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Concentrated solutions of individualized single walled carbon nanotubes

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ABSTRACT

Solutions of alkali metal salts of single-walled carbon nanotubes (SWNTs) show individualization of the nanotubes without sonication-induced shortening. Bundles are fully exfoliated and length measurements show mean length over one micron, a rare case for liquid formulation of SWNTs. These concentrated solutions of individualized nanotubes in organic solvents can be freeze dried leading to ultralight, highly porous, conducting and mechanically stable carbon nanotube cryogels.

1. Introduction

Carbon nanotubes and in particular single walled carbon nanotubes (SWNTs) are promised a great technological future due to their extraordinary (in the literal sense) properties [1,2]. Carbon nanotubes share with graphene high Young modulus, high electrical mobility, high aspect ratio and lightness. However, to use SWNTs in industrial applications, one of the main problems to overcome is that of optimum dispersion or solubilization. SWNTs readily form parallel bundles or ropes [3,4] with a van der Waals binding energy of 500 eV per micrometer of tube-tube contact [3,5]. These bundles are formed by hexagonal packing of individual nanotubes, with diameters of a few tens of nanometers, compared to ca. 1 nm for individual tubes. These bundles are very difficult to exfoliate, i.e. separate into individual tubes. The bundles greatly worsen mechanical properties of SWNT-polymer composites due to internal slippage [6], raise percolation thresholds for electrically conductive composites and diminish transmission of transparent films based on nanotubes. For these reasons, most applications (electrical, mechanical, optical or electromechanical and even separation of single-walled carbon nanotubes [7]) require full exfoliation of the SWNT bundles if they are to take advantage of the full potential of SWNTs. True exfoliation of single-walled nanotubes bundles by a combination of high shear mixing, high power cup-horn sonication and ultracentrifugation of a sodium dodecylsulfate (SDS) aqueous suspension of SWNTs has been demonstrated about ten years ago by band-gap fluorescence of semi-conducting nanotubes [8]. However, this breakthrough was obtained at the cost of low nanotubes fraction (10^{-4} wt.% or ca 1 μg/ml) and loss of most of the starting material (99%). Alternatively, Coleman et al. showed dilution-induced debundling of SWNTs and obtained diluted dispersions with mostly individual tubes at 10^{-5} weight fraction in *N*-methyl-pyrrolidone (NMP) [9]. High weight fraction aqueous solutions (up to 20 mg/ml) have been obtained with sodium dodecylbenzene sulfonate (SDBS) using bath sonication, i.e. a milder sonication, for 24 h [10]. Over 70% of the tubes were found to be exfoliated by atomic force microscopy (AFM), but the tubes were clearly shortened by this process (mean length of 165 nm and 500 nm, respectively for HiPco (High Pressure

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carbon monoxide process) and laser ablation tubes), most probably due to sonication. Successful exfoliation of SWNT have also been obtained by sonication in presence of synthetic or natural polymers, namely polyimide [11] and DNA [12] at the expense of shortening the nanotubes [13–16]. On the other hand, successful individualization of SWNT have been obtained by mild sonication without any significant shortening, albeit at the cost of rather low concentration (up to 30 μg/ml) [17,18].

In those latter cases, SWNTs are coated with surfactant or polymers, which can be difficult to remove afterwards, and furthermore, those are metastable dispersions, as opposed to thermodynamically stable solutions. In the case of bile salts, Wenseleers et al. have shown that true dissolution could be obtained without the help of sonication, albeit the dissolution is quite slow (days or weeks) and concentrations are low [19]. Likewise, solutions of SWNTs have been obtained in superacids [20]. Covalent functionalization has also been used to solubilize SWNTs [21–24].

Some years ago, we have shown that concentrated (up to 0.5 wt.%) *solutions* of SWNTs can be obtained by spontaneous dissolution of alkali metal salts of SWNTs in polar organic solvents [25,26]. The adjective "concentrated" thus describes the fact that those solutions are two orders of magnitude (1–5 mg/ml against 30 μg/ml) more concentrated than the suspensions of individualized tubes of the literature. In this reductive dissolution, no energy was used to dissolve the nanotubes salts, hence at no moment in the whole process are the nanotubes susceptible of being broken or damaged in any way. Shaffer, Skipper et al. have prepared similar solutions by reducing SWNTs in metal-ammonia and showed successful sorting of SWNTs by carefully adjusting the reducing agent [7]. We show here, by AFM measurements that diameter distribution of SWNTs in these concentrated solutions of electric arc tubes show exclusively exfoliated tubes or very small bundles (ca 3 tubes). Furthermore, since no process is used here that might cut the tubes, length measurements allow for a lower limit distribution analysis of the length of nanotubes. Additionally, these solutions can be freeze-dried, yielding ultralight (apparent density < 10 g/L), conducting cryogels. Raman analysis of the cryogels shows that nanotubes have not suffered any change (functionalization) in the process.

2. Experimental

Carbon nanotubes synthetized by the electric arc method (Nanoledge) for AFM measurements and chemical vapor deposition (Elicarb™ from Thomas Swan, Inc.) for cryogels were used as received. Diameters for electric arc nanotubes range from 1.2 to 1.5 nm. Concentrated solutions (between 0.1 and 0.2 wt.%) were prepared by the mild dissolution route [25,26] under inert atmosphere in an Innovative Technology™ glove box filled with argon. Alkali metal salts of nanotubes of approximate stoichiometry KC_{10} were synthesized by reduction in tetrahydrofuran (THF) via the naphthalene radical anion route [27]. Solutions of these salts were prepared in dimethylsulfoxide (DMSO) by gentle stirring at room temperature (ca 2 mg/ml, overnight) without sonication or any other high-energy technique, followed by a mild centrifugation (2500 *g*, one hour) as previously described [25]. Adequate concentration (between 1 and 10 μg/ml) for AFM imaging was obtained by diluting a drop of these master solutions with freshly centrifuged DMSO (for which the upper and lower fractions have been discarded in order to remove most dust particles). AFM samples were prepared as follows: a piece of mica was cleaved inside the glove box, exposing a freshly cleaved surface, and a drop of solution of adequate (trial and error) concentration was placed on the mica and allowed to dry overnight inside the box, before air exposure. For the raw nanotubes, suspensions were prepared in ethanol (to ensure fast evaporation time) with mild bath sonication (a few minutes). AFM images were obtained with a Nanoscope III™ microscope (Digital Instruments) in tapping mode. Standard silicon cantilevers with a resonance frequency of 300 kHz were used. Scan rate varied between 0.3 and 1 Hz. Diameters were measured from height profiles individually obtained by the height measurement tool. Length measurements were obtained by manual measurement on printed pictures (with a ruler). Cryogels were obtained by freezing the solutions in liquid nitrogen in a closed vessel filled under argon in the glove box, then thermostating the frozen solution at ca 10 °C (i.e. a few degrees below DMSO freezing point) and exposing it to secondary vacuum (10^{-5} mbars) overnight. Electrical conductivity measurements were carried out by four points methods with silver paste contacts. Current was applied to face to face contacts on each side of the monoliths while voltage was measured on annular contacts in between. Compression modulus measurements were obtained on a ZWICK Z2.5 apparatus.

3. Results

3.1. Solutions

SWNT solutions of electric arc nanotubes (Nanoledge) were prepared by reductive dissolution [25]. In short, an alkali metal salt of SWNT is prepared following the procedure of Petit et al. [27] This salt is then dissolved with gentle stirring overnight in a polar organic solvent such as DMSO. It should be noted that DMSO is known to be a poor solvent for dispersing raw carbon nanotubes [9,28]. After a mild centrifugation (2900*g*, one hour) to remove any insoluble material, a concentrated solution (up to 0.5 wt.% in nanotubes) is obtained. This solution is indefinitely stable if kept under inert atmosphere (the reduced nanotubes are air sensitive) [25]. For example, visual observation of SWNT solutions prepared 8 years ago show no hint of aggregation. Apart from the initial centrifugation described above, no other separation technique was used. Several dilutions of the initial master solution were prepared and deposited by drop casting on freshly prepared mica surfaces which were imaged by AFM.

Fig. 1 shows AFM height images of drop casted SWNTs. To be able to compare the dissolved tubes with the raw material, the latter was dispersed in ethanol (a non-dispersing solvent for nanotubes, as DMSO [9,28] but far easier to handle and remove) with a few minutes bath sonication and drop casted on mica (Fig. 1a). Together with the tubes, particles of sizes from