The dissolution of carbon nanotubes in aniline, revisited†

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Thorough examination of a previous report on the high solubility of carbon nanotubes in refluxing aniline reveals that the reported optical properties of the "nanotube" solution are due to aniline decomposition products, rather than functionalized nanotubes. No appreciable dissolution of single-wall carbon nanotubes can be achieved by this method, although some solubilization of multiwall nanotubes has been confirmed by SEM and TEM analyses.

Introduction

Carbon nanotubes[1] have been the subject of intense recent interest, as effective new methods for the preparation of these remarkable fullerene-like tubular molecules have appeared.[2] A major limitation for the purification, processing and chemical functionalization of carbon nanotubes has been their extremely poor solubility in common organic solvents. Despite the similarity of nanotubes to fullerenes, nanotubes are not at all soluble in typical fullerene solvents.[3] Several methods for the dissolution of nanotubes have been reported and can be grouped into three basic strategies. (1) Chemical modification of nanotubes.[4] This method leads to nanotube derivatives that are soluble in organic solvents, but the process of cutting the tubes and attaching functionalized groups to the nanotube disturbs the pristine nature of its chemical structure and certainly changes its properties. (2) Dispersion of nanotubes in aqueous surfactants.[5] This method has been quite successful in providing workable solutions of nanotubes for different applications. (3) "Polymer-wrapping," typically with aromatic polymer chains that can solvate the nanotubes well enough to disrupt the very strong tube–tube attractive forces.[6,7]

It was reported that nanotubes interact strongly with amines.[8] Since fullerenes are particularly soluble in aromatic solvents, one could hypothesize that combining these functions in aniline might provide a solvent in which carbon nanotubes could be dispersed.

The NYU group reported recently[9] on the high dissolution of single-wall (and multi-wall) carbon nanotubes in aromatic amines, and also reported the observation of a strong fluorescence from aniline solutions of nanotubes between 530 and 700 nm.[10] Specifically, the dissolution of SWNTs in hot aniline was reported to give a red-brown SWNT solution (**1**) which exhibited distinctive UV–Vis absorption (Fig. 1) and emission spectra, properties which were ascribed to a reaction

between the convex double bonds of nanotubes and aniline, by analogy with the known fullerene–amine reaction.[11] While some of these observations are reproducible, as described below, careful re-examination in both of our labs reveals some serious discrepancies between the reported results and our conclusions. In particular, we report now (a) that even if SWNTs are soluble in aniline, they could not be detected by SEM or TEM, and (b) that the reported optical properties are not in fact due to nanotubes.

Experimental

Materials

Three types of carbon nanotubes were used. The first were laser oven grown single-wall carbon nanotubes (SWNTs) purchased from Rice University (tubes@rice nanotubes, produced by laser ablation) which were delivered (to NYU) suspended in toluene. SEM analysis did not show any visible nanoparticles in the sample. The second sample was multi-wall carbon nanotubes (MWNTs), which were purchased from Nanolab at Boston College. SEM analysis also showed no nanoparticles in this sample. Finally, HipCO single-wall nanotubes (high pressure decomposition of CO gas) used at UCLA were
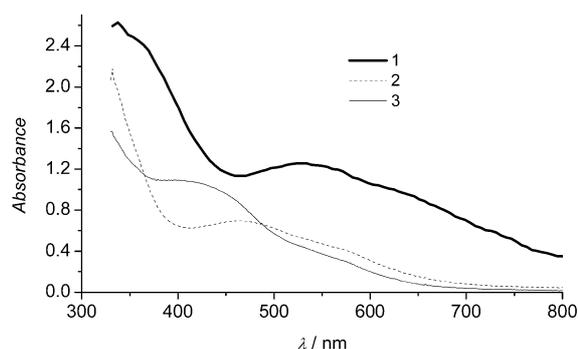

Fig. 1 UV–Vis absorption spectra of solutions **2** and **3** after reflux for 3 h (1 mm cell); a spectrum of **1**[9] is given for comparison.

obtained from Rice University. Transmission Electron Microscopy (TEM) images were obtained directly from MWNT aniline solution which was deposited on the copper grid after slow evaporation of the aniline.

Protocols for SWNT dissolution in aniline

(a) Studies done at NYU. In this work, SWNTs (10 mg) as obtained from Rice University (tubes@rice) in 10 mL toluene were filtered through a 0.22 μm PTFE membrane (Fischer Scientific # GVHP 04700) using a Millipore filter apparatus. It should be noted that sonication was avoided in the original published work and also in the new more careful experiments. The collected "buckypaper" was added to 10 mL of freshly distilled aniline. This nanotube/aniline mixture was heated at reflux overnight. The initially colorless aniline solution turned dark red after 12 h reflux. When the reaction mixture was protected with Ar (using gas-filled balloon setup), the color change was much slower. After being cooled to room temperature, the dark nanotube/aniline solution was filtered through a 0.22 μm PTFE membrane. SEM micrographs of these filter membranes show that the pores are actually polydisperse, ranging from over 1 μm to under 0.5 μm (see Supplementary Information). The dark red solution (solution **1**) passed through the filter, but the majority of the sample (presumed by the NYU group to be large and undissolved nanotubes; see below) was collected on the filter paper. The filtrate was evaporated by heating to 300 °C in air using a heating mantle and a black solid was obtained. The weight of the solid collected on the filter was 9.5 mg, while the filtrate residue weighed 15 mg. The elemental analysis of this filtrate residue supports the presence of a coating of aniline decomposition products on some carbon material, extracted from the nanotubes. Microanalysis results: SWNT starting sample (C, 75.08; H, 0.96; N, 0.03), undissolved buckypaper (C, 71.71; H, 1.60; N, 3.79), and filtrate residue (C, 78.39; H, 4.61; N, 11.49). An increase in the nitrogen content in the undissolved buckypaper accounts for $\sim$25% of the aniline in the filtrate residue, and, because the total weight was virtually unchanged, this should mean that $\sim$ ¼ of the SWNT sample (most probably metal impurities and carbon soot) was extracted into aniline solution. This is in agreement with the decreased nitrogen content of the filtrate residue [compared to the formula of polyaniline ($C_6H_{4.5}N$); C, 79.56; H, 4.95; N. 15.47].

For experiments with multi-wall carbon nanotubes (Nanolab), 10 mg MWNT powder was mixed with 10 mL freshly distilled aniline. The whole reaction system was protected by argon and was heated at reflux for 12 h. After reaction, the dark solution was centrifuged for 5 h at 4200 rpm using a Fisher IEC Centra-CL3 benchtop centrifuge. After centrifugation, the supernatant solution was decanted and the solid was weighed (7.2 mg). The very dark red solution was heated at 300 °C to remove the aniline. A shiny black powder (20 mg) was collected.

(b) SWNT dissolution studies done at UCLA. Even after ultrasound-assisted re-suspension in aniline, it was not possible to dissolve more than *ca.* 0.5 mg out of 10 mg of SWNTs (HipCO process, Rice University) in 1 mL of hot aniline, even after reflux for 12 h (it was previously claimed[9] that a 3 h reflux period was sufficient to achieve significant dissolution). Similar results were obtained using high-boiling aliphatic amines. It is possible that higher solubility may be achievable using this procedure for short, oxidized nanotubes.‡ The UV–Vis spectrum of this solution (**2**), shown in Fig. 1, is similar but
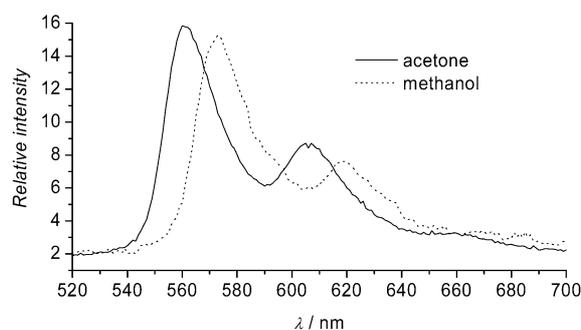

Fig. 2 Emission spectra of solution **3** (excitation at 500 nm).

not identical to that of solution **1**, obtained at NYU. The latter shows stronger absorption, particularly in the 500–600 nm range. Evaporation of solution **2** gave a red-brown tar that could be easily re-dissolved in a number of organic solvents, including acetone and dichloromethane (as reported for **1**[9]).

Results and discussion

Since the preparation of SWNTs involves initiation and propagation by transition metals,[2] and since the nanotubes were not separated from the aniline soup, some of us (at UCLA) suspected that the reported spectral properties of these solutions might be due to aniline decomposition products, rather than to nanotube adducts.[12] Thus, the transition metal catalyzed oxidative polymerization of aniline might lead to aniline-derived products that were the origin of the optical properties of those solutions.[13]

The following control experiment was performed to address the observed optical properties of the claimed "SWNT solutions" **1** and **2**. A freshly distilled sample of aniline was refluxed in the dark in air for 3–12 h, which gave rise to a red-brown solution (**3**), whose UV–Vis spectrum exhibited an absorption between 400 and 600 nm that was similar, but not identical, to that reported for solutions **1** and **2** (see Fig. 1). The relative intensity of the band at *ca.* 420 nm in the spectrum of solution **3** changed as a function of time, decreasing during the reaction concomitant with an increase in absorption between 500 and 600 nm. Similar spectral changes have been reported for the oxidative polymerization of aniline as a function of reaction time.[13] However, it is possible that the increased red-shift in the absorption of solution **1**, obtained from a refluxing suspension of a tubes@rice SWNT sample in aniline, might be partly due to extracted carbon materials (but not necessarily nanotubes). In fact, the higher content of amorphous carbon in nanotube samples produced by laser ablation (tubes@rice *vs.* HipCO material is documented by the manufacturer.

The photoluminescence spectra of solution **3**, shown in Fig. 2, are essentially identical to those previously reported for SWNT solutions in aniline (**1**).[9] Even the solvent dependence of the emission from **3**, namely the red shift of both emission bands in methanol *vs.* acetone, is the same as that reported for **1**. When aniline was heated at reflux in a strictly oxygen-free atmosphere, either in the presence or absence of SWNTs, no significant change in the color of the solutions was observed. This shows that the observed spectroscopic properties are due to oxidative decomposition (polymerization, *etc.*) of aniline itself, rather than to some material derived from nanotubes.§ Trace metal impurities in the nanotubes, however, may play a catalytic role.

As already noted, the color of the aniline solutions changed to dark red after 12 h reflux with either single-wall or multi-wall carbon nanotubes. Scanning Electron Microscopy (SEM) of

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‡ Certain batches of SWNTs can display unusual properties. Thus, a particular sample of HipCO (from Rice University), after oxidative purification in air (150 °C) showed significant solubility even in pure water, due to an abundance of defect sites (carboxylic acid groups).

§ Thermal decomposition of aniline results in the production of a whole diversity of oligomeric products, including phenazines, azobenzene, *etc.*
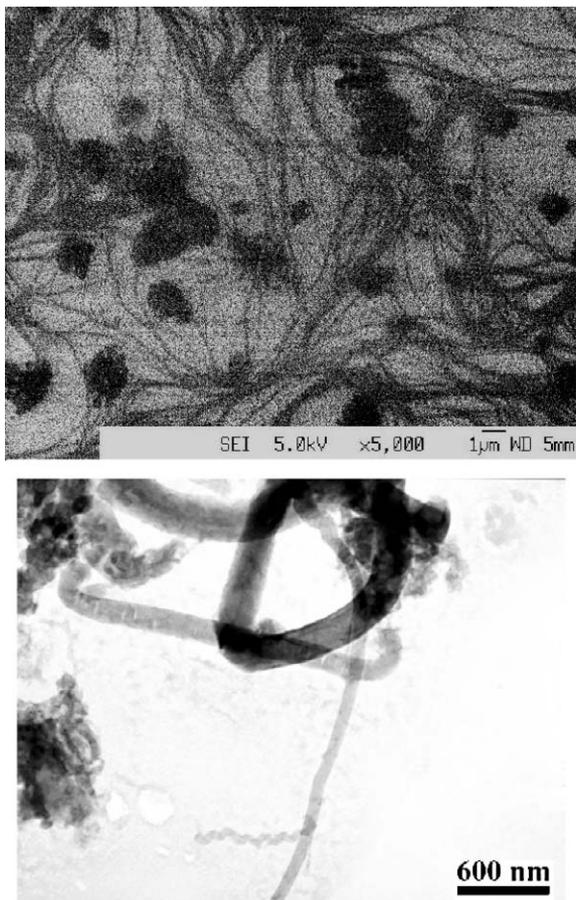
Fig. 3 The SEM (top) and TEM (bottom) images of the residue of evaporation of a solution of MWNTs in aniline.

the SWNT solution **1**, after evaporation of aniline from a sample plate, did not provide incontrovertible proof of nanotube dissolution.

In fact, it is not expected that SWNTs longer than ~ 200 nm could pass through the 0.22 μm PTFE membrane (see ESI†) used in the original protocol. In the case of MWNTs, where no membrane filtration was employed in the experiment, SEM images do suggest the presence of the nanotubes in the MWNT/ aniline solution, which is also confirmed by Transmission Electron Microscopy (TEM) analysis (Fig. 3), but micron size particles are also present. These particles may result from the reaction of aniline itself, catalyzed by trace metals in the nanotube sample. The TEM image in Fig. S3 taken after slow evaporation of the aniline reveals additional structural information.

The mechanism of the observed solubility of MWNTs in aniline is probably due to the formation of an anilinium carboxylate salt $(MWNT-CO_2^-)(^+NH_3Ph)$ from the aniline oligomers and the defect carboxylic acid groups of the MWNTs and/or non-covalent interactions with aniline oligomers. It is noteworthy that a similar mechanism of non-covalent donor–acceptor interaction has been recently proposed to explain the doping effect of carbon nanotubes in polyaniline composites.[14]

Taking into account that more elegant methods of polymer-assisted dissolution of SWNTs have already been developed using poly(*m*-phenylene-co-2,5-dioctyloxy-*p*-phenylenevinylene) (PmPV),[15] starch,[16] and other organic polymers,[17] the present method is not expected to be competitive as a solubilization procedure, but its modification could be of interest for the preparation of nanotube–polyaniline composites.[14b,18]

Conclusions

To conclude, experiments with SWNTs at UCLA using HipCO tubes and at NYU with laser ablation tubes show no

incontrovertible evidence of their presence in aniline solution. The observed partial decrease in mass of the nanotube precipitate with refluxing aniline can be attributed to extraction of impurities, which is more pronounced for laser ablation tubes than for HipCO material. However, the NYU group confirmed that it is possible to dissolve multi-wall carbon nanotubes in refluxing aniline, as evidenced by SEM and TEM analysis of material derived from aniline solutions, although the solubility is not as great as claimed in the earlier report.[9]

The new experiments have conclusively shown that the earlier report ascribing fluorescence of aniline–nanotube solutions to the dissolved nanotubes is incorrect. The observed emission is attributable to decomposition/oxidation products of aniline itself. This suggests that carbon nanotube components (tubes, metals and soot) catalyze the polymerization of aniline. The dark color of the aniline–nanotube solutions arises from the oxidation reactions of aniline induced by the nanotube material.

In contrast to a widespread preconception, the chemical behavior of the π-system of carbon nanotubes does not resemble that of fullerene.[11] The high reactivity of the latter is due to its non-aromatic electronic structure, whereas the fully aromatic structure of nanotube walls is more similar to that of graphite.

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