Cyclodextrin-Mediated Soft Cutting of Single-Walled Carbon Nanotubes

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Shortened single-walled carbon nanotubes (SWNTs, <1 μm) are expected to have rich chemistry,[1−5] and they are promising one-dimensional building blocks for constructing advanced nanoscale structures. Liu et al. developed a chemical method[1] to cut the SWNTs (diameter 1.1−1.3 nm) produced by pulsed laser vaporization.[6] The same technique has also been adapted to prepare shortened SWNTs from electric arc-produced[7] SWNT material (diameter 1.3−1.5 nm).[2,8−10] The resulting shortened SWNTs can be further sorted by length,[1] chemically functionalized,[1,2] solubilized[2,8] and chromatographically purified.[9] Stepanek et al. very recently reported a new mechanical cutting process for SWNTs involving hard diamond particles as abrasive material.[11] The disadvantage of this process is that it would be difficult to separate shortened SWNTs from small diamond particles.

Smalley et al. recently discovered a gas-phase catalytic process called HiPco which is capable of producing high purity of SWNTs in large scale.[12] This unique type of SWNTs (diameter 0.7−0.8 nm) is attractive material for studying nanotube chemistry because of expected[13,14] higher chemical reactivity. For the same reason, we found that the cutting technique of Liu et al. might not apply to such small-diameter nanotubes. For example, after 12 h sonication of 10 mg SWNTs (HiPco) in 12 mL of a 3:1 mixture of concentrated H_2SO_4/HNO_3, we noticed by transmission electron microscopy (TEM) that most of nanotubes have been severely damaged. While investigating the chemical processing of SWNTs (HiPco), we found unexpectedly that SWNTs (HiPco) can be efficiently cut simply by grinding in soft organic materials such as γ- and β-cyclodextrins. We report here the preliminary results of this "soft" cutting technique.

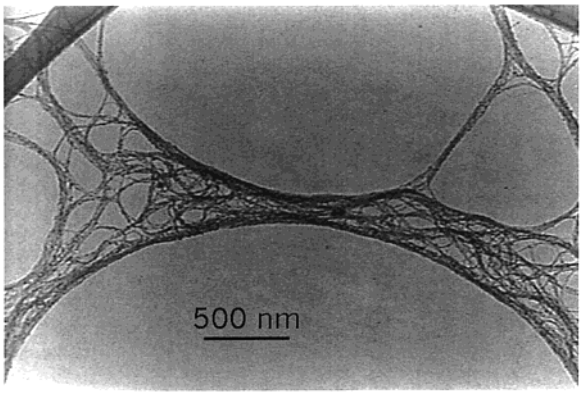

Figure 1. TEM image of as-prepared SWNTs (HiPco).

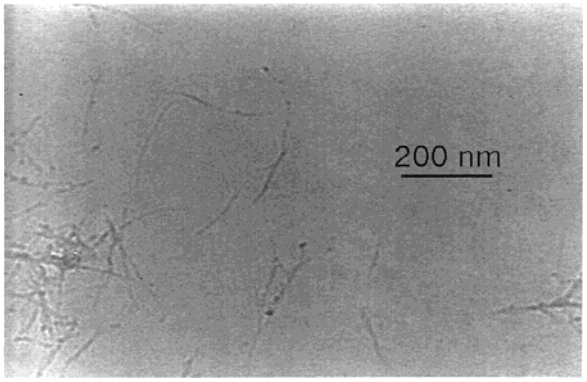

Figure 2. TEM image of shortened SWNTs (HiPco).

The SWNTs (HiPco) (Carbon Nanotechnologies, Inc.) consist mostly of long (>4 μm) and thick (20−100 nm) nanotube ropes, mixed with a small amount of residual iron catalyst particles (Figure 1). The typical cutting procedure was as follows: 5.4 mg of SWNTs (HiPco) and 162 mg of γ-cyclodextrin[15] was ground in 1 mL of ethanol for 10 min by using an agate mortar and pestle. The resulting sticky, grayish mixture was further ground for 1 h (without addition of ethanol) to give an homogeneous, fine, black powder. The black powder was then ground for another 1.5 h and then heated at 75 °C for 24 h.

In contrast to the starting SWNT material, nearly all of the product ($>95\%$) can be easily dispersed in deionized water by 10 min of sonication to form a quite "stable"[16] colloidal suspension (0.2 mg of SWNTs−γ-cyclodextrin/mL) for at least 12 h. The TEM (Figure 2)[17] shows that about 90% of the nanotubes have lengths less than 1 μm, and ~70% of which are thin ropes (5−10 nm) have lengths between 100 and 600 nm. The γ-cyclodextrin can be readily removed by membrane filtration (0.2 μm pore size), followed by thorough washing with deionized water. The resulting black solid, like fullerenes, is much more

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(16) Unlike soluble SWNT organic solutions[2, 8] and surfactant-stabilized aqueous SWNT suspensions, which are stable in both glass- and plastic-containers, the SWNTs−γ-cyclodextrin solid mixture can ONLY form stable aqueous suspension in a plastic container by sonication. We found that siliconized, low-retention polypropylene microcentrifuge tubes (Fisher cat. no. 02-681-321) give the best dispersion results. The microcentrifuge tubes and polyethylene transfer pipets (VWR cat. no. 14670-331) were used for the handling of final SWNT products in all of our experiments.

(17) One drop of the freshly prepared aqueous suspension (0.1−0.2 mg SWNTs−γ-cyclodextrin/ml, 10 min sonication) was placed on a Holey Carbon 400 mesh Ni TEM grid (SPI Supplies, Formvar coating was removed) in contact with a Kimwipes wiper. The water solvent was quickly soaked away by the wiper, preventing the aggregation of nanotubes. The TEM (JEM 2000FM) was operated at 80 kV to minimize the electron beam damage on this unique type of small-diameter SWNTs.

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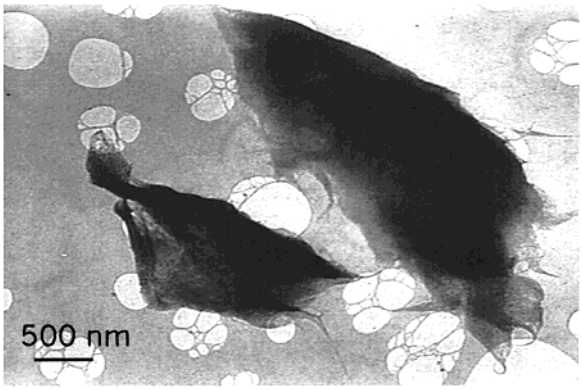

Figure 3. TEM image of high-density SWNTs particles.

difficult to disperse in water, and surfactant (sodium dodecyl sulfate, SDS) is needed to get a stable aqueous suspension by sonication.

To further understand these nanotube-cutting results, we did a series of comparison experiments under similar conditions (all based on SWNTs (HiPco)). We found the following: (1) Grinding SWNTs in β-cyclodextrin gives results similar to those for γ-cyclodextrin. (2) Grinding SWNTs in octadecylamine (ODA, the molecule used to solubilize SWNTs in organic solvents by covalent and ionic fuctionalizations[2,8]) gives an inhomogeneous, grayish mixture of white (ODA) and black (SWNTs) fine particles, indicating that the SWNTs solid cannot be well-dispersed in ODA. The product is difficult to disperse in chloroform and tetrahydrofuran and cannot form a stable suspension by 10 min of sonication. TEM showed that the product consists mainly of full-length SWNTs. (3) Grinding of SWNTs in SDS (the molecule which was used to disperse SWNTs in water) gives results similar to those for ODA. (4) Grinding SWNTs without any chemicals gives black particles with much higher density (Figure 3), which are extremely difficult to disperse in either water or organic solvents.

These observations demonstrate that cyclodextrins have surprisingly superior nanotube-dispersing capability. We believe that the excellent dispersion of SWNT ropes in organic matrix is the key to the success of our nanotube-cutting experiments; otherwise, flexible nanotube ropes[18] would tend to be entangled and compressed together during the grinding to form high-density particles. Once the nanotube material can be well dispersed, and the thick nanotube ropes are partially exfoliated into thin nanotube ropes, the normal grinding force would be strong enough to induce local conformational strains on nanotubes,[19] which eventually lead to the cutting of nanotube ropes, most probably at their defective sites.

We found that, without grinding, the aqueous dispersion of SWNTs can also be obtained by sonication with γ-cyclodextrin in deionized water, which gave essentially full-length SWNTs (>90%, see Supporting Information). This is in agreement with previous observations that excellent dispersion in solvents still gives SWNTs with lengths greater than 1 μm.[20,21] It might be possible to increase the percentage of shortened SWNTs by significantly extending the sonication time to facilitate the cutting of SWNT ropes.

It's unlikely that individual nanotubes or nanotube ropes can form the rotaxane structures with γ-cyclodextrin (inner cavity diameter $\sim$0.75$-$0.83 nm[15]). The cyclodextrins are therefore believed to be adsorbed at the surface of nanotube ropes by van der Waals force. It's still unclear at present why cyclodextrins act as excellent nanotube dispersing reagents.

In summary, we discovered that SWNTs (HiPco) can be efficiently cut simply by grinding in cyclodextrins. The solid-state process successfully avoids not only sonication in strong acids and oxidants which can severely damage the small-diameter nanotubes, but also the long time sonication in any solvent which could make scaling-up difficult. The extension of our soft cutting technique by using ball milling with appropriate grinding energy might lead to the large-scale production of shortened SWNTs in high yield.

Supporting Information Available: Figures showing the high-resolution TEM images of as-prepared SWNTs and shortened SWNTs, as well as TEM images from control experiment (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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