Highly Water Soluble Carbon Nanotubes

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Abstract

Microwave radiation-assisted functionalization of single wall carbon nanoubes (SWNTs) to form highly soluble nanotubes has been demonstrated. After three minutes reaction, solubilities of more than 10 mg of nanotubes per milliliter of water and ethanol were obtained. The Raman spectrum of SWNTs obtained from its solution phase for the first time shows changes due to loss of quasi-one dimensionality of the backbone structure, whereas transmission electron microscopy indicates extensive debundling. Because of capillary effects, aligned SWNTs are obtained each time after evaporation of a drop of the solution on a hydrophobic substrate.

Key Words: Carbon nanotubes, solutions, nanotube functionalization.

Solubility of carbon nanotubes in water would allow chemical derivatization and manipulation to be easily carried out. Considerable efforts have therefore been made [1-7] to make carbon nanotubes soluble in water and in organic solvents, but to date only with limited success. Moreover, the solubilities achieved are mostly due to water-soluble macromolecules attached to the nanotubes[3-5]. Here we report an environmentally friendly, microwave-induced method to prepare highly water-soluble single-walled nanotubes (SWNTs) in about three minutes, using a closed vessel reactor. Solubilities of more than 10 mg of SWNTs per milliliter of water and ethanol are obtained, which is many orders of magnitude higher than what has been previously reported[1-6]. The solutions obtained are free of suspended nanotubes as determined by light scattering measurements, and for the first time the Raman spectrum of functional SWNTs was obtained from its solution phase. This relatively simple microwave technique to produce highly water-soluble nanotubes will enable processing of nanotubes in bulk quantities and hasten applications of this unique material [1,5].

Functionalized SWNTs obtained after microwave treatment have very high solubilities in de-ionized water and ethanol under ambient conditions, and significantly higher solubilities in acidic water. Photographs of aqueous solutions of different concentrations of functionalized SWNTs produced by this method are shown in Fig.1.

Laser light scattering particle size measurements of the aqueous solutions of microwave functionalized SWNTs were compared with measurements made on an aqueous suspension of pristine SWNTs. The suspension prepared by sonication of a mixture of 0.1 weight % and 0.5 weight % of the surfactant Triton-X showed particle sizes ranging from 100 nm to 600 nm with a peak at 300 nm at detection angles of 62.2 and 90 degrees.

Figure1. Photographs of SWNTs solution in DI water: (A) 0.05mg/ml, (B) 0.1 mg/ml, (C) 0.2 mg/ml, (D) 0.3 mg/ml, (E) 0.5 mg/ml and (F) 2mg/ml [11].

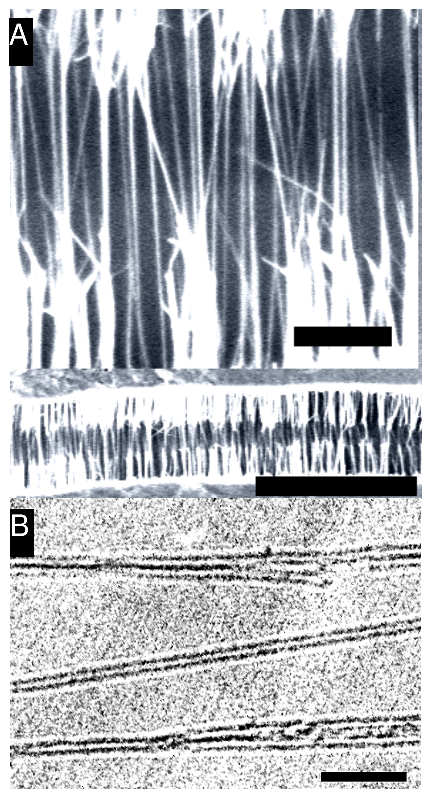

Figure 2. SEM and TEM images of functionalized SWNTs deposited from aqueous solution: (A) Bottom: Lower magnification SEM image showing alignment of the functionalized SWNTs, scale bar = 2 μm; Top: Higher magnification image of the aligned SWNTs, scale bar = 200 nm. (B) TEM image of debundled functionalized SWNTs, scale bar = 10 nm [11].

In contrast, the aqueous solution of microwave functionalized SWNTs did not show the existence of particles in the 3 to 800 nm size range, clearly indicating that the nanotubes are ideally dissolved.

SWNTs deposited from aqueous solution show scanning electron microscope (SEM) and transmission electron microscope (TEM) images displayed in Fig. 2A and 2B, respectively. The SEM images indicate clear alignment of the depositing nanotubes resulting from capillary forces during evaporation of the solvating water molecules. Alignment of the carbon nanotubes is seen each time after evaporation of a drop of the solution. The TEM image shows extensive debundling of the SWNT ropes, but no indication of structural modification of the sidewalls can be seen at this magnification level.

We believe that high water solubility is achieved by the extensive nitration and acidification of the SWNT sidewalls and tube ends. This is clearly indicated by the Fourier-Transform Infrared (FTIR) spectrum (Fig. 3). Strong lines due to the symmetric and antisymmetric stretching of the $-NO_2$ groups and the C=O stretching of the –COOH groups are seen at frequencies of 1355 cm^{-1}, 1637 cm^{-1} and 1719 cm^{-1}.

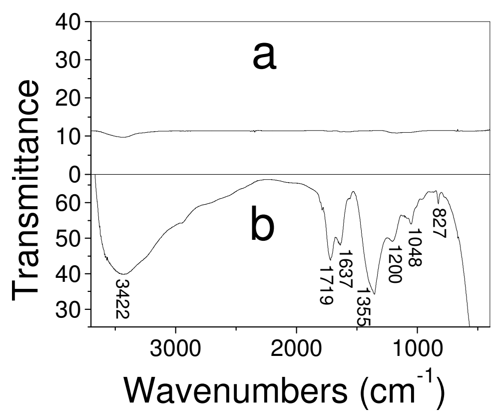

Figure 3. FTIR spectra of: (a) pristine SWNTs; (b) microwave functionalized SWNTs [11].

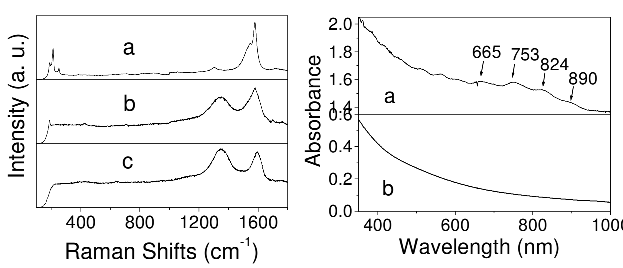

Figure 4. Raman and Vis-NIR spectra of: (left panel) Raman spectra of (a) pristine SWNTs, (b) functionalized SWNTs in solid phase, and (c) functionalized SWNTs in aqueous solution. (Right panel) Vis-NIR spectra of: (a) Pristine SWNTs suspended in dimethyformamide, (b) Aqueous solution of microwave reacted nanotubes [11].

Functionalization of the tubes is also indicated by the Raman spectrum taken in aqueous solution shown in the left panel of Fig. 4. The SWNT radial breathing modes are not observed, probably due to loss of structural one-dimensionality caused by extensive sidewall functionalization. The broad disorder-induced line around 1320 cm^{-1} is enhanced in intensity and broadens due to the appearance of the symmetric stretching mode of the $-NO_2$ groups. The C-C tangential mode frequency at 1597 cm^{-1} is upshifted by about 20 cm^{-1} relative to the frequency of this line in pristine SWNTs because of extensive charge transfer from the sidewalls to the $-NO_2$ groups. The functionalization with ionizable groups results in the solubility of these SWNTs in water and alcohols.

Visible-near infrared (Vis-NIR) absorption spectra (shown in the right panel of Fig. 4) of the solutions and a suspension of pristine SWNTs in dimethylformamide were measured. Inter-band transition absorptions associated with the van Hove singularities in quasi-one dimensional pristine SWNTs are clearly seen at 665, 753, 824 and 890 nm in spectrum of the pristine SWNTs. The corresponding spectrum of the microwave functionalized solution is featureless, indicating a loss of the quasi-one dimensional SWNT structure due to extensive functionalization of the sidewalls. The degree of nitration and carboxylation of the SWNT structure indicated by the infrared and Raman data was quantified by thermogravimetric analysis (TGA) measurements on pristine and microwave functionalized SWNTs performed under dry nitrogen at a heating rate of 10^oC per minute from 30^o to 500^oC. The TGA traces (see supporting materials) indicate that compared to pristine SWNTs, the functionalized SWNTs decrease about 50% in weight probably due to dissociation of the $-NO_2$ and –COOH groups from the nanotube backbone and tube ends, respectively. This would indicate that approximately every four carbons on the SWNT structure is functionalized by the microwave process. This might be an upper limit because of steric hindrance effects.

In addition to its high solubility we have also observed that the aqueous solutions of microwave functionalized SWNTs are electrically conducting, with conductivity in de-ionized water of 215.8 μS relative to that of 1.5 μS for de-ionized water. This raises the possibility for electrical manipulation (such as, electrodeposition) of the SWNTs from a solution phase.

Our results are of great significance for the chemical and physical manipulation of carbon nanotubes in nanotechnology. The very high water and alcohol solubility will enable SWNTs to be more easily processed in operations involving chemical reactions, physical blending, or thin film formation. Moreover, their alignment during deposition from solution will facilitate the creation of novel nanoelectronic device architectures. Microwave induced reactions as a means to achieve nanotube functionalization would also be extremely important from the stand-point of process development and scale-up.

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References:

(1) Mickelson, E. T.; Chiang, I. W.; Zimmerman, J. L.; Boul, P. J.; Lozano, J.; Liu, J.; Smalley, R. E.; Hauge, R. H.; Margrave, J. L. *J. Phys. Chem. B* **1999**, *103*, 4318.

(2) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.

(3) O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. *Chem. Phys. Lett.* **2001**, *342*, 265.

(4) Lin, Y.; Allard, L. F.; Sun, Y. -P. *J. Phys. Chem. B* **2004**, *108*, 3760.

(5) Qin, S.; Qin, D.; Ford, W. T.; Resasco, D. E.; Herrera, J. E. *Macromolecules* **2004**, *37*, 752.

(6) Wang, Y.; Iqbal, Z.; Malhotra, S. *Chem. Phys. Lett.* **2005**, *402*, 96.

(7) Wang, Y.; Iqbal, Z.; Mitra, S. *Carbon* **2005**, *43*, 1015.

(8) Lin-Vien, D.; Colthup, N. B.; Fateley, W.G.; Grasselli, J.G. *"The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules"*, Academic Press, New York (**1991**), Chap. 11.

(9) Bahr, J. L.; Yang, J.; Kosynkin, D. V.; Bronikowski, M. J.; Smalley, R. E.; Tour, J. M. *J. Am. Chem. Soc*. **2001**, *123*, 6536.

(10) Mitchell, C. A.; Bahr, J. L.; Arepalli. S.; Tour, J. M.; Krishnamoorti, R. *Macromolecules* **2002**, *35*, 8825.

(11) Yubing Wang, Zafar Iqbal and Somenath Mitra. *Journal of Am. Chem. Soc.* 43 1015-1020, (2006)