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About the solubility of reduced SWCNT in DMSO

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Abstract

Single-walled carbon nanotubes (SWCNT) have been reduced with sodium naphthalide in THF. The reduced SWCNT are not only soluble in dimethylsulfoxide (DMSO) to form a stable solution/suspension, but also react spontaneously at room temperature with DMSO to evolve hydrocarbon gases and are converted into functionalized SWCNT. The degree of functionalization is about 2C% and the addends are mainly methyl and small oxygen-containing hydrocarbons. The functionalized SWCNT are apparently more soluble and stable in DMSO solution. It may open a new era for further processing and applications.

1. Introduction

Single-walled carbon nanotubes (SWCNT) exhibit exceptional mechanical, thermal and electrical properties, the best of any known materials. Combined with their very high aspect ratios, SWCNT should be the ideal fillers for the fabrication of composite materials with superlative properties. Unfortunately, as a result of strong van der Waals interactions, high crystallinity and aromaticity, SWCNT bundle up as ropes and have little affinity for or compatibility with any matrices and solvents, thus making the realization of high performance composites very challenging unless proper chemistry is performed. Recently, Pénicaud *et al* reported that SWCNT bundles can be readily exfoliated by reduction with an alkali metal such as Na, Li or K in THF through electron transfer mediated by alkali–naphthalene–THF complexes [1]. Furthermore, they concluded that the thus reduced SWCNT dissolve spontaneously in polar aprotic solvents such as sulfolane, dimethyl sulfoxide (DMSO), *N*-methylformamide (NMF), dimethylformamide (DMF) and 1-methyl-2-pyrrolidone. Indeed, these solvents do appear to dissolve reduced SWCNT and therefore they have been used to conduct chemistry and processing of reduced SWCNT with the expectation that pristine neutral SWCNT can be recovered through oxidation by exposure to air [2, 3]. Here we report our discovery of the solubility and reactivity of reduced SWCNT in DMSO solution.

2. Experimental details

2.1. Sample preparation

The experiments have been conducted in the following way. SWCNT were synthesized using the laser-oven approach as described in [4]. Reduced SWCNT were prepared according to [5]. The resulting mixture was centrifuged in a 250 ml polyethylene bottle at 5000 rpm for 30 min. The precipitate was thoroughly washed five times with 200 ml of freshly dried THF through repeated sonication–shaking–centrifugation cycles. Under flowing N₂ atmosphere 200 ml of carefully dried DMSO was added to the final precipitate and the bottle was sealed immediately with a cap fitted with a septum. Afterwards, the bottle was vigorously shaken and bath-sonicated for 10 min. More details for typical sample preparation are described as follows.

2.1.1. Preparation of a suspension of SWCNT in THF. 100 mg of SWCNT purified by a procedure developed in-house were ground in a few ml of dry THF in an agate mortar in air. These SWCNT were then suspended in 150 ml of dry THF in a Schlenk round-bottomed flask and sonicated either in an ultrasonic bath for approximately 1 h or using an ultrasonic tip for about 30 min, resulting in a well-dispersed suspension.

2.1.2. Preparation of a green sodium naphthalide solution in THF. 95.8 mg of small pieces of sodium and 640 mg of naphthalene were added to 30 ml of dry THF contained in a Schlenk round-bottomed flask under N_2 . The mixture was stirred for 3 h resulting in a dark green solution.

2.1.3. Preparation of reduced SWCNT. The green sodium naphthalide solution was added to the SWCNT suspension which was sparged with N_2 for a few minutes before adding the sodium naphthalide. The mixture was stirred overnight at room temperature and then centrifuged at 9000 rpm for 30 min. After discarding the liquid phase under N_2 , the precipitate was washed five times with fresh dry THF through sonication–shaking–centrifugation cycles. After centrifugation the THF-wet dope of reduced SWCNT was collected in a 50 ml Falcon tube and stored under N_2 .

2.1.4. Reaction with DMSO. To the above dope kept under flowing N_2 , 45 ml of dry DMSO (99.9%, Aldrich, dried with molecular sieve 4 Å before use) was added. The mixture was strongly shaken and bath-sonicated for 10 min. Afterwards, an evolved gas sample was collected through a pre-assembled rubber septum using a gas-tight syringe for GC-MS measurement. The evolved gas was continuously monitored until the next day.

The sample mixture was subsequently filtered through a 0.2 μm pore size PTFE membrane. The filtrand was extensively washed with DMSO, THF, water and methanol until the filtrate became colourless, leaving a solid black cake on the filter membrane. A suspension of a small amount of the filter cake in methanol was prepared for Raman and XPS measurements. The remainder of the filtrand was dried in an oven at 95 °C overnight.

2.1.5. Blank reaction with DMSO: sodium naphthalide in THF with DMSO and without SWCNT. 95.8 mg of small pieces of sodium and 640 mg of naphthalene were added under N_2 to 30 ml of dry THF in a Schlenk round-bottomed flask. The mixture was stirred for 3 h resulting in a dark green solution. The dark green solution was transferred into a 50 ml Falcon centrifuge tube with a pre-assembled septum cap, to which 15 ml of dry DMSO was added. Gases were immediately generated and the dark green colour of the mixture slowly changed to yellow. After 10 min the evolved gas sample was collected using a gas-tight syringe and injected into the GC-MS instrument.

2.1.6. Control reaction: neutral SWCNT with THF and DMSO. 100 mg of neutral SWCNT purified by a procedure developed in-house was placed in a 50 ml Falcon centrifuge tube with 30 ml of dry THF and 15 ml of dry DMSO. The mixture was sealed with a septum and bath-sonicated for 30 min. The sample in the gas phase was collected with a gas-tight syringe and injected into the GC-MS instrument.

Figure 1. Chromatograms of gases evolved from: sodium naphthalide in THF and DMSO mixture (A); reduced SWCNT in THF and DMSO mixture (B); neutral SWCNT in THF and DMSO (C).

2.2. GC-MS analysis

GC/MS analysis of gas samples was performed on an Agilent 6890GC/5975MSD instrument equipped with a Carboxen 1010 PLOT (Supelco) 30 m $\times$ 0.32 mm column. The carrier gas was helium with a constant flow of 1.5 ml min⁻¹. A 500 μl gas-tight syringe was used to inject 500 μl samples. The injector temperature was 200 °C and split injection mode was used with split ratio 1:50. The GC oven temperature was programmed for an initial isothermal soak at 35 °C for 5 min, followed by a temperature ramp of 20 °C min⁻¹ to 225 °C. All components in the samples were detected in scan mode with a mass range of 10–300 mass units and identified using NIST library number 05.

Note that the CO_2 retention time in trace C in figure 1 is shorter than that in traces A and B because it was obtained after reinstalling the same column back into the instrument after cutting the column slightly shorter.

2.3. XPS analysis

The samples were analysed using a Kratos Axis Ultra-XPS equipped with a monochromated Al x-ray source. Three analyses were performed on each sample to ensure reproducibility. Analyses were carried out using an accelerating voltage of 14 kV, current of 10 mA and an x-ray spot size of 400 μm $\times$ 700 μm . Charge build-up was compensated for using the Axis charge balancing system. The pressure in the analysis chamber during analysis was 2.0×10^{-9} Torr. High resolution spectra were collected at a pass energy of 40 eV and peak-fitted using CasaXPS (ver. 2.2.107) data processing software. Shirley background correction procedures were used as provided by CasaXPS. Curve-fitting procedures used for the high resolution spectra used a Gaussian–Lorentzian function. The binding energy scale of the spectrometer was externally referenced to Ag 3d_{5/2} at 368.3 eV. High resolution analyses were calibrated to the adventitious C 1s signal at 284.6 eV. Quantification was performed using sensitivity factors provided by CasaXPS's Scofield element library.

Scheme 1. A schematic representation of the reaction steps, products and their appearance in DMSO solution (R = yet unknown fragments anchored to SWCNT in the final product).

2.4. TGA–MS–IR analyses

TG analyses of nanotube samples were performed on a Netzsch TG 209 F1 Iris[®] with simultaneous coupling of an Aeolus QMS403C mass spectrometer and a Bruker Tensor 27 Fourier Transform Infrared (FTIR) spectrometer via a TGA A588 TGA-IR module. The system was bought as a complete unit from Netzsch. The system was run with BOC UHP argon (5.3) gas and residual oxygen was trapped with a Supelco Big-Supelpure O oxygen/water trap. Transfer lines between the TG instrument, mass spectrometer and FTIR spectrometer and the IR cell were heated to a temperature of 200 °C.

2.4.1. Measurement conditions. Each TG analysis was performed using a clean platinum crucible, washed by rinsing with acetone, drying with Kimwipes[®] tissues and then curing in a Bunsen burner flame for 15 s. After cooling, the crucible was placed in the instrument and any residual air was removed by two evacuation and Ar-backfill cycles. The crucible was then placed under running gas conditions, which consisted of a 25 ml min⁻¹ flow of argon for the protective gas and a 50 ml min⁻¹ flow of argon for the purge gas. The balance on the TG was then tared. A buoyancy correction run was performed on the empty crucible, which accounted for balance drift due to increasing heat. The buoyancy run consisted of heating from room temperature to 120 °C at a heating rate of 10 °C min⁻¹, isothermal at 120 °C for 20 min, heating from 120 to 950 °C at a heating rate of 10 °C min⁻¹ and then keeping the temperature at 950 °C for another 30 min.

Analysis of nanotube samples proceeded as follows. A clean crucible was placed in the TG instrument and the balance was tared while under running gas conditions. The crucible was removed from the instrument, filled with the sample and returned to the TG. Residual air was removed by three evacuation and Ar-backfill cycles and the sample was placed under running gas conditions. The weight of the sample was recorded once the balance had stabilized. The sample was then placed under vacuum in the TG and heated to 120 °C at a rate of 10 °C min⁻¹. The sample remained at 120 °C under vacuum overnight. The sample was then cooled back

to room temperature under argon and placed under running gas conditions. The weight of the sample was recorded again once the balance stabilized and this weight was used as the starting weight for the analysis. The analysis programme was identical to the buoyancy correction run (heating from room temperature to 120 °C at a heating rate of 10 °C min⁻¹, isothermal for 20 min, heating from 120 to 950 °C at a heating rate of 10 °C min⁻¹ and then keeping the temperature at 950 °C for another 30 min). IR and MS data were collected concurrently with the TGA data. IR data were collected from 4500 to 500 cm⁻¹ at a resolution of 4 cm⁻¹. The integration ranges used for analysis of specific chemical signatures in the IR data were: 2402–2242 cm⁻¹ for CO₂, 3026–3002 cm⁻¹ for the Q branch of methane, 3001–2850 cm⁻¹ for the P branch of methane, 3042–2788 cm⁻¹ for total CH and 2849.83–2787.89 cm⁻¹ for low frequency CH (CH outside the P branch of methane). Mass spectrometry data were recorded from 1 to 80 mass units.

2.5. TEM and SEM analyses

TEM images were obtained using a Philips CM20 FEG Microscope operating at 200 kV. Samples were prepared by dropping a few drops of a suspension of SWCNT in methanol onto the holey carbon grid with a pipette.

SEM images were obtained using a Hitachi S-4800 FE microscope, operating at 1.2 kV, at a distance of 3 mm. Samples were prepared by pipetting a few drops of a suspension of SWCNT in methanol onto an aluminium SEM sample stub with a disposable Pasteur glass pipette.

3. Results and discussion

The reaction steps and their products have been illustrated schematically in scheme 1. The reduction of neutral SWCNT with sodium naphthalide in THF has been reported by Pénicaud *et al* [1]. The reduced SWCNT react spontaneously and immediately at room temperature with DMSO, a powerful radical scavenger, to produce gases and covalently functionalized SWCNT that retain high solubility in

Figure 2. (a) SEM micrograph and (b) TEM micrograph of filtrand following reaction of reduced SWCNT with DMSO and subsequent filtration through a $0.2\ \mu\text{m}$ PTFE membrane.

DMSO even after subsequent exposure to air or extraction as a solid. This chemical functionalization and, consequently, the solubility in DMSO will remain unless an annealing treatment is carried out.

It is well known that DMSO is an effective radical scavenger. It interacts readily with hydroxyl radicals ($\cdot\text{OH}$) to produce methyl radicals ($\cdot\text{CH}_3$) which give rise to methane by hydrogen abstraction. It has been shown that $\cdot\text{CH}_3$ generated by the reaction of $\cdot\text{OH}$ with DMSO adds to the sidewall of neutral SWCNT [6]. It has also been shown that neutral SWCNT induce the decomposition of radical precursors such as peroxides through a single-electron transfer mechanism [7]. As reduced SWCNT have increased radical and nucleophilic characters, reaction with DMSO is therefore not totally unexpected.

To determine whether the reduced SWCNT are simply soluble in DMSO and maintain their negative characters or soluble due to chemical modifications, several characterization tools were used. One important observation that has led to this study is the release of gases upon mixing reduced SWCNT with DMSO. Hence, our first goal has been to characterize these gases using GC-MS. Gas samples were taken with a gas-tight syringe above a mixture of thoroughly washed (*vide infra*) reduced SWCNT with dry DMSO and injected into the GC-MS instrument for analyses. The above process was repeated under identical conditions but with the complete *absence* of SWCNT in one case, and with *neutral* SWCNT in THF and DMSO in another; the latter serving as a control to establish a baseline. The results of the GC-MS analyses of these gas-phase samples are given in figure 1. As shown in the upper trace, sodium naphthalide in THF reacts with DMSO to produce predominantly methane and a much smaller amount of ethylene. In contrast, as shown in the middle trace, reduced SWCNT in THF and DMSO produce methane, ethylene and ethane in similar proportions. To make sure that the reaction was caused by the reduced SWCNT and not by residual sodium naphthalide even though different gases are produced, the

reduced SWCNT were extensively washed five times with a large amount of dry THF prior to adding the DMSO. As the solubility of sodium naphthalide in THF is very large, the washed reduced SWCNT paste must be free of residual sodium and naphthalene and, therefore, the observed gases must be the result of reactions between reduced SWCNT and DMSO.

The reacted reduced SWCNT are highly soluble in DMSO and the solutions remain stable for at least several months. They cannot be precipitated out easily through centrifugation but can be recovered through either vacuum evaporation of DMSO or filtration through a $0.2\ \mu\text{m}$ PTFE membrane (time tedious). In the latter case, as shown in the SEM of figure 2(a) and TEM of figure 2(b), the filtrand is composed of SWCNT with a very small proportion of residual amorphous carbon and metal particles covered by carbon shells or encapsulated inside an SWCNT bundle. Quite interestingly, this solid material can be readily re-dispersed in DMSO by simple bath sonication and even by hand shaking. To obtain dispersions with such ease, the SWCNT must be chemically modified and covalent functionalization, showing transformation from sp^2 to sp^3 hybridization through covalent anchoring of addends, is the only logical explanation. This transformation can be easily observed by Raman spectroscopy as illustrated in figure 3. Following the reaction with DMSO, the Raman spectra show an increase in the D-band over pristine SWCNT material. Incidentally, the increase in the D-band in the Raman spectrum obtained from reduced SWCNT subjected to DMSO is clearly apparent in figure 2 of [1] but was left without further explanation. The D-band increase was noted and somewhat discussed in [2] but was attributed to Na intercalation. Also noted in [2] is the stability of the dispersion even after oxidation which was attributed to a number of possible factors, none of them including chemical functionalization as we demonstrate here.

Further evidence for covalent sidewall functionalization is provided by evolved gas analyses using simultaneous thermo-gravimetry, mass spectrometry and infrared absorption

Figure 3. Raman spectra of neutral SWCNT used as starting material (red trace), and reduced SWCNT after the addition of DMSO (blue trace) (the spectra's intensities are normalized against the G-bands').

Figure 4. Thermogram and its derivative and the integrated infrared absorbances for the CO₂, CH₄ and the CH-containing addends released from the sample obtained from subjecting reduced SWCNT to DMSO.

(TGA-MS-FTIR), which provide quantification and some identification of functional groups anchored to SWCNT. The data are presented in figure 4 which shows a mass loss of more than 8 wt% following desorption in UHP Ar. The desorption occurs in two main steps: a first step at about 300 °C, yielding CO₂, water and CH-containing fragments, and a second step at about 450 °C, yielding CH₄, presumably originating from methyl addends. From the integrated absorbance of the ν_3 bands of CO₂ and CH₄ (figure 4) and taking into consideration the different extinction coefficients [8], the number of methyl groups is calculated to be the same as the number of addends yielding CO₂. The nature of the oxygen-containing addends cannot be established with certainty at this time but they may arise from residual THF molecules left in the samples after the centrifugation/washing cycles.

In the simplest case of an H-abstraction, the addend would be a tetrahydrofuryl radical and this would yield an

Figure 5. XPS in the region of C 1s (top) and in the region of S 2p (bottom) for the filtrand material following reaction of reduced SWCNT with DMSO and subsequent filtration through a 0.2 μ m PTFE membrane.

overall functionalization level of a little more than 2C%. This figure is totally consistent with the total increase in C-sp³ character of 7% found in the XPS spectrum (figure 5 (top)) following reaction. The XPS spectrum also shows the presence of various C–O bond types, further supporting the hypothesis of oxygen-containing addends. The starting purified SWCNT material shows the presence of C–O bonds (table 1) but the increase due to chemical functionalization of reduced SWCNT with DMSO is significant. The appearance of C–O bonds in the starting purified SWCNT is consistent with previous results by others (see, for instance, [9]) and is responsible to a large degree for the small D band in the Raman spectrum of purified SWCNT. The presence of S has also been confirmed by XPS but the signal is quite weak (figure 5 (bottom)). As no S-containing compound has been detected by either mass spectrometry or infrared absorption, one has to conclude that the majority of addends do not contain S.

Table 1. Contents and comparisons of all components identified by XPS between purified SWCNT and DMSO-reacted SWCNT.

	O content % in atoms	O content in area	N content % in atoms	Graphite sp ² -C % in atoms	Graphite sp ² in area	Diamond sp ³ % in atoms	Diamond sp ³ -C in area	Other sp ³ -C % in atoms	Other sp ³ -C in area	sp ² -C area/total area
SWCNT-DMSO	5.22	3949	0.1	52.2	13 488	13.65	3525	25.8	6666	13 488/247 56 = 0.54
Purified SWCNT	3.86	3234	0.32	59.17	16 923	11.28	3198	19.1	5473	16 923/27 706 = 0.61

Figure 6. (Left-hand side) Dry samples of filtrand (reacted reduced SWCNT with DMSO) re-dispersed in DMSO after 2 min of bath sonication and 12 days of settlement. (Right-hand side) Same treatment but with pristine SWCNT purified by a procedure developed in-house. The same amounts of filtrand and pristine SWCNT were used. Note the deposit in the bottle containing the pristine SWCNT and transparency of the solution compared to the bottle containing the re-dispersed filtrand.

(This figure is in colour only in the electronic version)

4. Conclusion

Here we have demonstrated the fact that care must be taken in choosing the proper solvent for reduced SWCNT, particularly in DMSO. Our observations do not diminish in any way the seminal finding by Pénicaud *et al.* Reduced SWCNT

increase the nucleophilic character of SWCNT in addition to provide easy exfoliation in solution, thus allowing for versatile chemistries to be carried out. But reduced SWCNT can also act as initiators of radical reactions with radical scavengers such as DMSO. Our evidence has proven that DMSO cannot be used as a solvent with reduced SWCNT without first quenching the negative character. The ability to disperse and re-disperse DMSO-reacted reduced SWCNT at values $> 1 \text{ g l}^{-1}$ of DMSO, as shown in figure 6, opens new opportunities in materials science that we will report in the near future.

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