DNA Dissolves Single-walled Carbon Nanotubes in Water

Naotoshi Nakashima,[†]* Shingo Okuzono,[†] Hiroto Murakami,[††] Tonau Nakai,[†††] and Kenichi Yoshikawa[†††]
[†]*Department of Materials Science, Graduate School of Science & Technology, Nagasaki University, Bunkyo, Nagasaki 852-8521*
[††]*Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812-8581*
[†††]*Department of Physics, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto, 606-8502*

(Received February 5, 2003; CL-030107)

Transmission electron microscopy, atomic force microscopy, and UV-vis-NIR absorption spectroscopy have revealed that deoxyribonucleic acid (DNA) molecules dissolve single-walled carbon nanotubes in an aqueous solution.

Although carbon nanotubes have been in the forefront of nanoscience and nanotechnology because of their many unique properties,[1] chemical and biochemical approaches using this material have been very limited. Noncovalent sidewall-functionalized soluble carbon nanotubes are of interest,[2] because the study would lead to the chemical and biochemical design to create functional carbon nanotubes in solution systems.

The combination of carbon nanotubes and deoxyribonucleic acid (DNA) has been of interest to many chemical and biochemical areas in both fundamental and application.[3] Very recently, Dwyer et al.[4] and Baker et al.[5] reported the synthesis of covalently bonded adducts of single-walled carbon nanotubes with DNA and oligonucleotide, respectively. Although carbon nanotubes have been solubilized in organic solvents and in water by i) chemical modification,[6] ii) the adsorption of detergents[7] or a π-aromatic compound,[2a] and iii) polymer wrapping,[8] to our knowledge, no report has been published thus far describing the preparation of a carbon nanotube-DNA aqueous solution. Here we describe the first finding that DNA molecules dissolve single-walled carbon nanotubes (SWNTs) in aqueous solutions.

SWNTs (HiPco™, the length and diameter of pristine SWNTs are ca. 1-10 μm and ca. 0.8-1.2 nm, respectively) obtained from Carbon Nanotechnologies Incorporated were purified as described elsewhere.[2a] DNA (sodium salt from salmon testes, 6.8 mg, Sigma, helix type: B in water) was sonicated with a probe-type ultrasonifier (SMT, UH-300) in water (10 mL) for 15 min to obtain aqueous solution of DNA.[9] Temperature was maintained below 8 °C with an ice-bath. About 0.4 mg of purified SWNTs (p-SWNTs) was placed in the DNA aqueous solution (5 mL) and then sonicated with a bath-type ultrasonifier (Branson 2210) at temperatures below 10 °C for 1 h. Centrifugation (800 g) of the suspension for 1 h was found to give a black-colored transparent supernatant aqueous dispersion/solution, which was collected and used for the following measurements. No such black-colored solution was obtained in water containing 2 mol dm^{-3} NaCl.

Figure 1 shows a photo of p-SWNTs in water in the absence of DNA (left) and a solution/dispersion of p-SWNTs in water in the presence of DNA (right). Without DNA, p-SWNTs were insoluble in water. It is evident that optically transparent black-colored dispersion/solution of p-SWNTs was obtained when

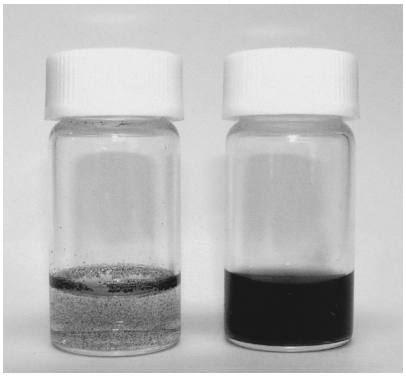

Figure 1. A photo of p-SWNTs in water in the absence of DNA (left) and solution/dispersion of p-SWNTs in water in the presence of DNA (right).

DNA was used as a solubilizer. No precipitation was produced for the p-SWNTs-DNA solution/dispersion even after two months upon storage at 5 °C.

Transmission electron microscope (TEM) measurements for the aqueous solution/dispersion of p-SWNTs-DNA were conducted on a Jeol JEM-100S electron microscope. A carbon-coated TEM grid (Ouken-Shoji, 200-A mesh) was immersed in the solution for ca. 1–2 s, and then air-dried. Figure 2 shows a typical TEM image, in which dispersed bundled SWNTs with molecular length of ca. 0.5-2 μm are clearly observed. It is in fact that p-SWNTs are solubilized/dispersed in the DNA aqueous solution.

Atomic force microscope (AFM) was used to reveal the structure of p-SWNTs in the DNA solution. A sample for AFM measurements was prepared by dipping a freshly cleaved

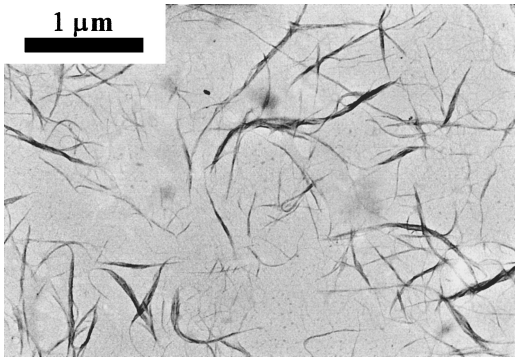

Figure 2. A typical TEM image of an aqueous solution/dispersion of p-SWNT-DNA.

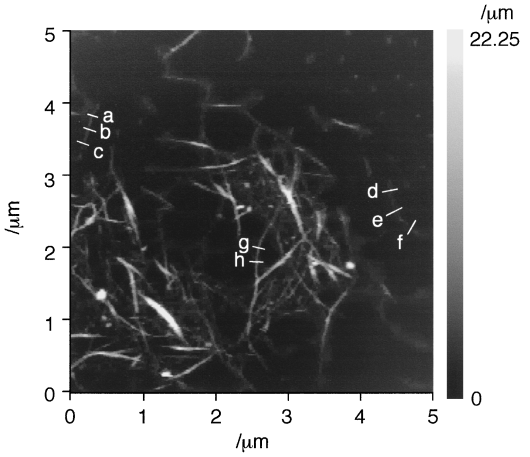

Figure 3. A typical AFM image of an aqueous solution/dispersion of p-SWNT-DNA.

mica substrate into the DNA-SWNT aqueous solution and of solution of DNA solely for a few seconds and then air-dried. A typical AFM image for a p-SWNTs-DNA solution recorded on a SPI3800N (Seiko Instruments Inc.) with a Si_3N_4 cantilever (SN-AF01) is presented in Figure 3. The height of the nanotubes indicated by lines a–f was 2.75, 2.35, 2.72, 2.24, 2.12 and 1.96 nm, respectively. An AFM image for the solely DNA solution could not be detected under the condition.[10] The height of the plasmid DNA image on a mica surface has been reported to be 1.32 ± 0.35 nm.[11] All together, it has become clear that the nanotubes are individually dissolved with the aid of DNA in water. Nanotube bundles that are formed from aggregation of several nanotubes were also seen in the AFM image as indicated by lines g (height, 4.68 nm) and h (height, 5.03 nm).

The UV maximum for the nucleic base of the p-SWNT-DNA aqueous solution appeared at 260 nm, which is identical with that of aqueous solution of the used DNA. The characteristic absorption derived from the nanotubes dissolved in water is seen around a 500–1000 nm region in the vis-NIR spectrum

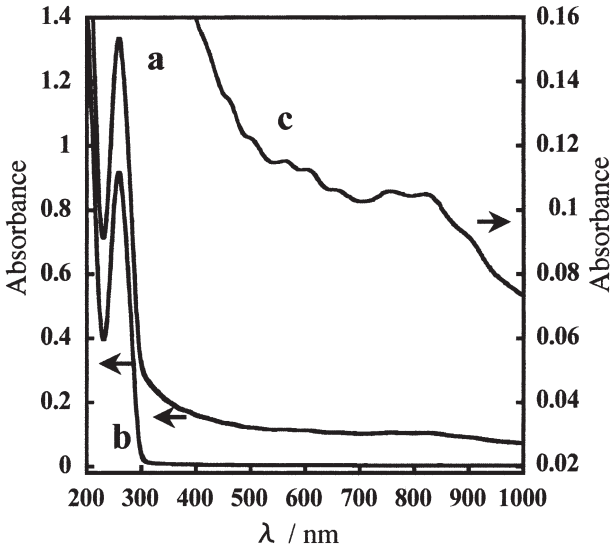

Figure 4. UV-vis-NIR absorption spectra of aqueous solutions of p-SWNT-DNA (a and c) and DNA (b). Optical cell length, 1 mm.

(Figure 4), which is almost identical with that of the reported HiPco SWNTs[12]. This also supports the dissolution of the DNA. Peak maxima of the circular dichroism (CD) of an aqueous solution of p-SWNT-DNA appeared at 266 nm (positive band) and 246 nm (negative band) which were identical with those of the used DNA solely in water.[13]

Although the detailed mechanism for the dissolution of the nanotubes in a DNA aqueous solution and the fine structure of the obtained p-SWNT-DNA in water are not clear at present, possible π-π interaction between the sidewall of the nanotubes and the nucleic acid bases of DNA with partial deformation structure generated by sonication might be suggested as an important factor for the dissolution of nanotubes. The weak interaction of the major (and/or minor) grooves of the DNA and the nanotubes might contribute to the dissolution.

In conclusion, we have revealed that SWNTs are dissolved in a DNA aqueous solution. The carbon nanotube aqueous solution prepared by the present method would be useful for chemical, biochemical and biological designs to create functional carbon nanotubes in aqueous systems. Further studies along this line are currently underway in our laboratories.

References and Notes

1 "Carbon Nanotubes: Synthesis, Structure, Properties and Applications," ed. by P. Avouris, G. Dresselhaus, and M. S. Dresselhaus, Spriger-Verlag, Verlin (2000).
2 a) N. Nakashima, Y. Tomonari, and H. Murakami, *Chem. Lett.*, **2002**, 638. b) J. Chen, H. Liu, W. A. Weimer, M. D. Halls, D. H. Waldeck, and G. C. Walker, *J. Am. Chem. Soc.*, **124**, 9034 (2002). c) A. Star, J. F. Stoddart, D. Steuerman, M. Diehl, A. Boukai, E. W. Wong, X. Yang, S.-W. Chung, H. Choi, and J. R. Heath, *Angew. Chem., Int. Ed.*, **40**, 1721 (2001).
3 a) S. C. Tsang, Z. Guo, Y. Chen, M. L. H. Green, H. A. O. Hill, T. W. Hambley, and P. J. Sadler, *Angew. Chem., Int. Ed. Engl.*, **36**, 2198 (1997). b) Z. Guo, P. J. Sadler, and S. C. Tsang, *Adv. Mater.*, **10**, 701 (1998).
4 C. Dwyer, M. Guthold, M. Falvo, S. Washburn, R. Superfine, and D. Erie, *Nanotechnology*, **13**, 601 (2002).
5 S. E. Baker, W. Cai, T. L. Lasseter, K. P. Weidkamp, and R. J. Hamers, *Nano Lett.*, **2**, 1413 (2002).
6 a) J. Chen, M. A. Hamon, H. Hu, Y. Chen, A. M. Rao, P. C. Eklund, and R. C. Hadoon, *Science*, **282**, 95 (1998). b) J. Chen, A. M. Rao, S. Lyuksyutov, M. E. Itkis, M. A. Hamon, H. Hu, R. W. Cohn, P. C. Eklund, D. T. Colbert, R. E. Smalley, and R. C. Haddon, *J. Phys. Chem. B*, **105**, 2525 (2001).
7 a) V. Krstic, G. S. Duesberg, J. Muster, M. Burghard, and S. Roth, *Chem. Mater.*, **10**, 2338 (1998). b) N. Nakashima, H. Kobae, T. Sagara, and H. Murakami, *ChemPhysChem*, **3**, 456 (2002).
8 a) M. J. O'Connel, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, and R. E. Smalley, *Chem. Phys. Lett.*, **342**, 265 (2001). b) A. Star, D. W. Steuerman, J. R. Heath, and J. F. Stoddart, *Angew. Chem., Int. Ed.*, **41**, 2508 (2002).
9 The MW of DNA evaluated by polyacrylamide gel electrophoresis was 300-600 bp.
10 AFM images of DNA are usually measured in water containing magnesium ion.
11 C. Bustamante, J. Vesenka, C. L. Tang, W. Rees, M. Guthold, and R. Keller, *Biochemistry*, **31**, 22 (1992).
12 I. W. Chiang, B. E. Brinson, A. Y. Huang, P. A. Willis, M. J. Bronikowski, J. L. Margrave, R. E. Smalley, and R. H. Hauge, *J. Phys. Chem. B*, **105**, 8297 (2001).
13 A. J. Adler and G. D. Fasman, in "Methods in Enzymology," ed. by L. Grossman and K. Moldave, Academic Press, New York (1967), Vol. 12B, p 268.

Published on the web (Advance View) April 23, 2003; DOI 10.1246/cl.2003.456