ChemComm

Dissolution of small diameter single-wall carbon nanotubes in organic solvents?

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Received (in Columbia, MO, USA) 19th September 2000, Accepted 27th November 2000
First published as an Advance Article on the web 8th January 2001

The solubility of small diameter single-wall carbon nanotubes in several organic solvents is described, and characterization in 1,2-dichlorobenzene is reported.

Owing to their phenomenal electrical and mechanical properties, single-wall carbon nanotubes (SWNTs) have been an area of intense research since their discovery in 1991,[1] and a variety of potential applications have been proposed.[2] Many of these applications will likely require chemical modification to facilitate manipulation of the tubes. Consequently, there have been significant efforts to derivatize SWNTs.[3] These efforts, including our own, have been hampered by minimal or complete lack of solubility in common organic solvents. We report here a screening of organic solvents, many of which have previously been found advantageous towards the dissolution of C_{60} and C_{70} fullerenes.[4] Solubilization of SWNTs is expected to facilitate both their chemical derivatization and investigation of their photophysical properties.

The SWNT samples used for this study were produced by a gas-phase catalytic process developed by Smalley and coworkers.[5] This process is capable of producing SWNTs with diameters of *ca.* 0.7 nm, considerably smaller than SWNTs typically produced by laser oven methods.[5,6] The production material was used directly, with no purification. The material used for this investigation consisted of mostly carbon nanotubes, and contained *ca.* 5 atom% residual iron catalyst, as verified by scanning electron microscopy (Philips XL 30 ESEM) and EDAX (energy dispersive analysis with X-rays). An SEM image of the SWNTs is shown in Fig. 1

UV–VIS absorption spectroscopy was used to determine solubility as follows. Several different concentrations of SWNT solutions in 1,2-dichlorobenzene were prepared by sonication (Cole-Parmer B3-R, 55 kHz). The solutions were then filtered through glass wool until no visible particulate remained, and the absorption spectrum was recorded (Fig. 2). A 100.0 mL aliquot of each sample was placed in a warm water bath, and the solvent was removed with a gentle stream of nitrogen. The samples were dried in an oven at 130 °C for 1 h and then weighed to determine the mass of solubilized SWNT. This concentration (in mg L^{-1}) in conjunction with the absorbance at 500 nm, allowed preparation of the plot shown in the inset of Fig. 2. The slope of the linear-least-squares fit is then analogous to the familiar extinction coefficient of Beer's Law.[7] This value was used to determine the concentration of all subsequent samples, which were prepared in the following manner. Several mg of SWNT material were placed in a scintillation vial containing 10 mL of solvent. The amount of SWNTs used was sufficient to ensure undissolved material. The vial was capped and sonicated for 1 h. The solution was filtered through glass wool until no particulate remained, and the absorption spectrum was recorded. The concentration was determined as described above. The results are shown in Table 1. A single production batch was used to generate the results shown in Table 1. The stability of these solutions varied from *ca.* 4 h to more than 3 days for 1,2-dichlorobenzene. Since the solubility of SWNT samples might vary from batch to batch, two other batches of gas-phase grown material were checked for their solubility properties in 1,2-dichlorobenzene. The results were within *ca.* 10% of the original batch.

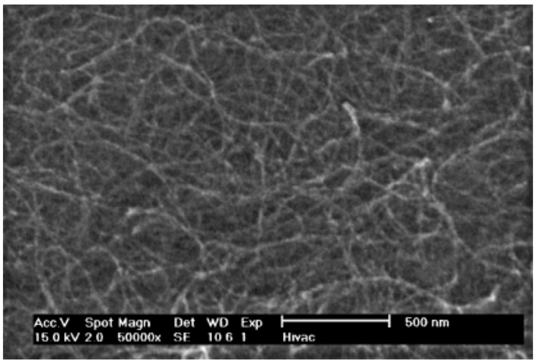

Fig. 1 SEM image of the SWNT material used for this investigation.

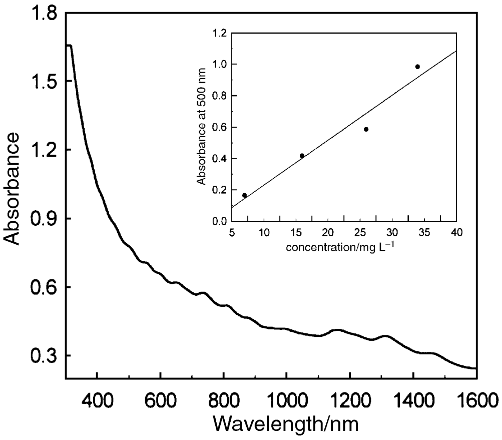

Fig. 2 Absorption spectrum of the SWNT material at a concentration of 27 mg L^{-1} in 1,2-dichlorobenzene. Inset: Optical density at 500 nm of the SWNT material in 1,2-dichlorobenzene at different concentrations. The straight line is a linear-least-squares fit to the data; slope = 0.0286.

Table 1 Room-temperature solubility of the SWNT material[a]

Solvent	mg L^{-1}
1,2-Dichlorobenzene	95
Chloroform	31
1-Methylnaphthalene	25
1-Bromo-2-methylnaphthalene	23
N-Methylpyrrolidinone	10
Dimethylformamide	7.2
Tetrahydrofuran	4.9
1,2-Dimethylbenzene	4.7
Pyridine	4.3
Carbon disulfide	2.6
1,3,5-Trimethylbenzene	2.3
Acetone	—[b]
1,3-Dimethylbenzene	—[b]
1,4-Dimethylbenzene	—[b]
Ethanol	—[b]
Toluene	—[b]

[a] The sonicator bath water temperature rose to *ca.* 35 °C over the course of 1 h. [b] Solubility in these solvents was < 1 mg L^{-1}

DOI: 10.1039/b008042j

1,2-Dichlorobenzene was found to be a reasonable solvent for the SWNTs. A photograph of the SWNT samples dissolved in 1,2-dichlorobenzene at differing concentrations is shown in Fig. 3. The 1,2-dichlorobenzene solutions could be filtered (0.2 μM PTFE, Sartorius), dried for 1 h at 140 °C, and then re-dissolved.

The issue of solution *vs.* suspension for SWNT in organic solvents is unresolved. Although there was no visible particulate in the solutions reported here, the terms 'metastable solution' or indeed even 'suspension' may be equally applicable. The question of whether solvation means exfoliation of nanotube ropes into individual nanotubes is perhaps inherent in this issue. In an attempt to determine whether these solutions/suspensions were comprised of individual tubes, we performed atomic force microscopy (Digital multi-mode SPM)[8] on samples deposited from 1,2-dichlorobenzene solutions. Samples from a *ca.* 5 mg L^{-1} solution showed mostly small bundles which are likely comprised of several nanotubes, based on height analysis of *ca.* 1.5–1.9 nm and lengths of *ca.* 500 nm. Analysis of samples deposited from more concentrated solutions revealed larger bundles or ropes with heights of *ca.* 6 nm and lengths of 1–3 μM. These bundles are a result of the significant van der Waals interaction between the sidewalls of the tubes. It is therefore possible that solubilization in 1,2-dichlorobenzene does not completely exfoliate the SWNT bundles to give individual nanotubes. Alternatively, individual tubes could be present when in solution, but these coalesce when spin-coated on the substrate for imaging.

Solutions in 1,2-dichlorobenzene did not pass through a 1.2 μM PTFE membrane (Sartorius). This does not conclusively mean that all tubes in the solution were longer than 1.2 μM. A few longer tubes may form a mat on the membrane, preventing passage of shorter tubes. In addition, these membranes are 'torturous path' filters, which may require significant solute deformation; a difficult task for these exceedingly rigid tubular structures. We also attempted to pass a *ca.* 30 mg L^{-1} 1,2-dichlorobenzene solution (this solution was sonicated for *ca.* 20 min) through a 3 μM, track-etched polycarbonate membrane (Poretics). The pores in these membranes are nearly 'straight' holes (relative to their diameter) which do not require significant solute deformation for passage. The filtrate contained 13 mg L^{-1} of SWNTs. This solution did not exhibit a Tyndall effect (632 nm) 20 min after filtration. This suggests that most particles in the solution are on the order of 0.6 μM in length or smaller, though this is of course an extremely crude estimate of particle size. In addition, at this concentration, the solution absorbs *ca.* 50% of the incident light at 632 nm. After *ca.* 1 h, the solution did exhibit a Tyndall effect, and particulates became visible shortly thereafter. It is then reasonable to suppose that individual tubes might indeed exist in the solution at low concentrations, but they eventually form ropes, then bundles of larger size. In more concentrated solutions, the tubes are likely to exist only as ropes or bundles. Whenever dealing with such large, rigid molecules however, the question of 'true' solubility persists.

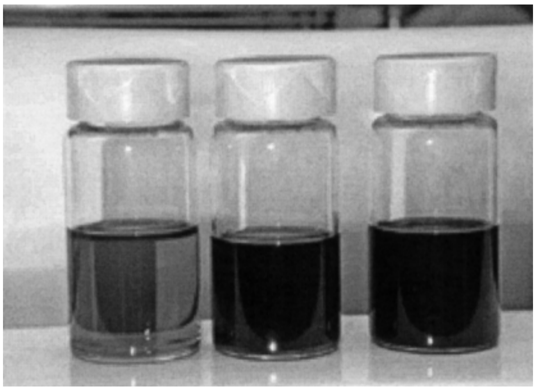

Fig. 3 SWNT solutions in 1,2-dichlorobenzene. From left to right: 10 mg L^{-1}, 25 mg L^{-1}, 95 mg L^{-1}.

A report recently appeared in the literature concerning dissolution of laser-oven produced SWNTs (diameter *ca.* 1.2 nm) in organic solvents.[9] The authors presented extensive spectroscopic characterization of the dispersions, and concluded that highly polar solvents such as dimethylformamide, *N*-methylpyrrolidinone, and hexamethylphorphoramide were the most attractive solvents. We have also investigated the solubility of laser-oven produced tubes (obtained from Tubes@Rice) in 1,2-dichlorobenzene, which was briefly touched upon in the aforementioned report. We found the raw production material to possess a solubility similar to that of the gas-phase catalytically grown tubes in 1,2-dichlorobenzene, at *ca.* 75 mg L^{-1}. However, this material consists of as little as 40% SWNTs, the remainder being comprised of amorphous carbon amd metal catalysts. We found purified material from Tubes@Rice (consisting of *ca.* 90% SWNTs) to be considerably less soluble in 1,2-dichlorobenzene, at 35 mg L^{-1}. It is therefore likely that impurities play a role in dissolution of the laser-oven grown SWNTs. Alternatively, the purification process may affect the integrity of the SWNTs, altering their solubility properties. Concerning the differences observed between the laser-oven produced material and the gas-phase catalytically produced material, it is not clear whether these arise from the nature of the tubes themselves (*i.e.* the diameter or possibly differing helicity mixtures), or merely arise from the different impurities or intermolecular packing characteristics of each production method.

We are currently seeking to take advantage of the dissolution ability of 1,2-dichlorobenzene to facilitate chemical derivatization of the gas-phase catalytically produced SWNTs.

We thank Dr Robert Hauge for helpful discussions. We gratefully acknowledge the financial support of NASA (NASA-JSC-NCC 9-77, OSR#99091801) and the NSF (NSR-DMR-0073046#) for this work.

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7 Beer's Law states that $A = \varepsilon bc$, where A is the optical density, ε is the extinction coefficient, b is the path length, and c is the concentration. The extinction coefficient is somewhat solvent dependent.

8 Samples were spin coated on a mica substrate, rinsed with ethanol, and warmed to evaporate the solvent. Imaging was performed in tapping mode.

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