Nanodispersion of Single-Walled Carbon Nanotubes Using Dichloroethane

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In this paper we present a simple approach of nanodispersing single-walled carbon nanotubes (SWCNTs) in a non-polar 1,2-dichloroethane (DCE) solvent. After filtration with isopropanol and acetone, the purified SWCNTs were immersed in DCE, followed by sonication for about 15 hours. The samples were further centrifuged at 17,000 revolutions per minute for about 3 hours. Atomic force microscopy (AFM) demonstrated that the spin-coated nanotubes were mostly individual nanotubes with an average diameter of 1.6 nm and a length of about 250 nm. We also found that the presence of water, and the dry process during DCE treatment, prevented nanotubes from being nanodispersed.

Keywords: Single-Walled Carbon Nanotube, Nanodispersion, Dichloroethane, AFM.

1. INTRODUCTION

Carbon nanotubes exhibit peculiar one-dimensional properties and diverse applications. Single-walled carbon nanotubes (SWCNTs) are easily bundled by van der Waals interactions during synthesis and purification processes.1–3 The bundling often obscures the superb characteristics of carbon nanotubes, and has been a bottleneck from scientific and technological points of view. For instance, nanodispersion (dispersion into individual nanotubes) is necessary for the fabrication of individual nanotube transistors.4–6 Nanodispersion also provides excellent information about electronic structures from optical absorption and fluorescence spectra.7–9 A percolation limit can be easily achieved in many nanocomposites by nanodispersing small quantities of nanotubes in the host matrix.10

Although nanotubes in the bundle interact via weak van der Waals forces, lengths of nanotubes are typically an order of ten micrometers, resulting in strong interaction energy of an order of 1000 eV.11 This is barely breakable with physical approaches. Surfactants in water with sonication treatment have been used to break the bundle by wrapping up the individual nanotubes.9,12 13

Although this method can achieve nanodispersion to some extent, surfactants are usually left in the sample, therefore this procedure requires an extra step to remove the remaining surfactants. Polymers with functional groups, DNA, and liquid crystals have been introduced to disperse carbon nanotubes with a similar spirit.11 12 13 Sonication in strong acid has also been introduced.16 In this case, the length of carbon nanotubes can be shortened by an attack of nanotube sidewalls. The solubility of nanotubes is greatly enhanced in organic solvents such as N-methyl-2-pyrrolidone (NMP) or N,N-dimethylformamide (DMF) by attaching the functional groups at the defective sidewalls or at the ends of nanotubes.17–20 The reaction in such organic solvents, however, provoked strong chemical disruption of the π-bonding of nanotubes, significantly modifying the electronic structures of the nanotubes. High temperature annealing is required to recover the electronic structures, making it difficult for transistor applications. The solubility of nanotubes in water can also be enhanced by fluoride chemisorption on the sidewalls of nanotubes.21 All these approaches leave some dispersants in the sample, or perturb the electronic properties of the nanotubes in many cases. Therefore, it is necessary to search for a new approach of nanodispersion without remnants in the
sample, and without altering the electronic structures of the nanotubes.

In this report, we introduced dichloroethane (DCE) to achieve nanodispersion of SWCNTs. The hydrophobic nanotubes were well nanodispersed in non-polar DCE solvent. This is explained by the “like dissolves like” principle. We demonstrated the degree of nanodispersion by atomic force microscope (AFM).

2. EXPERIMENTAL DETAILS

The raw HiPCO SWCNTs were purchased from CNI (Carbon Nanotechnologies Inc.) Figure 1 shows the schematic diagram of the sample preparation procedure. The raw sample containing 22.3 wt% of iron catalysts was first annealed at 350 °C in air for one hour to remove the carbonaceous particles. The heat-treated sample was further stirred in a 35% HCl solution at room temperature to remove catalytic metals, similar to the previous work, and rinsed with deionized (DI) water by filtration. The remaining metal content, analyzed by thermo-gravimetric analysis, was 1.7 wt%, where the main composition, determined from X-ray photoelectron spectroscopy, was Fe$_2$O$_3$ and Fe$_3$O$_4$. The bundle size was enlarged, as expected, from typical solution treatment, as shown in Figure 2.

We prepared three samples by using further treatments (Fig. 1): (i) immersed in DI water (surface tension 72.3 mN/m) before drying, (ii) filtrated further with isopropanol (surface tension 21.1 mN/m) followed by acetone (surface tension 22.3 mN/m) and dried in the atmosphere, and (iii) immersed in DCE (surface tension 32.6 mN/m) after isopropanol and acetone treatments before drying. These samples of 0.1 mg were further sonicated in 100 ml of DCE for fifteen hours. After centrifuging the sample at 17,000 rpm for 3.5 hours, supernatants were spin-coated on a SiO$_2$ substrate. All the samples were DCE-treated prior to measurements. Our aim was to see the pretreatment effects of the nanodispersion of the SWCNTs. The dynamic force mode (DFM) in the AFM (Seiko SPA-400) was used to get information for diameter and length distributions of SWCNTs. Raman spectra were taken using a micro-Raman system (Renishaw RM1000-Invia). The D-band in the Raman spectrum, which is the defect characteristics on the nanotube walls (and/or carbonaceous particles), decreased after the acid treatment.

3. RESULTS AND DISCUSSION

The modification of the electronic structures was monitored by the Raman spectra Figure 3. The radial breathing mode (RBM) of the Raman spectra in Figure 3(a) shows that the small-diameter metallic SWCNTs near 250 ~ 260 cm$^{-1}$ were destroyed during the oxidative heat
Intensity (arb. units)

Raman shift (cm$^{-1}$)

(a) 514 nm (2.41 eV)

(b) line-shape of the tangential mode (or G-band)

Fig. 3. The Raman spectra of variously treated samples with an excitation energy of 514 nm: (a) radial breathing modes, and (b) tangential G-bands. From the top panel, each spectrum represents (I) the raw SWCNTs, (II) the oxidized SWCNTs, (III) the acid-treated SWCNTs, and (IV) the DCE-treated SWCNTs. All peaks were normalized by the G-band.

Fig. 4. AFM images obtained using DFM mode for (a) the raw SWCNTs directly dispersed in DCE solution, indicated as #1 in Figure 1, and (b) the purified SWCNTs that were further immersed in DI water, again dispersed in DCE solution, indicated as #2 in Figure 1. The scale bar is 2 μm. The inset shows the typical height distribution along the black line indicated in the panel.
intercalative acid treatment when one prefers to use polar solvents. For this reason, we removed water by a continuous filtration with IPA and subsequently with acetone, and the sample was then dried in the atmosphere. Figure 5(a) shows the AFM image of sample #3. In this case, nanotube bundle size was greatly enlarged with a typical diameter of 5.5 nm. The nanotube lengths were longer than those of samples #1 and #2. Although water was removed, nanotubes were again severely bundled during the dry process in acetone, with a typical bundle size of 2.5 nm. Although the bundle diameters were reduced significantly, nanodispersion was barely achieved with the dry process. The last step we tried was to immerse SWCNTs in DCE solution before drying to avoid the bundling effect (see sample #4). Nanotubes were well-nanodispersed with relatively small lengths. The nanodispersion was achieved by a solvation of nanotubes in a non-polar solvent, in contrast to non-soluble nanotubes in a polar solvent. This is understood by a simple principle that “like dissolves like.” In particular, the non-polar solvent with halogen groups enhanced a solvation of nanotubes by increasing the binding energy between the nanotubes and the solvent molecules. An advantage of using DCE is that its boiling temperature is 83 °C, much lower than the 202 °C and 153 °C of organic NMP and DMF solvents, respectively, making the DCE more easily removable by vaporization after treatment. Another point to address is that DCE (32.6 mN/m) has a smaller surface tension than water (72.3 mN/m), making for a better wettability of nanotubes.

Figure 6 shows the time evolution for the diameter and length distributions for the nanotubes of sample #4. The most probable nanotube length was about 250 nm. This value was not altered with a time evolution of several days, suggesting high stability in the solubility. The most probable height (diameter) with an extraction time of 2 hours after centrifuging was duplicate, near 1.6 nm and 3 nm, where the latter could be a bundle composed of two or three nanotubes. Some nanotubes were aggregated at a longer extraction time of 72 hours and further precipitated, giving the most probable peak near 1.6 nm. Although the dispersed SWCNTs in DCE solution seemed to be quite stable, the aggregation did occur microscopically. Our results showed that by simply avoiding the dry process during DCE treatment, we were able to achieve nanodispersion and to obtain nanotubes with smaller lengths.

4. CONCLUSIONS

We have demonstrated how to achieve nanodispersion using non-polar DCE treatment. Purification before treatment is an important step to achieve nanodispersion. The presence of water agglomerates the individual nanotubes into bundles. A simple removal of water or any other types of solvents by the dry process, is also harmful for nanodispersion. Instead of using water as a solvent, we used a non-polar solvent, DCE, to achieve nanodispersion. Nanotubes were mostly nanodispersed with typical tube lengths of 250 nm. Raman spectra showed that nanotube walls were well preserved without much damage during DCE treatment.

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References and Notes


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