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

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SUPPORTING INFO

Preparation of Surfactant Mesophases: The aqueous solution is prepared by dissolving 0.5% sodium cholate (Sigma Aldrich) and the appropriate weight of single-walled carbon nanotubes (SWNTs) in deionized water. Multiple rounds (minimum 3) of probe sonication followed by centrifugation for 30 minutes at 17,000 relative centrifugal force (Sorvall RC 6+ Centrifuge, F13 carbon fiber rotor, Thermo Fisher, Waltham, MA) were performed to separate out aggregated SWNT. Next, a stable lyotropic LC mesophase is formed by combining 5.5 grams of polymerizable surfactants (PS) BC-05 and RN-10 in a 7:1 ratio (Montello, Tulsa, OK) with 3.1 grams of butyl methacrylate (Sigma Aldrich) in a sealed vial. The mixture is heated to 80 °C and 1.4 grams of aqueous sodium cholate solution with varying concentrations of SWNT is added. The mesophase is vortexed as cooled and immediately used for experiments.

Near-Infrared Photoluminescence (PL): The mesophase was heated into the disordered phase and pipetted into a warmed florometer cuvette (Starna Cells). A 638 nm laser incorporated into a NS1 NanoSpectralyzer system (Applied NanoFlorescence, Houston, TX), produced emission spectra from 900 nm to 1600 nm wavelength. The PS0 phase was used as the background subtraction for subsequent phases that contained SWNT, though the sample had very little florescence signal in the region of interests.

Small Angle X-Ray Scattering: SAXS measurements were performed on a Rigaku S-MAX 3000 with 2D small-angle (SAXS) and wide-angle (WAXS) detectors. Samples were pipetted into glass capillaries and flame sealed on either end to ensure sample integrity at high temperatures and under vacuum. The samples were heated on a hot stage (Linkam Scientific Instruments, Surrey, England) that is integrated into the vacuum chamber.

Polarized Optical Microscopy: Polarized optical microscopy was performed on a Zeiss Axiovert 200M with crossed polarizers, while a Linkam hot stage was used to control temperature. The samples were heated and cooled at 3 °C/min under constant air flow to ensure controlled cooling.

SWNT areal density and occupancy: We reduce the system to the case where the length of the nanotube is equal to the length of the micelle core. Given a nanotube wall thickness (t_{SWNT}) we can calculate the cross-sectional area of the wall of the nanotube, A_{SWNT} . The area fraction of a single SWNT in the idealized water channel will be denoted as $\varphi_{SWNT}^{w,ideal}$, and is given by the ratio of the wall area to that of the channel:

$$\varphi_{SWNT}^{w,ideal} = A_{SWNT} / (\pi r_w^2) \quad (3)$$

Next, we determine the real volume fraction of SWNT in the water channel based on measured weight fraction of SWNT in the aqueous phase incorporated into the microemulsion. With knowledge of the ideal and actual areal fractions of SWNT in the hydrophilic core, we can calculate the percent occupancy (p_{SWNT}^{hyd}) of the water cores in the present system.

$$p_{SWNT}^{w} = \frac{\varphi_{SWNT}^{w}}{\varphi_{SWNT}^{w,ideal}} \quad (4)$$

Finally, the areal density of SWNT can be determined by multiplying the number density of water channels by their percent occupancy:

$$v_{SWNT}^w = p_{SWNT}^w v^w \quad (5)$$

Assuming one SWNT per channel, these calculations yield a 0.0027 occupancy rate and an areal density of 3.85 E9 nanotubes/cm² cross-sectional area of the mesophase.



Figure S1: Top: Photograph of solvent phases and associated SWNT solubility. After extensive vortexting of butyl methacrylate and SWNT suspended in 0.5 wt% sodium cholate (SC), the SWNT remain in the aqueous phase. Bottom: No PL signal is detectable in the BMA phase following this partitioning experiment. This control measurement used a different SWNT dispersion (SouthWest Nano CG200 tubes) and so the peak locations/intensities are due to a different population of nanotubes.



Figure S2: Near-infrared spectra of SWNTs in different surfactants employed in this research. The spectra show a decrease in the PL intensity of the smallest SWNTs and a slight increase in the peak intensity of the larger SWNTs.



Figure S3: POM micrographs for each composition: (A) PS0; (B) PS33; (C) PS66; (D) PS100