous channels or pores. The aqueous nanopores are generated by lyotropic self-assembly of a ternary mixture of polymerizable nonylphenol oligo-ethylene glycol surfactants, water, and *n*-butyl methacrylate (BMA). The system forms a thermodynamically stable water-in-oil (w/o) microemulsion where water is confined within the hydrophilic core of an inverse worm-like micelle (WLM), with the lipophilic BMA forming the continuous phase. This represents an important step toward the realization of polymer nanocomposites with well-dispersed and potentially orientationally ordered SWNTs.

The continuous oil medium possesses negligible SWNT solubility as confirmed by partition experiments (Figure S1), but is completely miscible with the surfactant mixture of ionic and nonionic oligo-ethylene glycol species, Scheme 1. The

## Scheme 1. Mesophase Composition (wt %)<sup>a</sup>

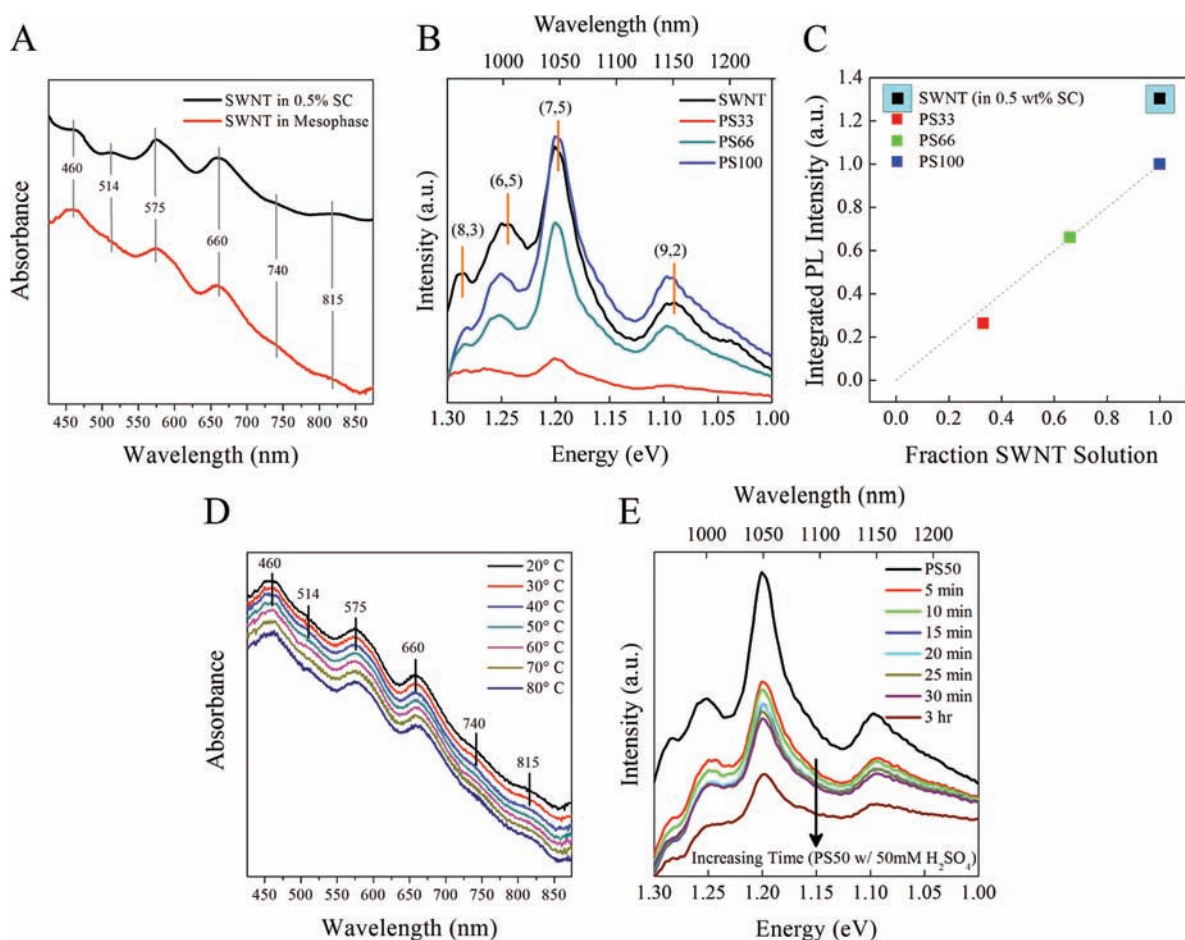


<sup>a</sup>Water is present at 14%. (A) Polymerizable surfactant BC-05 (49.5%); (B) polymerizable surfactant RN-10 (5.5%); (C) butyl methacrylate (31%); (D) sodium cholate (0.007%).

mesophase is formed by addition of aqueous media to a mixture of BMA and the surfactant. The aqueous media is a suspension of SWNTs in a 0.5 wt % solution of sodium cholate in water. Samples were prepared with different nanotube concentrations by using 0.5 wt % sodium cholate solutions that additionally contained either 0 mg/mL (PS0), 45  $\mu\text{g/mL}$  (PS33), 89  $\mu\text{g/mL}$  (PS66), or 134  $\mu\text{g/mL}$  (PS100) SWNTs. The SWNTs used in this study were prepared using CO disproportionation on an MCM-41 catalyst and have an average diameter of 0.8 nm.<sup>12</sup>

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**Figure 1.** (A) UV-vis spectra of the SWNT dispersion and SWNT incorporated in the mesophase at the PS100 concentration; (B) near-infrared PL of SWNTs in 0.5 wt % sodium cholate (SWNT) and in the mesophase at different SWNT concentrations (PS33, PS66, PS100) confirms that SWNTs remain well dispersed in the mesophase; (C) integrated PL emission from 1.3 to 1.0 eV for SWNTs in solution of 0.5% sodium cholate, PS33, PS66, and PS100; (D) temperature dependence of UV-vis spectra during heating shows that the SWNT do not aggregate on clearing of the mesophase. Data are shifted for clarity; (E) PL intensity decreases over time when 50 mM H<sub>2</sub>SO<sub>4</sub> is incorporated into the aqueous phase as a quenching agent.

Well-dispersed semiconducting SWNTs exhibit band gap photoluminescence (PL) in the near-IR and characteristic resonant absorptions in the UV-vis range. Aggregation of SWNTs is associated with quenching of the PL and significant broadening of the optical absorption, while both quenching and spectral shifts in PL may occur with changes to the surrounding solvent or surfactant environment.<sup>9–11</sup> PL and UV-vis absorption thus provide sensitive probes for the dispersion state and local environment of the nanotubes.<sup>13</sup> The UV-vis spectra for the aqueous SWNT dispersion in 0.5% sodium cholate and SWNTs incorporated in the mesophase show clearly resolved spectral features (Figure 1A), consistent with well-dispersed tubes, although the presence of some bundling cannot be ruled out. The partial suppression of the peak-to-valley ratios in the UV-vis also indicates that some, likely unavoidable, aggregation occurs in the process of blending components and forming the phase. The aqueous dispersion exhibits well-resolved fluorescence peaks corresponding to chiral SWNTs with  $(n,m)$  values of (6,5) and (7,5), and diameters of 0.75 and 0.82 nm, respectively (Figure 1B). These diameters are consistent with TEM measurements and BET analysis of these nanotubes.<sup>12</sup> The well-resolved spectral features persist when this aqueous SWNT suspension is incorporated into the microemulsion (Figure 1B). The PL

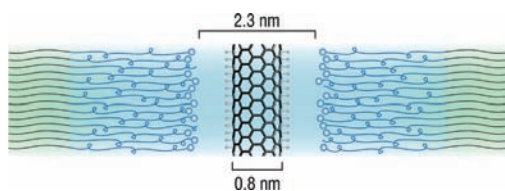
emission peaks for SWNT samples PS33, PS66, and PS100 were integrated from 1.3 to 1.0 eV to determine the total PL emission. This integrated PL value was then normalized to the PS100 value, and plotted against percent of SWNTs in the mesophase (Figure 1C). The linear correlation between PL intensity and SWNT concentration supports the hypothesis that the SWNTs remain well dispersed upon inclusion into the mesophase. Temperature resolved UV-vis (Figure 1D) shows no discernable changes on heating, indicating that the SWNTs do not aggregate during thermal disordering of the mesophase.

A quenching experiment was performed to verify that the nanotubes are indeed sequestered in the aqueous domains and not in the hydrophobic continuum. The aqueous content of the microemulsion was introduced in separate aliquots, the first half containing 100 mM H<sub>2</sub>SO<sub>4</sub> and the second half containing 134  $\mu$ g/mL SWNTs. In this manner, if sequestered in the aqueous nanopores, the SWNTs would be exposed to acidic conditions at 50 mM H<sub>2</sub>SO<sub>4</sub> and thereby be subject to protonation over time. Such protonation is well-known to lead to fluorescence quenching of SWNTs due to hole-injection that is both band gap selective and reversible.<sup>13–15</sup> The PL intensity of the mesophase was monitored following a short equilibration time after preparation. While we could not monitor the PL intensity during the short 3–5 min of equilibration and sample transfer

to the PL setup, significant quenching was observed after preparation of the mesophase with acidified water (Figure 1E). We observe an order of magnitude reduction in signal intensity and loss of peak definition after 3 h (bottom, brown trace) compared to a sample with an equivalent SWNT loading at pH 5.3 (top, black trace, PSS0). An alternative explanation is that the decrease in PL is driven by SWNT aggregation. Nevertheless, this experiment corroborates our finding that SWNTs are effectively sequestered in the nanometer-scale aqueous cores of the microemulsion.

Careful inspection of changes to individual peak intensity (i.e., peaks attributed to a single diameter SWNT) suggests that the PL of small diameter tubes is partially quenched by inclusion in the mesophase, while the PL intensity of larger diameter tubes is slightly accentuated (Figure 1B). We speculate that this is due to the presence of the surfactant in close proximity to the nanotubes and that the surfactant plays a role in the stability of the SWNTs, acting in tandem with, but also displacing some sodium cholate. Indeed, similar differences in the relative intensities of peaks were noted when SWNTs were dispersed in a 1% surfactant solution versus 0.5% sodium cholate. The PL data (Figure S2) indicate that the surfactant by itself is an effective dispersant for SWNTs due to its strong aromatic and ionic dual character. The differences in the PL spectra (Figure 1B) can be interpreted as the result of subtle changes in the population of SWNT bundles present in the system on addition of the surfactant, suggesting that the surfactant is less effective as a dispersant for small diameter SWNTs than sodium cholate.

The picture which emerges is of individual SWNTs residing within the water located at the center of the worm-like micelle. This is schematically depicted in Figure 2. The nanotubes carry

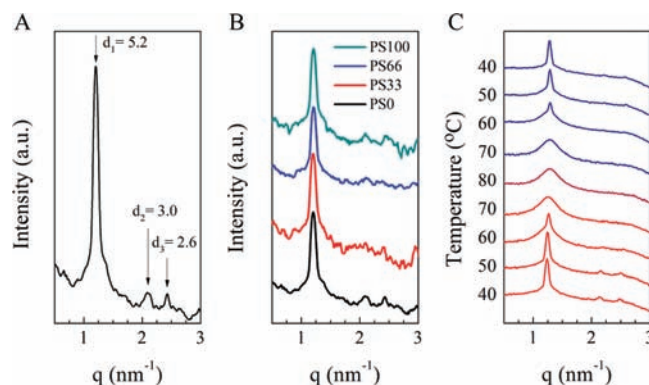


**Figure 2.** Schematic representation of SWNT sequestered in the nanometer-scale aqueous channel of the water-in-oil microemulsion.

a thin layer of physisorbed surfactants that provide stability in the aqueous nanopore and which inhibit nanotube escape into the oily continuum. Overall, the system forms a clear viscoelastic gel. Polarized optical microscopy shows a fan-like texture that is typical of hexagonally ordered mesophases (Figure S3). The texture is conserved across different loadings of SWNTs.

Small angle X-ray scattering (SAXS) confirms that the system has hexagonal symmetry. There is a strong primary peak at  $q = 1.207 \text{ nm}^{-1}$ , corresponding to a  $d$ -spacing of 5.2 nm (Figure 3A). Two higher order peaks are also clearly visible. The three peak locations occur with relative  $q^2$  ratios of 1:3:4, corresponding to the (100), (110), and (200) reflections of a hexagonally ordered mesophase. The system transitions reversibly around 60 °C to a disordered micellar phase (Figure 3C). The distance between centers of the cylindrical worm-like micelles was determined to be  $d_0 = 6 \text{ nm}$  as  $d_0 = d(4/3)^{1/2}$ .

This dimension,  $d_0$ , is principally a function of the length of the surfactant and its volume fraction in the system,  $\phi = 0.55$ . A second dimension of interest is the nominal radius of the



**Figure 3.** SAXS from mesophase. (A) PSO system at 25 °C forms hexagonal mesophase with reflections as indicated; (B) the  $d$ -spacing of the mesophase is unaltered upon SWNT addition; (C) the PSO mesophase undergoes reversible thermal transition into a disordered micellar phase.

aqueous pores,  $r_w$ . Equation 1 relates the water volume fraction,  $\phi_w$ , to the ratio of the area of the aqueous phase relative to the unit cell. For a water content of 14 wt % and  $d$ -spacing of 5.2 nm, the  $r_w$  of the cylindrical channels is 1.15 nm (2.3 nm diameter). Hydration of the oligo-ethylene glycol headgroups of the surfactant by the water in the core of the WLM means that in principle the SWNT may access a slightly larger volume than that offered by the water alone. This may account for the disparity between the 2.3 nm dimension and recent estimates for the diameter of sodium cholate wrapped SWNT.<sup>16</sup> In either case, the aqueous channel is sufficiently large to sequester a SWNT of 0.8 nm in diameter.

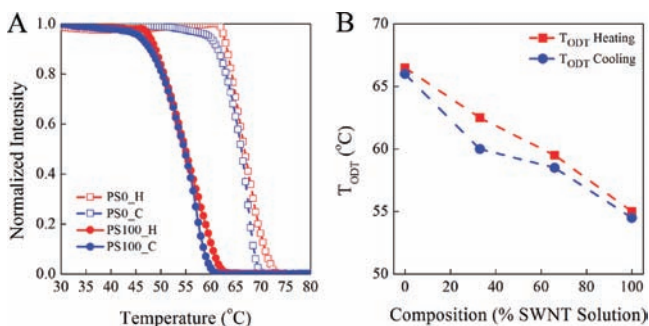
$$\phi_{\text{hyd}} = \frac{\sqrt{3} \pi r_w^2}{2 d^2} \quad (1)$$

In fact, comparison of the structure of a mesophase formed without SWNTs shows that the nanotube sequestration occurs without any detectable swelling of the micellar core. This is reflected by the insensitivity of  $d$ -spacing to SWNT loading (Figure 3B). Given the absence of physical distortion of the mesophase, as well as geometrical considerations, we speculate that the stabilizing surfactants are only adsorbed in a “face-on” configuration at the SWNT sidewalls and do not extend significantly away from the nanotube surface. That is, hemimicelle formation does not occur, as conjectured for the stabilization of SWNTs in bulk water.<sup>17,18</sup>

Finally, we calculate the areal density of SWNT and the occupancy of nanopores (Supporting Information). We assume a nanotube wall thickness of 0.0617 nm.<sup>19</sup> The calculation is facilitated by considering the ideal case of a thin film of the mesophase equal in length to the nanotube, but the result is equally valid for the areal density and probability of encountering a nanotube for any arbitrary cut through the bulk of the mesophase. We obtain an areal density of  $\sim 4 \times 10^9 \text{ cm}^{-2}$  and occupancy of 0.00273, indicating that effectively 1 in every 400 nanopores is occupied by a nanotube. AFM experiments have conclusively shown that a small but nonzero population of bundles exists even in well-dispersed suspensions.<sup>20</sup> From this perspective, the areal density and occupancy reported here provide upper limits for the compositions studied as the calculations implicitly assume that all nanotubes are singly dispersed. This large areal density is promising relative to that typically observed ( $5 \times 10^{11} \text{ cm}^{-2}$ ) in high density forests

grown by using water assisted CVD based “super-growth” methods.<sup>21</sup> The high packing density is a result of both the superior dispersal of SWNT by the tandem action of the sodium cholate and nonyl phenol oligo-ethylene glycol ionic surfactant pair, as well as the small length scale of the hexagonally packed structures that sequester the nanotubes.

While there is broad interest in the use of soft mesophases to confine and template the assembly of SWNTs and other nanomaterials,<sup>22–26</sup> reports of phase behavior to date have highlighted mesophase transitions driven by demixing.<sup>27,28</sup> The role of nanomaterial sequestration on the thermal stability of homogeneous ordered mesophases remains largely unexplored, particularly for surfactant-derived mesophases. Toward this end, we characterized the order–disorder transition of our mesophases as a function of SWNT loading by temperature resolved polarized optical microscopy (POM). One can readily imagine that the inclusion of a rigid anisotropic element at the core of a micelle might stabilize the structure against disordering. Contrary to our expectation, the data show a clear monotonic and linear decrease in the order–disorder transition temperature ( $T_{\text{ODT}}$ ) of the mesophase with increasing SWNT loading (Figure 4). Analogous behavior



**Figure 4.** (A) Transmitted intensity from POM on heating (red) and cooling (blue). (B)  $T_{\text{ODT}}$  as a function of SWNT inclusion.

was observed also for mesophases incorporating SWNTs from a commercial source (SouthWest Nano CG200) and stabilized without the aid of sodium cholate. The reasons for this are currently unclear, and further investigation is warranted. Nevertheless, SWNTs were stable through heating and cooling of the system with PL intensity invariant after multiple rounds of heating and cooling through the order–disorder transition. The sharp sensitivity of the ODT underlines the fact that the SWNT are intimately associated with the worm like micelles.

In conclusion, this work demonstrates that SWNTs are stably sequestered in nanometer-scale water channels of an oil-in-water (o/w) microemulsion. This approach represents an important contribution to realizing the isolation and stabilization of pristine nanotubes in nonpolar media. Stabilizing SWNTs in these confined channels is also an important step toward the development of well-dispersed nanotubes in polymer nanocomposites. Finally, the surfactant-based approach adopted here lends itself to further application in template directed assembly of the nanotubes and polymerization in thin-film geometries. Although not explicitly discussed here, the use of a polymerizable surfactant and vinyl monomer as the continuous phase brings us closer to the realization of aligned SWNTs sequestered in a continuous, water-impermeable polymer film. Additional progress is being

made toward the development of aligned SWNT membranes for application in aqueous analytical separations.

## ■ ASSOCIATED CONTENT

### § Supporting Information

Materials and methods, SWNT partitioning, polarized optical micrographs, NIR PL of SWNT dispersions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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