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Mechanical agitation induces counterintuitive aggregation of pre-dispersed carbon nanotubes





Ricardo M.F. Fernandes^{a,b}, Matat Buzaglo^c, Oren Regev^{c,d}, István Furó^b, Eduardo F. Marques^{a,*}

^a Centro de Investigação em Química, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre, s/n, P-4169-007 Porto, Portugal ^b Division of Applied Physical Chemistry, Department of Chemistry, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

^c Department of Chemical Engineering, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel

^d Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, 84105 Beer-Sheva, Israel

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ABSTRACT

Mechanical agitation is commonly used to fragment and disperse insoluble materials in liquids. However, here we show that when pristine single-walled carbon nanotubes pre-dispersed in water are subject to vortex-shaking for very short periods (typically 10–60 s, power density ~0.002 W mL⁻¹), re-aggregation counterintuitively occurs. The initial dispersions are produced using surfactants as dispersants and powerful tip sonication (~1 W mL⁻¹) followed by centrifugation. Detailed imaging by light and electron microscopies shows that the vortex-induced aggregates consist of loose networks (1–10² µm in size) of intertwined tubes and thin bundles. The average aggregate size increases with vortexing time in an apparently logarithmic manner and depends on the dispersant used, initial concentration of nanotubes and size distribution of bundles. The aggregation is, nonetheless, reversible: if the vortex-shaken dispersions are mildly bath-sonicated (~0.03 W mL⁻¹), the flocs break down and re-dispersal occurs. Molecular insight for the mechanism behind this surprising phenomenon is put forth.

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1. Introduction

Many practical exploitations of carbon nanotubes, such as composite reinforcement [1,2] and advanced molecular electronics [3,4], require prior separation of the highly aggregated and

* Corresponding author. E-mail address: efmarque@fc.up.pt (E.F. Marques). entangled powders of this nanomaterial into isolated nanotubes or thin bundles. Dispersing the powders in aqueous media by noncovalent binding [5,6] of amphiphiles—surfactants [7,8], polymers [9,10] or proteins [11,12]—has become a widely used strategy for that goal. Besides playing an active role in the exfoliation process [13,14], the dispersants also promote colloidal stability by hindering re-bundling and precipitation due to electrostatic or steric repulsions between the coated tubes [15].

The dispersing process usually involves powerful sonication of the as-received powder in presence of the dispersant solution. This step is followed by centrifugation to remove larger agglomerates and impurities and yield the final SWNT dispersions. The experimental parameters used both in the sonication and centrifugation steps are critical for the characteristics of the final dispersion obtained. viz. the distribution of tubes and bundles thereof in suspension [16–19]. These dispersions possess only kinetic and not thermodynamic stability [15]. Consequently, re-aggregation typically occurs within hours to weeks-depending on the dispersants and processing conditions used [7,15]-and is undesired for most applications. It might be thought that if a short energy boost were imparted to the dispersions, e.g. by vortex-shaking, any flocculated material would redisperse. In fact, mechanical agitation by vortexshaking is a well-known method for dispersing materials such as soft colloids [20-23] or hard particles [24-26]. The vortex mixers used usually consist of an electric motor connected off-center to a cupped rubber holder of vials. With the motor on, the rotating holder randomly shakes the vial (with a few thousand rpm), creating a turbulent vortex flow in the contained liquid that fragments and disperses the material.

Counterintuitively, herein we have found the opposite effect in aqueous dispersions of pristine single-walled carbon nanotubes (SWNTs). Vortex-shaking leads to instability and re-aggregation of the pre-dispersed particles (individual tubes and bundles) into discrete, weakly-bound aggregates in the $1-10^2 \,\mu m$ size range. Previously, a few papers reported on crosslinked networks of SWNTs in as-produced semidilute dispersions and gels [27] or on fractal-like aggregates in dilute, poorly dispersed SWNT suspensions [28–30]. As concerning aggregates resulting from flowdriven flocculation or percolation of pre-dispersed tubes, studies are also relative scarce, and typically involve multiwalled nanotubes and rheological effects in semidilute and concentrated regimes [31,32]. To our knowledge, this is the first report where aggregation induced by mechanical agitation in dilute dispersions of SWNTs-and redispersal by weak bath sonication-is recognized and studied. Our own surprise over the observations prompted us to further investigate this intriguing phenomenon, yielding the current report. The SWNT dispersions were prepared by assorted surfactants under identical conditions and then submitted to vortexing over varying time. We also investigated the effects of initial nanotube concentration and bundle size distribution (by varying the centrifugation parameters prior to vortex shaking) on the average aggregate size. Given that the molecular mechanism of the phenomenon is likely complex, different hypotheses will be presented.

2. Experimental section

2.1. Materials and sample preparation

The dispersions were prepared using single-walled nanotubes (SWCNT/HDPlas, CheapTubes), specified by the supplier as mixed single- and double-walled tubes with outer diameter d = 1-4 nm and length $L = 3-30 \mu$ m, produced by catalytic chemical vapor deposition. Three types of common surfactants (covering for molecular diversity) were used: the anionic surfactants sodium

dodecylbenzenesulfonate, SDBS, and sodium dodecyl sulfate, SDS; the cationic surfactants dodecyltrimethylammonium bromide, DTAB, and cetyltrimethylammonium bromide, CTAB; and the nonionic surfactants Pluronic[®] F127 and F68 (both amphiphilic triblock copolymers), and Triton^M X-100. All the surfactants were acquired from Sigma-Aldrich (purities \geq 99%) and used as received.

All dispersions were prepared by weighing 9 mg of carbon powder into a vial followed by addition of 3 mL of the desired surfactant solution (yielding 3 mg mL⁻¹ suspensions). The mixtures were then tip sonicated for 8.5 min, using a Bandelin Sonoplus Vb 2070 probe set to a vibration amplitude of 30% and estimated power density of ~1 W mL⁻¹ [33], followed by 20 min centrifugation in a Centurion K24 IR centrifuge at 4000g (typical value, except in the g variation study). For the vortex-shaking studies, a Breda Scientific mixer (3000 rpm) with a rubber single cup head was used. The vortex mixer delivers an estimated average power density of ~2 mW mL⁻¹ (see Section 1 and Table S1, Supplementary Data). For bath sonication, an Elma Sonic (model S10; 30 W 37 kHz) sonicator was employed (~0.03 W mL⁻¹) [33].

2.2. Quantification of SWNT and dispersant concentrations

For all systems, we set the SWNT concentration, c_{SWNT}, to 0.30 ± 0.03 mg mL⁻¹, for proper comparison between surfactants on the vortexing effects. This was achieved as follows. (1) An aqueous SWNT/dispersant mixture was sonicated and, after centrifugation, the c_{SWNT} in the supernatant—the as-produced dispersion-was determined by UV-Vis spectrometry (double-beam Spectrophotometer U-2001; λ = 660 nm) according to a previously published method [33,34]. (2) This dispersion was then diluted to $c_{SWNT} = 0.30 \pm 0.03 \text{ mg mL}^{-1}$ using the initial surfactant solution in order to keep surfactant "saturation" in the bulk; the error arises from *c*_{SWNT} determination in the initial dispersion. The surfactant concentration, c_s , in the initial surfactant solutions was ca. 3 mg mL⁻¹, except for DTAB, set to 12.5 mg mL⁻¹ (due to weaker dispersing ability [33]: cf. also Section 2 and Fig. S1. s.d.). The final $c_{\rm s}$ values after centrifugation and dilution effects, however, are not anymore the initial ones, one main reason for that being the loss of surfactant in the precipitate in the initial step. A sensible estimation yields the final all inclusive $c_s \approx 2.7 \pm 0.5 \text{ mg mL}^{-1}$ (for all surfactants except DTAB) and $c_{\text{DTAB}} \approx 12 \pm 1 \text{ mg mL}^{-1}$.

2.3. Imaging by light microscopy, cryo-SEM and cryo-TEM

Imaging of the vortex-shaken SWNT dispersions was carried out with an Olympus BX51 light microscope, with differential interference contrast (DIC), under 100× and 400× magnifications. The images were acquired with an Olympus C5060 videocamera and software CellA. For the graphs in Figs. 2 and 3, the major length, L_{a} , of a minimum of 50 aggregates per dispersion was counted in the light microscope and the results are shown as the average $\langle L_a \rangle$ (detailed values and respective standard deviation can be found in Section 3, Tables S2–S5, s.d.).

Selected vortex-shaken samples were also imaged by cryo-SEM, using a JEOL JSM 6301F SEM microscope equipped with a Gatan Alto 2500 cryo-preparation chamber. Each sample was vitrified by plunging it into nitrogen slush ($-200 \,^{\circ}$ C), followed by freeze-fracture at $-140 \,^{\circ}$ C. The subsequent sublimation of water (solvent) was done at $-95 \,^{\circ}$ C for 2 min. The specimen was finally sputtered with an Au-Pd alloy, during 30 s in Ar atmosphere, in the cryo-preparation chamber, before transfer into the microscope.

Cryo-TEM imaging was also performed for vitrified specimens of the vortexed dispersions. The latter were prepared using a Leica EM GP cryo-preparation station operated at 100% relative humidity. A drop of 4 μ l of solution was applied on a holey carbon TEM

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