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Purification of HiPCO Carbon Nanotubes via Organic Functionalization

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The use of carbon nanotubes in molecular electronics is a hot topic under very intense investigation.[1] In this context, the purification of single-walled carbon nanotubes (SWNTs) is a matter of great importance. Although several successful approaches have been devised to produce SWNTs, including arc-discharge,[2] HiPCO process,[3] or pulsed laser vaporization (PLV),[4] all lead to materials that contain either amorphous carbon or metal nanoparticles as major impurities. The key steps in the purification processes available today rely on oxidation with strong acids,[5] filtration,[6] or chromatography.[7] However, the oxidative treatment of SWNTs results in shortened tubes and also increases the number of structural defects. Recently, reliable methods to purify SWNT by selectively oxidizing metal catalyst particles have been reported.[8] Here, we propose a new method for the purification of HiPCO SWNT,[3] which consists of the following sequence: (a) organic functionalization of the as-produced nanotubes (pristine tubes, **p-SWNT**), (b) purification of the soluble functionalized nanotubes (**f-SWNT**), (c) removal of the functional groups and recovery of purified nanotubes (**r-SWNT**) by thermal treatment at 350 °C, followed by annealing to 900 °C. Each of these steps contributes to the purification, but only their sequential combination leads to high-purity materials. While the purity of the so-treated SWNT may not reach the high levels of recent purification methods,[8] our procedure has the advantage of not using oxidants. In addition, organic functionalization makes the SWNT more easy to handle, which results in a better manipulation for potential practical uses (vide infra).

We have recently reported the organic functionalization of SWNTs, based on the 1,3 dipolar cycloaddition of azomethine ylides in DMF suspension.[9] This modification results in a strongly improved solubilization of the **f-SWNT** while leaving the metal particles insoluble.

As unmistakably shown by transmission electron microscopy (TEM) images, **p-SWNT** contain a remarkable amount of metallic nanoparticles (Figure 1a. See also Figure S1, Supporting Information [SI]). Besides, amorphous carbon is visible from a more distant view in the TEM micrographs (Figure S2). Figure S3 shows that **f-SWNTs** are free of metal particles, although carbon impurities are still present in the product, since these are also soluble in DMF.

To further purify **f-SWNTs**, basically removing the amorphous carbon particles, a slow precipitation process was employed, occurring when diethyl ether was added to a chloroform solution of **f-SWNT** (85 mg in 300 mL). The solid material was discarded, whereas the soluble material was recovered and resubmitted to the same procedure. After this process was repeated three times (see SI for experimental details), the remaining **f-SWNT** material (50 mg) was checked by TEM (See Figure S4).

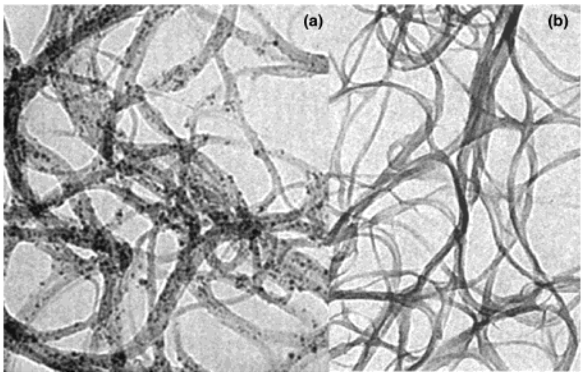

Figure 1. Representative TEM images of (a) **p-SWNT**, (b) **r-SWNT**.

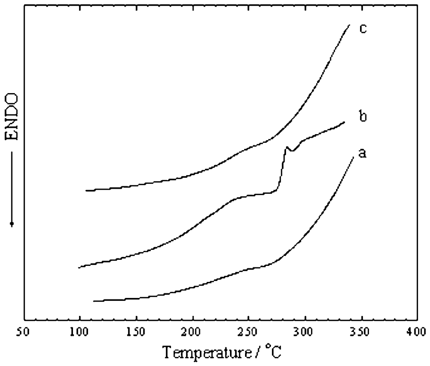

Figure 2. DSC curves of (a) the starting **p-SWNT**, (b) the purified **f-SWNT**, (c) the **r-SWNT** after the thermal treatment. ENDO means an endothermic direction.

The pristine nanotubes gave a smooth exothermic curve starting at 200 °C (Figure 2a), which can be tentatively attributed to an increased mobility of the nanotubes with increasing temperature. No weight loss was observed up to 400 °C. The DSC curve of **f-SWNT** (Figure 2b) shows an exothermic peak at 280 °C. This peak is most probably related to the removal of the attached organic groups, since a simultaneous 25−30% weight loss of the sample was observed (see SI for experimental details).

This weight loss is in excellent agreement with our previous estimate of the number of organic groups present in the functionalized nanotubes.[9]

The resulting black solid after DSC treatment (**r-SWNT)** was insoluble in organic solvents. TEM analysis showed that nanotubes were recovered, free of any impurities (Figure 1b). The heated

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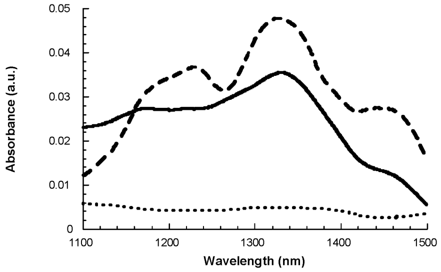

Figure 3. NIR spectra of **p-SWNT** (dashed line), **f-SWNT** (dotted line), **r-SWNT** (solid line).

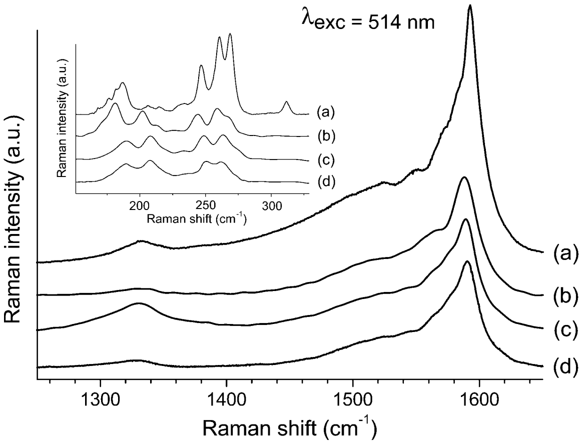

Figure 4. Raman spectra of (a) **p-SWNT**, (b) heated **p-SWNT**, (c) **r-SWNT**, and (d) **r-SWNT** annealed at 900 °C for 12 h in a vacuum.

purified tubes were again analyzed by DSC. The relative curve, reported in Figure 2c, is nearly identical to that of the **p-SWNT**.

The NIR absorption spectra of **p-SWNT**, **f-SWNT**, and **r-SWNT** are shown in Figure 3. The peaks of the **p-SWNT** in this region (Figure 3a) are attributed to the band gap transitions in semiconducting nanotubes.[10]

The spectrum of **f-SWNT** shows a dramatic loss of these bands, revealing that a high functionalization degree improves remarkably the solubility but alters effectively the electronic properties of the SWNTs.[9,10] However, the NIR spectrum of **r-SWNT** clearly proves that the nanotubes, after the removal of the organic groups, have recovered the electronic properties of **p-SWNT**. Some bands are less intense due to the disappearance of the smaller-diameter SWNT upon heating (see below).

The resonant Raman spectra of nanotubes before (curves a and b) and after (curves c and d) the full purification sequence are displayed in Figure 4. All three characteristic spectral regions of SWNT are essentially retained during the process: the radial breathing mode (150−350 cm^{-1}, inset), the D-line (1330 cm^{-1}), and the G-line (1595 cm^{-1}).[11] The disappearance of the peaks corresponding to very thin tubes (Figure 4, inset) is a consequence of the heating, as thin tubes are known to be unstable versus high temperatures.[12] The D-line was shown recently to originate from carbon defects in the nanotube walls.[13] Therefore, the relative intensity of the D-line is proportional to the number of such defects. This is the reason the D-line is more pronounced for the **r-SWNT** (curve c) than for the heated **p-SWNT** (curve b). As defects in the nanotube walls can be effectively healed by high-temperature annealing in a vacuum, the D-line of **r-SWNT** heated to 900 °C for 12 h is smaller again (curve d) and becomes similar to that of the **p-SWNT**.

The iron content in **p-SWNT** and in **f-SWNT** was measured by atomic absorption analysis (see SI for details). While **p-SWNT** contain 26% Fe (w/w), in agreement with what stated by CNI company, the **f-SWNT** contain only 0.4% (w/w).

In conclusion, the organic functionalization contributes remarkably to the purification of the SWNTs, while at the same time, it provides a much easier manipulation of the nanotubes. As a matter of fact, the modified nanotubes should be easy to deposit onto a substrate to create a pattern. Subsequently, the organic groups can be removed by simple heating, leaving the nanotubes intact and patterned. The missing electronic properties in the functionalized tubes are recovered after thermal treatment.

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Supporting Information Available: Experimental details and supplementary figures (PDF). This material is available free of charge via the Internet at http://pubs.asc.org.

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