

END-GROUP AND DEFECT ANALYSIS OF SOLUBLE SINGLE WALLED CARBON NANOTUBES

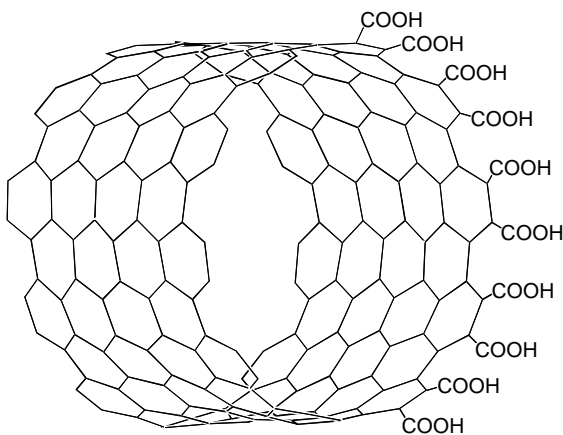
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Introduction

The scientific and technological potential of single walled carbon nanotubes (SWNTs) has attracted considerable attention to this field.(1-7) Previous studies have been carried out on solid, intractable forms of SWNTs. We have shown that chemical processing of short (100-300 nm in length(6)), SWNTs allows the preparation of stable organic solutions of these materials.(8,9) Related routes to soluble SWNTs have been reported,(10,11) together with approaches involving side-wall functionalization.(12-14)

susceptible to reaction with amines to give amides. If the latter reaction is carried out at elevated temperatures for 4 days with a long chain amine, some of the SWNT bundles exfoliate to give individual SWNT macromolecules, and small bundles that are soluble in organic solvents (s-SWNT).(8) Alternatively, direct reaction of the SWNT-COOH with a long chain amine also leads to THF-soluble SWNTs by formation of zwitterions.(9) Most of the conventional analytical tools of organic chemistry can be used in the characterization of the s-SWNT.(8,9,15,16)



Schematic End Section of (10,10) SWNT-COOH

Both the purification process and the shortening process terminate the open ends of the SWNTs with carboxylic acid groups.(6,8) This is illustrated schematically above for the (10,10) SWNT-COOH. The carboxylic acid groups can be converted into acylchloride groups by treatment with thionylchloride.(6,8) The acid chloride-functionalized SWNTs are then

Experimental

The single-walled carbon nanotubes (SWNTs), were prepared by a modification of the electric arc procedure(17). The purification, shortening and polishing of the SWNTs followed literature methods.(6,18) The shortened SWNTs were transformed to the acid chloride form (SWNT-COCl) by use of thionyl chloride(6,8-11), and then converted to s-SWNT-CONH(CH₂)₁₇CH₃ as described previously (Figure 1).(8,9)

Near- and Mid-IR are powerful analytical tool for the characterization of SWNTs (8,9,19), and most of the chemical functionalities are easily discernible in these spectra (Figures 2 and 3). The SWNT-CONH(CH₂)₁₇CH₃ showed peaks at 2918 cm⁻¹ and 2845 cm⁻¹ (ν(C-H) stretch modes of the alkyl chain); 1660 cm⁻¹ (ν(C=O)stretch of the amide); 1583 cm⁻¹ (ν(C=C) stretch of the SWNTs); 1471 cm⁻¹ (δ(C-H)bend of the alkyl chain).(Figure 3)

Results and Discussion

By using the octadecylamine (ODA) standards we were able to determine the weight of the

octadecylamido- groups in the different s-SWNT preparations. It is convenient to further simplify the problem by assuming that our SWNT sample is composed of (10,10) SWNTs,(1,8,9) in which the ends are cut vertically to the nanotube axis as shown in the schematic. With these simplifications there are 20 carboxylic acid groups at each end of the SWNT. Furthermore the unit cell of a (10,10) SWNT contains 40 carbon atoms and the translation repeat distance (a_0) of the unit cell along the 1D lattice is $\sqrt{3} a$, where a is the length of the carbon-carbon bond, and thus $a_0 = 2.46A^\circ$.(3) Thus a perfect 100nm long (10,10) SWNT-COOH would contain $40 \times (1000/2.46) \approx 16000$ carbon atoms (neglecting oxygen functionality), and 40 carboxylic acid groups (neglecting anhydrides). Thus the mole fraction of reactive (end-group) sites would be about 0.25% in a perfect 100nm long SWNT-COOH.

Conclusion

Solution phase mid-IR spectroscopy is shown to be a powerful tool for estimating the amount of functionality introduced into SWNTs.

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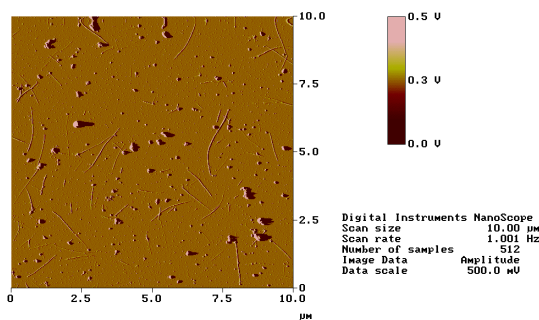


Figure 1. AFM amplitude scan of s-SWNTs-CONH(CH₂)₁₇CH₃ on mica substrate (Digital Instruments Nanoscope).

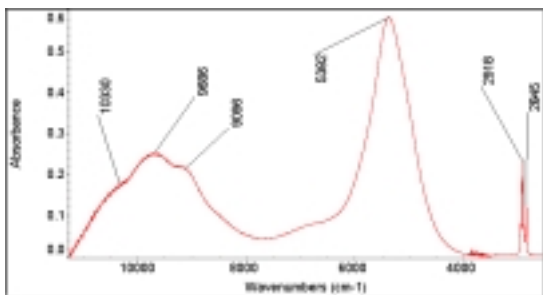
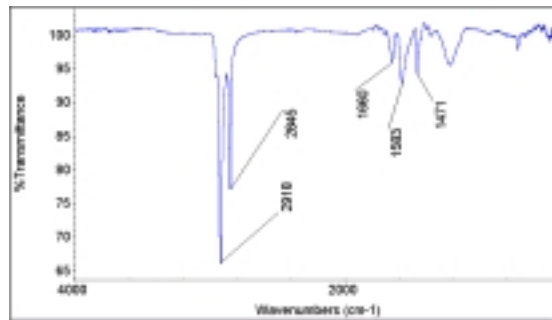


Figure 2. Near- and Mid-IR (ν(C-H) stretch region) spectrum of s-SWNTs-CONH(CH₂)₁₇CH₃ (quartz cell, light path 1 mm, baseline corrected, Nicolet Magna-IR 560 E. S.

P. spectrometer), at a concentration of 1 mg/mL



in CS₂.

Figure 3. Mid-IR spectrum of s-SWNTs-CONH(CH₂)₁₇CH₃ (thin film on quartz substrate, Nicolet Magna-IR 560 E.S.P. spectrometer).