Colloidal Particles Coated and Stabilized by DNA-Wrapped Carbon Nanotubes

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Single-walled carbon nanotubes (SWNTs) are dispersed in water via wrapping with short segments of single-stranded DNA (ssDNA). Small angle neutron scattering suggests a power-law exponent that is consistent with clustered nanotubes and hence marginal stability. The SWNT−ssDNA complex is used to stabilize dispersions of hydrophilic colloidal particles with the nanotubes adhered to the surface of the colloids. Near-infrared fluorescence microscopy demonstrates the interfacial band-gap fluorescence of these SWNT-coated particles, suggesting potential routes to novel platforms and applications.

Carbon nanotubes exhibit remarkable physical properties, and there is considerable interest in using them as nanoscale building blocks for a new generation of materials and applications.[1−6] A significant hurdle, however, is the inherent amphiphobicity of carbon nanotubes, which can be challenging to disperse, even with surfactants or surface functionalization. This fact has recently been exploited to make solid-stabilized emulsions of immiscible liquids using raw single-walled carbon nanotubes (SWNTs) as interfacial stabilizer, or surfactant,[7] suggesting potential routes toward engineering microscale interfacial structures with unique physical properties.

One particularly promising method of dispersing SWNTs in aqueous environments exploits a short (30 base pair) single-stranded DNA sequence of alternating guanine (G) and thymine (T) units, as recently demonstrated by Zheng and co-workers.[8,9] In theory, the hydrophobic base pairs preferentially segregate to the graphene surface, with the hydrophillic phosphate groups providing a degree of electrostatic stabilization in water. Liquid-phase chromatography applied to such aqueous suspensions further suggests potentially powerful methods for separating individual DNA coated SWNTs by band structure and size.[8]

Small angle scattering has been used extensively to measure and quantify SWNT dispersion. X-ray and light scattering have shown that SWNTs dispersed with synthetic wrapping polymers can form complex structures with dense branching and large sizes.[10,11] Small angle neutron scattering (SANS) measurements on aqueous surfactant dispersions commonly find high power laws at low scattering angle, suggesting large scale clustering.[12−15] The clustering may either be strongly bound SWNT structures that remain from the as-synthesized SWNT bundles or weakly associated aggregates that represent marginal stability. Measurements of deuterium labeled, covalently modified SWNTs demonstrate that the SWNT bundles are not weakly associated, but the energetic chemistry necessary for the grafting reaction may make this scenario different from other dispersion methods.[16]

Here, we exploit what might be interpreted as a degree of amphiphobicity in aqueous ssDNA-wrapped SWNT suspensions to synthesize polymer colloids coated and stabilized by the SWNT−ssDNA complex. In contrast to comparable colloids made with conventional surfactants, these microscopic particles retain their hydrophillic coating after repeated rinsing, suggesting that the SWNT−ssDNA complex is robustly attached to the colloid interface. Near-infrared (NIR) fluorescence microscopy is used to demonstrate band-gap NIR fluorescence for both the ssDNA-wrapped SWNTs and the SWNT-stabilzed colloidal particles, suggesting potential routes toward novel platforms and applications.

Aqueous SWNT-ssDNA suspensions provided by Zheng and co-workers were made using published procedures.[8,9] The SWNTs used were produced by the HiPCO process.[17] They were mixed with DNA containing 30 base pairs of alternating (guanine and thymine) in buffered aqueous salt solution (0.1 m/L NaCl) at initial concentrations of 1 mg/mL. As described elsewhere,[8,9] dispersion is typically induced via sonication at 3 W in an ice bath for 90 min and insoluble material is removed through centrifugation at 15000*g* for 90 min. SANS samples were prepared by exchange of H_2O with D_2O through dialysis. Final suspensions have concentrations on the order of 0.5 mg/mL.

SANS measurements were carried out at the NIST Center for Neutron Research (NCNR) in Gaithersburg,

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(17) Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

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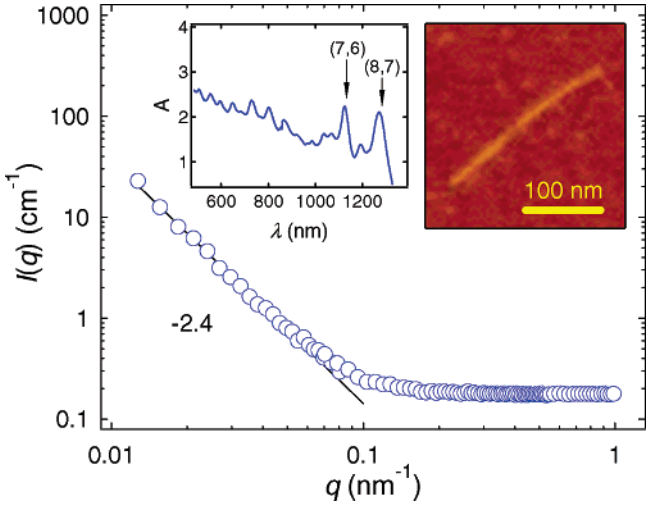

Figure 1. Typical SANS profile of the SWNT-ssDNA suspensions of interest here. The upper left inset shows the corresponding UV−vis absorption spectrum and the upper right inset shows an AFM image of an isolated ssDNA-coated SWNT deposited on a silicon wafer. The chirality vectors of the enriched semiconducting SWNT species are indicated. Unless otherwise indicated, error bars are the size of the data markers and represent two standard deviations in the total experimental uncertainty.

Maryland. Scanning electron microscopy (SEM) and optical absorption measurements were performed on commercial instruments using standard protocols. Tapping-mode atomic force microscopy (AFM) measurements were conducted in air using a Nanoscope IV system (Digital Instruments) operated under ambient conditions with standard silicon tips. The aqueous SWNT suspensions were diluted 100× in water (18 MΩ cm^{-1}) prior to being deposited (2 μL) onto plasma cleansed $Si^{1,1,1}$ wafers for AFM. After drying, residual salt was washed away with water to afford clear imaging conditions. AFM was also used to probe the structure of the SWNT interphase on the surface of SWNT-coated colloidal particles. Similar samples for SEM were gold coated under an argon atmosphere using a sputter coater operated at 25 mA for 120 s. Bright-field and NIR fluorescence microscopy images of these particles were collected on an InGaAs CCD array using the appropriate band-pass optical filters.

AFM images depicted primarily individual SWNTs possessing broad distributions in length. Quantitative analysis of such images gave a mean length of 300 nm and a mean diameter of 1.5 nm for the SWNTs used in this study. By number, 85% of the tubes were single SWNTs with the rest being bundles of diameter 10 nm or less. The upper right inset to Figure 1 shows the UV−vis absorption spectrum for the aqueous ssDNA-SWNT suspensions of interest. Peaks corresponding to specific chirality vectors (n,m), and hence different SWNT band structures, become more pronounced in suspensions of higher purity. A typical SANS profile obtained from the D_2O dialyzed ssDNA−SWNT suspensions is shown in the main panel of Figure 1.

For isolated tubes, the mass contained within a sphere of radius r is $N(r) \propto r^D$, where D is the fractal dimension of the tube. The radial distribution function is then $g(r) \propto r^{1-d}(\partial N/\partial r) \propto r^{D-d}$ where $d = 3$ is the spatial dimension. Taking the Fourier transform, the scattering intensity is $I(q) \propto q^{-D}$, where q is the scattering wave vector. For dispersed rigid rods with $D \approx 1$, we would thus expect q^{-1} behavior.

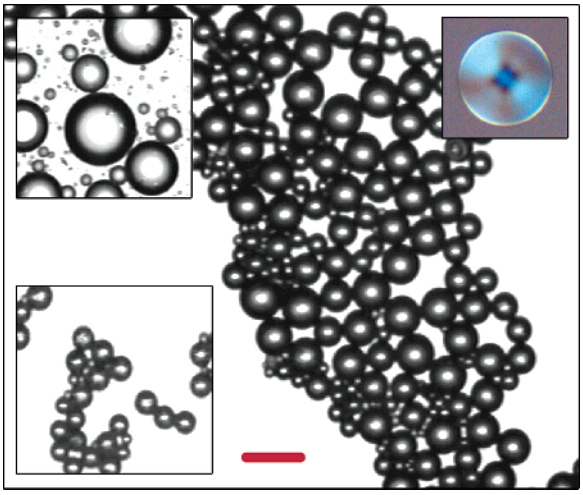

Figure 2. Optical micrograph of dried SWNT-coated colloids made of cross-linked polymer, where the red scale bar represents 70 μm. The upper left inset is an emulsion of toluene in water stabilized by the ssDNA-wrapped SWNTs and the upper right inset is a dried SWNT-coated colloid under cross polarizers. The lower left inset shows control colloids made with SDS.

As shown in Figure 1, the exponent we measure with SANS at these concentrations (approximately 0.05% SWNT by mass) is around 2.4. For nanotubes well approximated by rigid rods, this suggests a degree of clustering at these concentrations. In general, such attractive interactions are characteristic of SWNTs in suspension. When coated with ionic surfactant, for example, concentrated SWNTs typically retain an interparticle attraction on the order of $40k_BT$.[18] For the DNA-stabilized tubes, further evidence for a level of insolubility stems from the observation that the SWNT suspensions of interest here can be used to stabilize the interface between water and an immiscible organic fluid. The upper left inset of Figure 2 shows a stable emulsion that forms when toluene is added to the aqueous SWNT suspension (1:2 by mass) and shaken vigorously. Adding toluene to an aqueous suspension containing just the NaCl and ssDNA does not have this effect.

Taking this one step further, we made 1:1 mixtures of C_{12}DMA (1,12-dodecanediol dimethacrylate) monomer with 1 BPO (benzoyl peroxide) initiator and C_{12}DMA with 0.5% DMPT (*N*,*N*-dimethyl p-toluidine) accelerator and 0.1% ferrocene catalyst. This solution was quickly and vigorously shaken into the aqueous ssDNA−SWNT suspension (1:2 by mass) to make a soft emulsion. Once the polymer had cross-linked, we removed the suspending fluid and rinsed the remaining ssDNA−SWNT coated colloidal particles repeatedly in distilled deioniozed water. As a control, we carried out the same procedure using the conventional surfactant sodium dodecyl sulfate (SDS; 1% SDS by mass). To the naked eye, the presence of SWNTs at the interface is evident from a blackish hue for the rinsed and dried SWNT-stabilized colloids. By comparison, rinsed and dried colloids made with SDS appear white. The main panel of Figure 2 shows dried SWNT-coated colloids, whereas the lower left inset shows control colloids synthesized using SDS. Under crossed polarizers (upper right inset, Figure 2), the SWNT-coated and SDS stabilized colloids are indistinguishable, suggesting an isotropic distribution of nanotube orientations at the interface.

Figure 3 shows an SEM image of the dried SWNT-coated particles. High resolution SEM measurements at the

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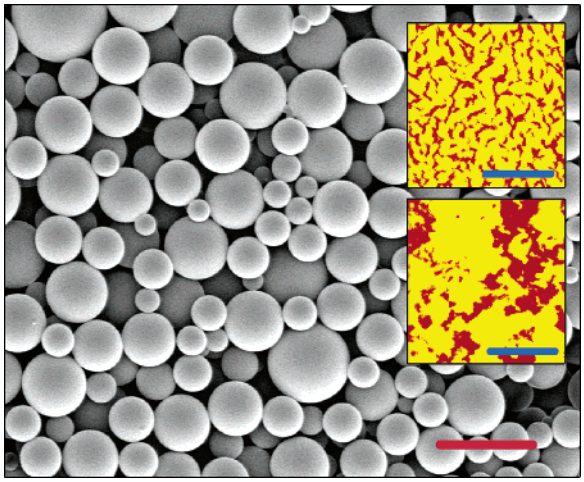

Figure 3. SEM image of dried SWNT-stabilized colloids (scale bar = 100 μm), where the upper inset shows an AFM image of a colloid surface and the lower inset shows an analogous image for an SDS stabilized colloid (phase contrast, scale bar = 150 nm).

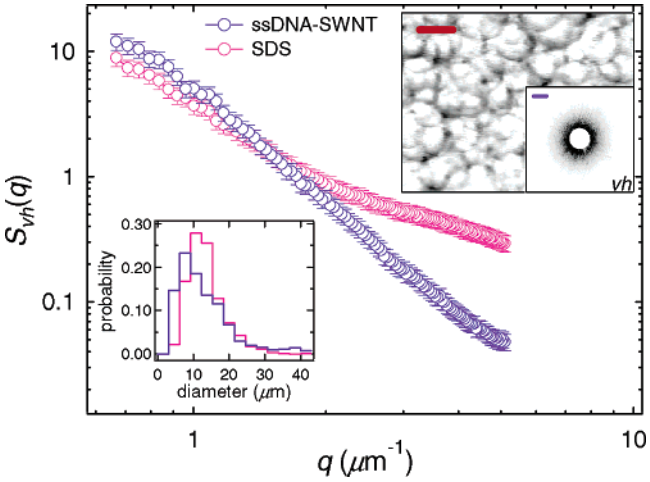

Figure 4. Cross-polarized small-angle light scattering profiles from the SWNT-stabilized and SDS-stabilized colloids saturated with Triton x100, where the upper right inset shows an optical micrograph/light-scattering pair for the SWNT coated particles (red scale bar = 60 μm, purple scale bar = 1 μm^{-1}). The lower left inset shows diameter histograms for the two colloid types.

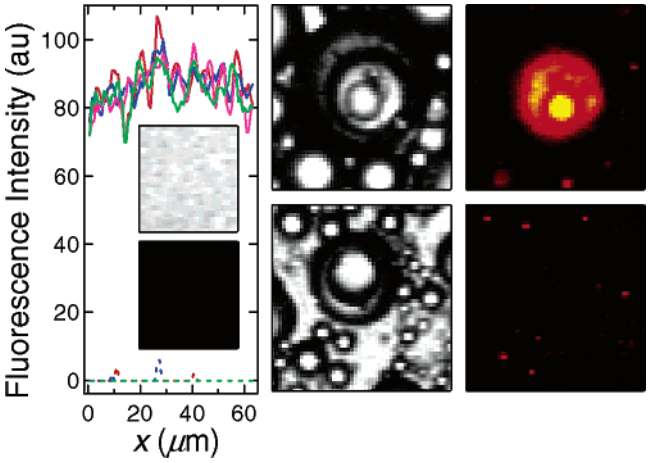

Figure 5. NIR fluorescence emission as a function of position for a dilute SWNT-ssDNA suspension, where the different colors represent measurements taken at 20 s intervals. The lower traces show the background emission intensity. This difference is shown visually in the inset. On the right, the upper two images show bright field (left) and NIR fluorescence (right) micrographs of stacked SWNT-stabilized colloids, whereas the lower images show the same for SDS-stabilized colloids.

surface of these particles (not shown) revealed an anisotropic structure of the same characteristic dimension as the SWNTs. In contrast, comparable measurements made at the surface of the dried SDS particles (not shown) revealed little or no anisotropy. We also performed phase-contrast AFM at the surface of the dried SWNT-coated colloids (upper inset, Figure 3), which similarly showed anisotropy at length scales characteristic of the SWNTs. Again, comparable measurements performed on the SDS control particles (lower inset, Figure 3) lack anisotropy at these length scales. The rinsed and dried SWNT-coated colloids can be resuspended in water, consistent with interfacial SWNTs coated with ssDNA and SWNT−DNA complexes that are adhered to the colloid interface.

To further quantify the difference between colloids stabilized with the ssDNA-wrapped SWNTs and those stabilized with SDS, we saturated rinsed and dried samples of each with the surfactant Triton x100, which matches the index of refraction of the cross-linked polymer particles and which should wet any exposed interface. Samples roughly 0.5 mm in thickness were then probed optically using bright-field microscopy and depolarized small-angle light scattering.[23] Although the Triton saturated SWNT-coated particles had a transparent gray appearance, the SDS colloids had a whitish hue characteristic of multiple scattering. In bright field microscopy, SWNT-coated colloids in Triton show only interfacial features (upper right inset, Figure 4), whereas those made with SDS show significant optical contrast arising from small aggregates and clusters. Small-angle light scattering profiles obtained in a crossed-polarized (hv) configuration[23] further suggest significant interfacial differences between the two types of colloids (Figure 4), consistent with stronger scattering in the mixture containing particles stabilized with SDS. Since the size distributions are similar (lower left inset, Figure 4), we attribute this to aggregation that occurs in the rinsed/dried SDS samples upon removal of surfactant. The DNA-wrapped SWNTs, on the other hand, form a robust hydrophillic surface that does not rinse away and which acts as an effective barrier to flocculation.

Individual SWNTs exhibit a band gap fluorescence in the NIR,[19] a region of wavelength where biological fluids and tissue are relatively transparent.[20] This suggests potential applications for isolated SWNTs in the area of bioimaging and biosensing. Ropes and aggregates of SWNTs, on the other hand, do not show this fluorescence. Using a 30 mW He−Ne (632.8 nm) as an excitation source, we measured the NIR fluorescence in both the original SWNT−DNA suspensions and in the SWNT-coated polymer colloids using NIR fluorescence microscopy. Figure 5 shows NIR (λ > 1000 nm) images of fluorescence intensity fluctuations in the initial aqueous SWNT suspension diluted to 1 μg/mL. At this concentration, the suspension is a clear transparent gray. The background signal from the same cell containing just water, NaCl, and ssDNA is also shown. The signal is consistent with limited physical bonding between adjacent SWNTs, further suggesting that the clustering of SWNTs is in some sense weak. This fluorescence is also observed in the SWNT-stabilized

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colloids, as can be seen by comparing NIR fluorescence micrographs with those made using SDS (right images, Figure 5).

There is current interest in using spherical nanoparticles to stabilize emulsions of immiscible liquids while engineering nanoscale structure at the interface.[21,22] Carbon nanotubes offer an additional tunable parameter to vary and explore within this effort; particle anisotropy and aspect ratio. When coupled with the novel optical properties of SWNTs, including a region of the electromagnetic spectrum where there are a host of technological needs and opportunities, this anisotropy opens routes to new applications. Here, we demonstrate that individual single-walled carbon nanotubes wrapped with a short specific sequence of single-stranded DNA can act much as a surfactant molecule, stabilizing the interface that forms between two immiscible liquids. A degree of such amphiphobicity associated with these SWNT−ssDNA complexes would also seem to raise interesting questions about their structure and solubility in purely aqueous solutions.

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