Cutting Fluorinated/Ozonated Single-Walled Carbon Nanotubes by Pyrolysis

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ABSTRACT

Pyrolysis and/or piranha treatment of fluorinated /ozonated single-walled carbon nanotubes (SWNTs) were found to have cut the nanotubes to short length (~100nm). Pyrolysis of partially fluorinated SWNTs (~C_5F) at 700°C cut the nanotubes without causing significant crosslinking among the SWNTs. When pyrolyzed at lower temperatures, the fluorinated SWNTs need room temperature piranha treatment to finish the cutting. SWNTs that was ozonated in perfluoropolyethers (PFPE) at room temperature has also been cut when pyrolyzed at 375°C. Functionalization of cut-SWNT with alkylhalide in $Li/NH_3(l)$ was used to debundle the nanotubes into individuals in chloroform for the length measurement. The cut-SWNTs have been characterized by Raman and AFM. AFM shows cut-SWNTs with a length distribution mainly between 30nm and 100nm. Large scale cutting of SWNTs would lead to novel applications of nanotubes in microelectronics, biological imaging and sensing, drug delivery and composite material, etc.

Keywords: nanotubes, cutting, fluorination, ozonation, pyrolysis.

1 INTRODUCTION

Since their discovery in 1991[1], carbon tubes are one of the most promising constituents of carbon nanoscale composites because of their unique electrical, mechanical and optical properties. Because they are hollow and much smaller than the blood cells, some methods were developed to attach DNA and protein molecules to the inside and outside of the nanotubes, this allows us to target and destroy individual cancer or virus cells. [2]. However, the SWNTs with uniform length scale are required to accomplish these applications. Short SWNTs were obtained by chemical etching using H_2SO_4/HNO_3[3], Also Gu[4] got the bundled cut-SWNTs by fluorination and pyrolysis at 1000C. In this paper, we introduce the cutting of single-wall carbon nanotubes without crosslink to an average length of 100nm by pyrolysis. Recently the STM analysis of Kelly[5] shows that fluorine could be removed slowly by pyrolysis , So cutting of SWNTs can be viewed as a two step process----introduction of sidewall damages and exploiting the damage sites to create cut-SWNTs. [6] First of all, the purified single-wall carbon nanotubes need to be partially fluorinated or ozonated. The cut nanotubes(cut-SWNTs) can be produced directly by pyrolysis of fluorinated SWNTs(F-SWNTs) in an argon atmosphere at 700° C or by room temperature piranha treatment after lower temperature pyrolysis. Also ozonated SWNTs(O-SWNTs) has been demonstrated to be cut by pyrolysis at 375°C. Functionlization in $Li/NH_3(l)$ by dodecyl groups[7] was used to debundle the SWNTs for characterization. Raman imaging and atomic force microscopy (AFM) has been successfully employed to study SWNTs' length distributions.

2 EXPERIMENTAL

2.1 Raw material and Purification

The SWNTs used in our experiment were produced by HiPco process [8]. Purification process [9] was used to remove the amorphous carbon and iron particles. The average length of the nanotubes is more than 200nm. All the AFM images in this paper are taken from SWNTs samples .that have been individualized with dodecylation in $Li/NH_3(l)$

2.2 Fluorination

The fluorination on the sidewalls of SWNTs was done at temperature between 50° C and 70° C in 10% Fluorine/90% Helium flow for 2~4 hrs. It was used to make F-SWNTs with a stoichiometry of C_5F. This process introduces functionlization sites on the sidewall of SWNTs.

2.3 Pyrolysis

The pyrolysis was done in a quartz boat in tube furnace. The sample was heated in an argon atmosphere at a rate of 20° C/min from room temperature to target temperature.

2.4 Piranha/Ammonium Persulfate Treatment

Piranha is 1:4 (vol/vol 30% H_2O_2/96% H_2SO_4 solution. Room temperature treatment for 1 hour was used. The solution was added to the noanotubes(1mL piranha: 1 mg nanotubes). Ammonium Persulfate solutions were prepared by dissolving 0.1g of the salt in 1mL of 96% H_2SO_4. The persulfate solution was then added to the nanotubes(1mL solution: 1mg of nanotubes). Both these two methods can

cut the nanotubes.

2.5 Ozonation

Ozonation plus piranha treatment is another potential method of cutting SWNTs. Previous work has been done in methanol at -78° C [9, 10] though it is an unstable system due to the explosive nature of ozone/methanol when warmed. Here cutting was done with O_3 bubbling (3.7% O_3 in O_2) in nanotubes/PFPE solution with homogenizing at room temperature for three hours, clean out by quenched with Nanopure (Barnstead International, Dubuque, IA) water and ethanol(200 proof) for 10 times. After that, cut-SWNTs were extracted into ethanol and PFPE was separated from the two-phase system. The reason PFPE was used as solvent is O_3 has very high solubility in PFPE.

3 RESULTS AND DISCUSSION

AFM image of purified nanotubes---the precursor is shown in Fig. 1. Fig. 2 shows the length distribution of the precursor. Functionalization debundles the SWNTs to make it soluble in chloroform for AFM histogram measurement. The length distribution shows there are tubes whose lengths are between 50nm~1000nm. The tube lengths were measured by Nanotube Length Analysis package of SIMAGIS software. Typically more than 500 nanotubes need to be measured to get statistical results.

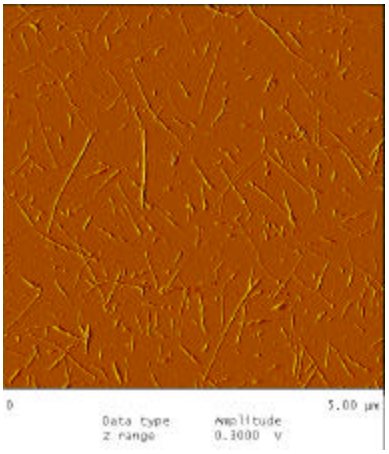

Fig. 1 AFM image of the purified SWNTs

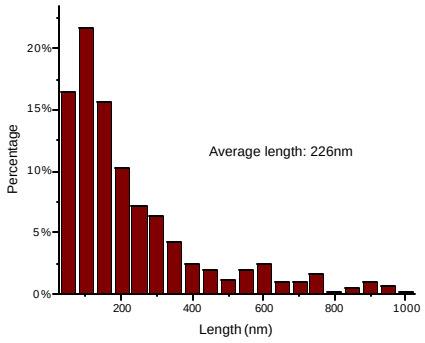

Fig. 2 Length distribution of purified SWNTs

To cut the nanotubes to shorter length, Pyrolysis of F-SWNTs in an argon atmosphere at 700°C can exploit the damage sites and produce the cut-SWNTs without crosslink but with shorter average length of 87nm. After pyrolysis, the SWNTs sample was functionalized with the same mechanism as mentioned above. Gu[4] pyrolyzed the F-SWNTs at 1000°C and cut the nanotubes to short bundled nanotubes with length of 50nm. We found that the pyrolysis beyond 700°C induce the crosslink. But the pyrolysis below 700°C is able to cut SWNTs without causing significant crosslinking between nanotubes.

Fig. 3 is the AFM image of cut-SWNTs by pyrolysis at 700°C. Fig. 4 shows the length distribution of the cut-SWNTs. Fig. 5 shows the Raman spectrum of purified SWNTs, fluorinated SWNTs, pyrolyzed SWNTs and functionalized SWNTs. The disorder peaks of SWNTs at different processing stages indicate that the sidewall functionalization by fluorination process, the exploiting the damage sites by pyrolysis process and covalent attachment of dodecyl groups by functionalization process respectively. The height data on Fig. 3 indicates that there is no apparent bundling of nanotubes, which suggests that there is no crosslinking during the pyrolysis.

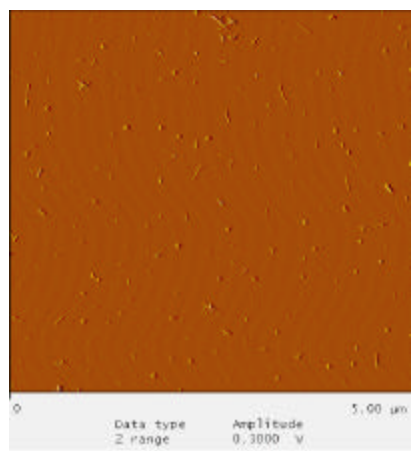

Fig. 3 AFM image of cut-SWNTs(pyrolysis at 700°C of fluorinated SWNTs)

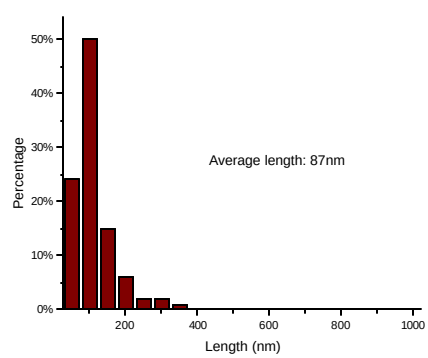

Fig. 4 Length distribution of cut-SWNTs(pyrolysis at 700°C of fluorinated SWNTs)

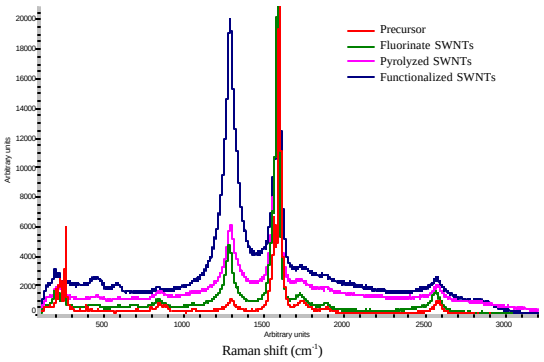

Fig. 5 Raman image of purified SWNTs, fluorinated SWNTs, pyrolyzed SWNTs and functionlized SWNTs.

Pyrolyzing SWNTs at lower temperature (~500°C) followed by room temperature piranha or ammonium persulfate treatment has also been tried, Fig. 6 shows the AFM image. It was found that with this process the SWNTs can be cut to shorter length than the precursor, but longer than the cut-SWNTs we got from 700° C pyrolysis of fluorinated SWNTs.

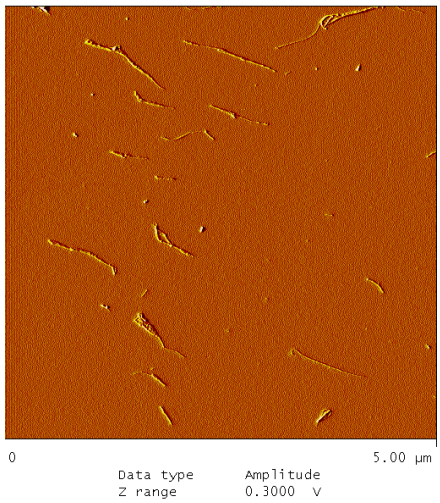

Fig. 6 AFM of Cut-SWNTs(pyrolysis at 500°C of fluorinated SWNTs followed by room temperature piranha treatment).

Besides the F-SWNTs, O-SWNTs can also be cut by pyrolysis. Same functonalization process has been done to debundle the cut-nanotubes for characterization (see AFM picture in Fig. 7). As shown in the Fig. 8, the average length of the cut-SWNTs is 103nm. So compare to precursor, the ozonated SWNTs were cut and we believe that cutting was occurred during the pyrolysis. So far we demonstrated the ozonation plus pyrolysis is another effective way to cut the SWNTs.

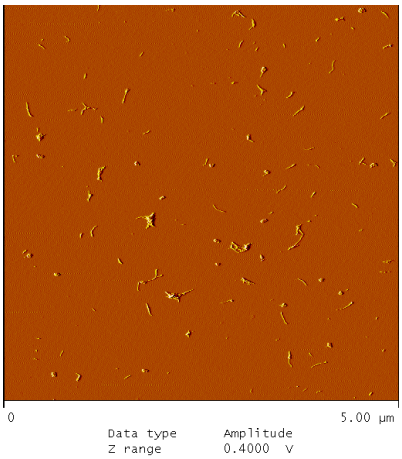

Fig. 7 AFM of Cut-SWNTs(ozonation followed by pyrolysis at 375°C)

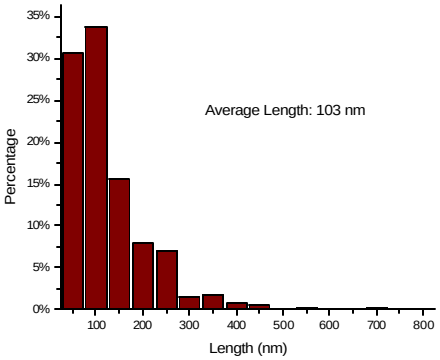

Fig. 8 Length distribution of cut-SWNTs(ozonation followed by pyrolysis at 375°C).

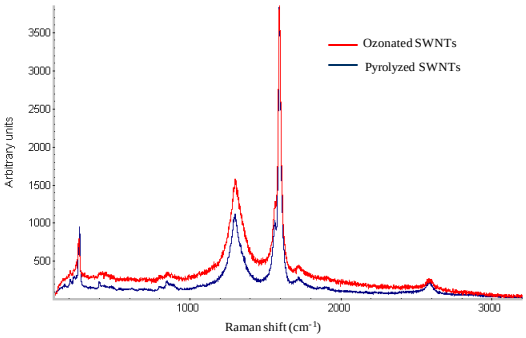

Fig. 9 Raman Spectrum of ozonated and pyrolyzed SWNTs

Raman spectrum in Fig. 9 shows the extensive ozonation of the nanotubes in PFPE solvents. The difference in the intensity of disorder peaks suggests pyrolysis cut the ozonated-SWNTs at damage sites.

4 CONCLUSION

Pyrolysis has been shown as an effective method of cutting. Fluorination and ozonation process can covalently attach fluorine and oxygen on the sidewalls of SWNTs. during the subsequent pyrolysis, C-C bonds are broken and cutting occurs at the damages sites. Pyrolysis at 700°C can cut the F-SWNTs without crosslink. At lower temperature, pyrolysis at 500°C apprarently create damage sites along SWNTs sidewalls, but those damage sites are not completely exploited to finalize cutting. One hour room temperature piranha treatment finalizes the cutting. Pyrolysis at 375°C can cut the ozonated SWNTs through the same mechanism. The overall carbon yield is 70-80% in all cutting methods described here. The final average length of the cut-nanotubes is ~100nm.

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