

Letters

Amphiphobic Carbon Nanotubes as Macroemulsion Surfactants

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Received November 21, 2002. In Final Form: February 24, 2003

Single-walled carbon nanotubes (SWNTs) are insoluble in either water or oil. When mixtures of SWNTs, water, and toluene are sheared vigorously, a macroscopic emulsion of water droplets forms in toluene, with the SWNTs residing at the interface between the immiscible fluids, acting as a natural "surfactant" or interphase material. The average droplet dimension decreases as the SWNT/water mass ratio increases, implying a coarsening-and-pinning mechanism. The concept of emulsification via amphiphobicity will find applications in processing nanotubes, compatibilizing immiscible fluids, and creating new macroscopic emulsion materials with unique interfacial and structural properties.

Carbon nanotubes (CNTs) are structurally unique, with tube diameters on the order of a few nanometers and lengths of many microns. They offer the promise of novel materials with unique mechanical, electrical, thermal, and optical properties,^{1–3} and they can be used for nanoelectronics,⁴ electron field emitters,⁵ and other applications.⁶ In recent years, advances in synthesizing large quantities of CNTs⁷ allow utilizing their extreme mechanical strength⁸ and thermal management power⁹ to develop

CNT-based composites.^{10,11} This new development poses queries about the surface properties of CNTs. Recent studies have shown that aligned CNTs can be super amphiphobic, strongly repelling both polar and nonpolar solvents.¹² Here we offer evidence for single-walled carbon nanotubes (SWNTs) acting as a natural "surfactant" or interphase material in macroscopic emulsions of water and toluene, a phenomenon with potential applications in the processing of nanotubes and the compatibilization of immiscible fluids.

The SWNTs were produced by the pulsed-laser vaporization technique⁷ and were obtained from Tubes@Rice¹³ as a "suspension" in toluene with a tube mass fraction of 0.673%. Individually, they have an average diameter of 1.3 nm and a length of microns. Single tubes tend to form bundles due to longitudinal van der Waals forces, and

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(1) Ebbesen, T. W. *Carbon Nanotubes*; CRC Press: Boca Raton, FL, 1997.

(2) Dresselhaus, M. S.; Dresselhaus, G. *Carbon Nanotubes: Synthesis, Structure, Properties and Applications*; Springer: New York, 2001.

(3) Sinnott, S. B.; Andrews, R. *Crit. Rev. Solid State Mater. Sci.* **2001**, *26*, 145.

(4) Avouris, P. *Chem. Phys.* **2002**, *281*, 429.

(5) Bonard, J. M.; et al. *Carbon* **2002**, *40*, 1715.

(6) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.

(7) Thess, A.; et al. *Science* **1996**, *273*, 483.

(8) Yakobson, B. I.; Brabec, C. J.; Bernholc, J. *Phys. Rev. Lett.* **1996**, *76*, 2511.

(9) Hone, J.; Batlogg, B.; Benes, Z.; Johnson, A. T.; Fischer, J. E. *Science* **2000**, *289*, 1730.

(10) Thostenson, E. T.; Ren, Z.; Chou, T. W. *Compos. Sci. Technol.* **2001**, *61*, 1899.

(11) Biercuk, M. J.; et al. *Appl. Phys. Lett.* **2002**, *80*, 2767.

(12) Li, H.; et al. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743.

(13) The references to commercial equipment or materials do not imply recommendation or endorsement by the National Institute of Standards and Technology.

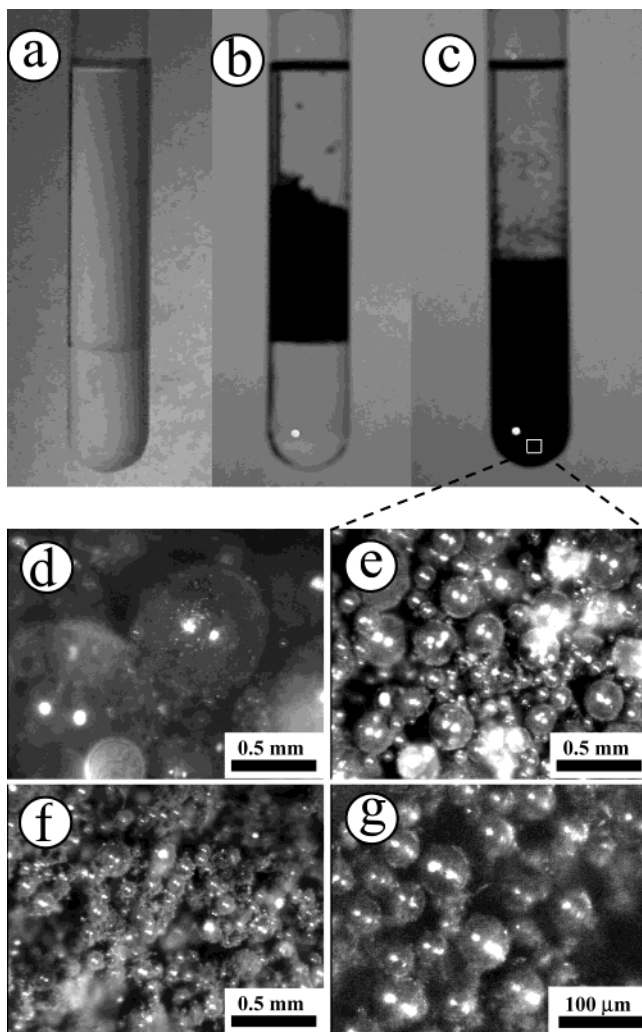


Figure 1. Upper panel: photographs of a SWNT/water/toluene mixture with a SWNT/water mass ratio of ca. 0.005. (a) Toluene (top) and water (bottom) in a test tube. (b) Prior to rigorous mixing, the bottom clear phase is water, and the tubes form aggregates (black) preferentially in the upper toluene phase. (c) After sonication and shearing, the bottom (black) is a macroemulsion of SWNT-stabilized water droplets in toluene, while the upper toluene phase is clear. Lower panel: micrographs of SWNT/water/toluene emulsions with a SWNT/water mass ratio, α , of (d) 0.0007, (e) 0.0033, (f) 0.012, and (g) 0.18. The size of the SWNT-stabilized water droplets decreases with α .

these are interwoven into a loose mesh. They are poorly soluble in toluene, forming diffuse macroscopic aggregates. Ternary mixtures of SWNT, water, and toluene were prepared at various SWNT/water mass ratios, $\alpha = M_c/M_w$. Toluene and water are immiscible under ambient conditions (Figure 1a, where the lower clear phase is water and the upper phase is toluene). After preparation and before rigorous mixing, the SWNTs stay preferentially in toluene (Figure 1b). After bath sonication for 1 min and vigorous shaking, the SWNTs incorporate with the heavier minority water phase at the bottom of the test tube, leaving the toluene clear (Figure 1c). Close optical inspection reveals that the lower SWNT-rich phase consists of fine water droplets, with the SWNT residing at the water–toluene interface, encapsulating and stabilizing a *macroemulsion* of water in toluene, as shown in the lower panel of Figure 1. This striking behavior is quite easy to observe and appears to be unique. In mixtures containing water and toluene with carbon black, “buckyballs” (C_{60}), or no third component, for example, we do not observe

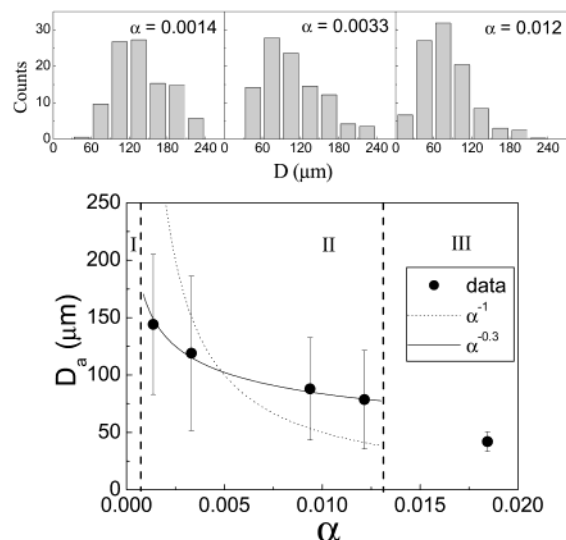


Figure 2. Upper panel: histograms of droplet diameter D (normalized to each 100 droplets) for $\alpha = 0.0014$, 0.0033 , and 0.012 based on ensembles of 200–300 droplets within regime II. Lower panel: the average droplet diameter, D_a , as a function of α . The dashed lines indicate boundaries separating the three distinct regimes: (I) water, toluene, and emulsion coexist; (II) emulsion and toluene coexist; and (III) emulsion, SWNT aggregates, and toluene coexist. In regime II, the experimental data are compared to the relations $D_a \sim \alpha^{-1}$ (dashed curve) and $D_a \sim \alpha^{-0.3}$ (solid curve).

this effect; the water quickly coarsens to fill the bottom of the test tube, with any third component remaining in the toluene.

Three regimes are apparent as a function of α . In regime I ($\alpha < 0.0008$), the bulk water phase coexists with the emulsion and bulk toluene phases. In this regime, droplets can grow to indefinitely large size, depending on the sample volume. Figure 1d shows droplets of ca. 0.8 mm diameter formed at $\alpha \approx 0.0007$. In regime II ($0.0008 < \alpha < 0.013$), the water is entirely consumed into the emulsion phase, which coexists with excess toluene. Images e and f of Figure 1 show emulsions prepared at $\alpha = 0.0033$ and 0.012 , respectively. In regime III ($\alpha > 0.013$), an emulsion phase of fine droplets coexists with SWNT aggregates in toluene. Figure 1g shows that for $\alpha = 0.018$, the droplets have an average diameter of $42 \mu\text{m}$.

In regime I, reliable droplet-size distributions cannot be obtained because of coarsening. In regime III, the morphology is a heterogeneous coexistence of emulsion and aggregate, with significant variation from sample to sample. In regime II, however, the morphology is reproducible. Droplet statistics were performed over an area of ca. 13 mm^2 , with a total of 200–300 droplets per ensemble. The upper panel of Figure 2 shows histograms of droplet diameter, D , at several values of α . It is evident that droplet size varies over a considerable range, from 10 to over $200 \mu\text{m}$. The most probable D decreases with α . The mean droplet diameter, D_a , is shown in the lower panel of Figure 2 as a function of α . Dashed vertical lines indicate boundaries between the three regimes.

To qualitatively model this phenomenon, we assume that the water droplets are monodisperse and the thickness of the nanotube-rich layer encapsulating them is uniform. Conservation of water and SWNT requires $M_w = \rho_w N \pi D^3 / 6$ and $M_c = \rho_c N h \pi D^2$, respectively, where h is the interphase thickness, N is the total number of droplets, and ρ_w and ρ_c are the mass density of water and interphase, respectively, where the latter depends on the macroscopic density and fractal geometry of the interfacial SWNT

aggregates and is assumed to be constant. It follows that $D = 6(\rho_c/\rho_w)(h/\alpha)$. For a particular mixture, $D \propto h$, implying that as droplets coarsen, the interphase thickness increases proportionally. If there exists a critical interfacial thickness h_c at which coarsening ceases, mixtures reach a steady state with $D_c \propto h_c/\alpha$. If α is so small that D_c is greater than the scale of confinement, droplets coarsen into a continuous water phase. In regime II, however, the water is consumed into a stable emulsion, with D_a thus providing a measure of D_c . The dotted curve in Figure 2 depicts the behavior predicted for constant h_c , with $D_a \sim \alpha^{-1}$ and $h_c \approx 0.08\rho_w/\rho_c$ (μm). The latter is valid around $\alpha \approx 0.005$. Since ρ_c is likely small compared to the density of water (the SWNT aggregates are diffuse and the tubes are hollow), the interphase thickness can be on the scale of microns, as expected for the macroscopic scale of the emulsion. This is also consistent with small-angle neutron scattering measurements, which indicate no structural differences between the pristine aggregates and the emulsions, from a few nanometers to 1000 nm. The actual trend exhibited by the data (solid curve in Figure 2) is more consistent with $h_c \sim \alpha^{0.7}$, which suggests that increasing the number of SWNTs in the mixture increases the interphase thickness. This imposes a limit for creating large curvatures or small droplets at higher α , giving rise to regime III, where fine emulsion droplets coexist with excess SWNTs.

The nanotubes are insoluble in either toluene or water. Similar to other forms of C_{60} , they are somewhat more compatible with aromatic hydrocarbons.¹⁴ Before the imposition of strong shearing forces via vigorous shaking of the samples, the tubes stay preferentially in the toluene as dark fluffy aggregates, with the water and toluene phases remaining distinct. Shearing breaks the minority water phase into fine droplets and creates a large amount

of interface between the immiscible fluids, where the SWNT bundles then preferentially reside. Upon cessation of shear, this interphase material limits the coarsening of water droplets, thus stabilizing the macroemulsion. This behavior arises from the natural amphiphobicity, large aspect ratio, and high rigidity of the CNTs. Because the interphase is made of woven nanotubes, it has a very high strength-to-mass ratio, and the stabilized water droplets are highly resilient to external perturbations. For example, emulsion droplets can be several millimeters in diameter while remaining perfectly round, and fine droplets can be easily transferred using a pipet or by directly pouring the solution. In addition, the emulsions are stable for months without noticeable change. These surprising features are common to carbon nanotubes. We have observed similar behavior with both single- and multiwalled CNTs and in other immiscible or partially miscible solvent pairs such as benzene/water, chloroform/water, cyclohexane/methanol, and so forth.

In this letter, we demonstrate a novel material form of a macroscopic emulsion, where water droplets are stabilized in toluene by amphiphobic SWNTs as a surfactant. The concept of emulsification via amphiphobicity might be applied to the processing and dispersing of nanoscale objects, the interfacial modification of incompatible liquids, and the creation of new macroscopic materials with unique interfacial and structural properties. We note that a somewhat similar phenomenon has recently been reported at smaller length scales in mixtures of toluene, water, and an inorganic nanoparticle.¹⁵ Fundamental issues, such as the detailed structure of the woven interphase, the long-term stability, the interfacial and mechanical properties of the emulsion, and the dynamics of emulsification, remain to be addressed.

LA026883K

(14) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.

(15) Lin, Y.; et al. *Science* **2003**, *299*, 226.