

Controlled Oxidation of Single-Wall Carbon Nanotubes: A Raman Study

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Abstract. Oxidation of single wall carbon nanotubes using H_2O_2 is a common purification and tube opening procedure. We studied the effect of oxidation in well controlled conditions on SWNT samples with different mean diameters, prepared by laser-ablation, CVD and the HiPco process. Detailed multifrequency Raman spectroscopy evidences that oxidation damage depends strongly on the mean tube diameter, damage occurring to small tubes first and successively for larger diameter tubes. We use the peapod filling of the above samples as a control to what extent the tubes are open to the C_{60} molecules.

INTRODUCTION

Related to the synthesis method, SWCNT samples contain inevitable catalytic particles as well as of non-desired carbon compounds. SWCNTs are known to be resistant to oxidation better than any other carbon modifications or metallic particles. This inspires the purification of SWCNTs with oxidating treatment such as refluxing in H_2O_2 or heat treatment in air. Naturally, a reasonable balance have to be achieved when non-wanted side products or catalytic particles are nominally removed and the desired SWCNT sample remains yet in sufficient abundance. Another important aspect of the oxidation is the opening up of the SWCNTs for the environment thus making the encapsulation with materials such as alkali halides or C_{60} possible¹. Here, we report a systematic gravimetric and Raman study of oxidation of different SWCNT samples using H_2O_2 . Raman spectroscopy and in particular multifrequency Raman measurements have been proven to be crucial in the characterization of several properties of SWCNTs². The level of oxidation is controlled by the dilution of the H_2O_2 aqueous solution. We found a strong dependence of oxidation on the nominal tube diameter of the samples, the small tubes being oxidized first, most probably from the tube ends.

EXPERIMENTAL

We studied 3 different SWCNT samples from commercial sources: laser ablation, LA, (Tubes@Rice, Rice University, Houston, Texas), CVD (Nanocyl, Namur, Belgium) and HiPco (Carbon Nanotechnolgies, Houston, USA). The purities as provided by the manufacturers are summarized in Table 1. Oxidation was studied by 2 hours refluxing of the SWCNT in diluted H_2O_2 aqueous solutions. After refluxing, the

material was filtered and the resulting bucky paper was dried at 140 °C in air. Comparability and reproducibility was assured by the use of the same amount of starting SWCNT material, 15 mg, and the same volume for the aqueous solution, 30 ml, for all treatments. The unit of treatment is defined as 1mg SWCNT in 1 ml of 30 % aqueous H₂O₂ and 1 ml of distilled water. Numbers above unity are achieved by repeating the refluxing, filtering and drying steps. Peapod filling was done following the step in Ref. 3. The peapod concentration in the resulting materials was determined from the Raman signal of the C₆₀ A_g(2) following Ref. 4.

TABLE 1. Properties of the studied SWCNT materials

Material	Purity (%)	Mean diam. (nm)	Peapod concentration (%)
HiPco	70	0.98	0
CVD	70	1.20	10
LA	15	1.34	30

RESULTS AND DISCUSSION

Figure 1. shows the weight loss of the SWCNT materials after the described oxidation procedure. Weight loss is generally considered as a poorly controllable quantity since SWCNT materials are known to absorb an ill defined and different amount of solvents. This originates in the different morphology of the SWCNT bundles. In order to reduce systematic errors related to this, we performed a control experiment, where no H₂O₂ was added to the distilled water. As shown in Fig. 1., the final and starting masses are in a close agreement, which supports the validity of the current gravimetric studies. A surprising observation in Fig. 1. is the complete disappearance of the HiPco material at treatment unit 1, whereas the LA and CVD compounds seem to tend to a constant value of the final to initial mass ratio. This may originate in two facts: i.) the overallly smaller diameters of the HiPco material may be more susceptible for the oxidation treatment than the larger diameter tubes present in the LA and CVD material (see. Table 1.); ii.) it is also possible that a different morphology related to the catalytic particles and the SWCNT may give rise to the difference. This later proposal is based on the fact the for the LA and CVD grown

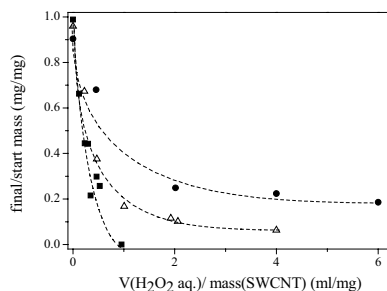


FIGURE 1. Mass loss of SWCNT samples after H₂O₂ treatment (/: HiPco, ●: laser ablation, △: CVD). Dashed lines are guides to the eye.

materials, the SWCNTs are known to grow out of larger catalytic particles, whereas the HiPco based SWCNT are known to be attached to smaller catalytic particles as well as to encapsulate the catalyst itself. The close presence of catalyst particles may catalyze the decay of H_2O_2 into the nascent oxygen reaction agent thus helping the oxidation of nanotubes. In what follows we focus our attention on the HiPco material in order to clarify the full disappearance of the material with treatment. The peapod concentration attests to what level the SWCNT samples are opened, and whether the tube diameters are large enough to accommodate C_{60} . Our results for the studied samples are summarized in Table 1. Clearly, even when significant number of tube openings are present, the HiPco tubes are too small for a detectable level of C_{60} encapsulation.

Figure 2. shows the RBM mode region of the Raman spectra of the HiPco sample with the oxidation steps defined on Figure 3a. at $\lambda=488$ nm. Changes associated with the treatment are observed: RBM lines at higher Raman shifts vanish with increasing treatment. SWCNT with larger Raman shifted RBM lines correspond to the thinner tubes as $\nu_{RBM} > 1/d$, where d is the tube diameter. The evident disappearance of thin SWCNT in the HiPco sample is quantitatively described when the mean tube diameter, d , and its variance, σ , is calculated assuming a monomodal distribution of the tube diameters following Ref. 5. Figure 3b. summarizes the data at 488 and 647 nm: the mean tube diameter gradually decreases that is accompanied by the narrowing of the diameter distribution function. This is understood as oxidation happening to the smallest nanotubes first. A simple calculation has shown that the shifting of d to higher values and the narrowing of the distribution can account for the $\sim 80\%$ weight loss observed for the '6' treatment.

The Raman D and G modes also hold significant information about the oxidation damage. In Figure 4a. and b. we show the Raman D and G modes at $\lambda=488$ nm. The

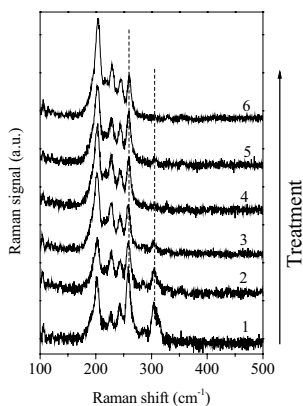


FIGURE 2. Raman spectrum of the oxidized HiPco sample at $\lambda=488$ nm. Dashed lines indicate Raman lines that vanish with increasing treatment.

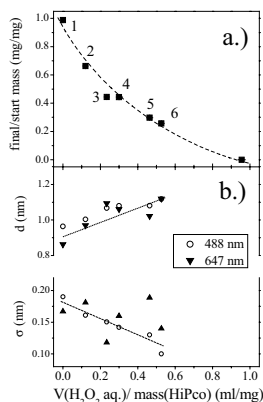


FIGURE 3a. Enlarged view and labelling of the oxidation of the HiPco sample. **3b.** Mean and width of the assumed monomodal diameter distribution of the HiPco sample at different laser frequencies. Dashed lines are guide to the eye.

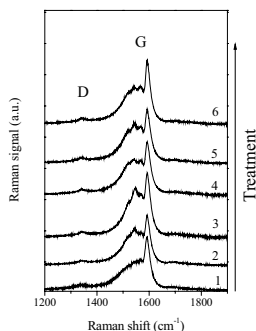


Figure 4a. The Raman D and G modes of the HiPco samples at $\lambda=488$ nm.

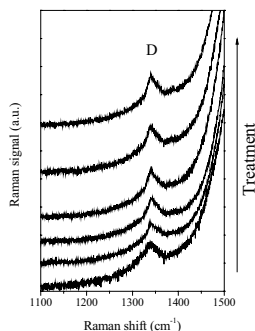


Figure 4b. Enlarged view of the D mode.

disappearance of the small, metallic tubes is evident as the Fano contribution to the G mode gradually disappears with increasing treatment. The lineshape has been analyzed in detail previously⁵. However, no significant changes are observed for the defect sensitive D mode as shown in Fig. 4b. This evidences that oxidation has no effect on the tube side walls and only tube ends are damaged, no matter how substantial the damage is.

CONCLUSIONS

The oxidation of LA, CVD and HiPco SWCNT samples was studied. We found that oxidation happens to small nanotubes first, starting from the tube ends. This results in a very rapid disappearance of the HiPco material with oxidation as it consists of nominally small diameter tubes.

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