Defect Location of Individual Single-Walled Carbon Nanotubes with a Thermal Oxidation Strategy

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Received: July 12, 2002; In Final Form: August 29, 2002

In the present study, we proposed a simple method to locate defect sites in individual SWNTs with an AFM technique by using a thermal oxidation strategy. After thermal oxidation of well-dispersed SWNTs on a silicon surface in air at 500 °C, almost all of the original SWNTs were fractured into short fragments. The range of the fragment sizes was different and closely related to the length and growth time of the tubes. The rupture of SWNTs was confirmed to be a result of the presence of defects in tubes and to be caused by the attack of oxygen molecules in air. Owing to the damage event that occurred in SWNTs after heating treatment, a thermal oxidation method may be developed as a potentially useful technique for the cutting of SWNTs, and chemical functionality of the SWNTs could also be achieved during this process. In this regard, a thermal treatment method would be employed as another useful cutting and functionalizing approach to tailor the chemical and physical properties of SWNTs.

Investigation of defects in single-walled carbon nanotubes (SWNTs) is of great importance not only to fundamental research but also in tailoring their chemical and physical properties for future applications.[1−4] Defects inevitably arise during the growth of SWNTs [5,6] and may also be introduced after some postsynthesis treatments such as chemical etching,[7] ultrasonication,[8] or electron beam irradiation.[9] The presence of defects such as topological structural defects, substitutional impurities, structural deformations caused by bending or twisting the nanotubes, and vacancies on the walls, etc., would ultimately affect the helicity, electronic structures, chemical activities, and other properties of pristine tubes to different extents.[1−4] However, the research in this field is currently limited as a result of the technical difficulties presented in the analysis of such nanoscale structures. Some attempts have been made to locate defects in nanotubes with high-resolution TEM,[10] STM techniques,[11] and using nanoparticles as markers.[12] A chemical titration method[13] and mid-IR spectroscopy[14] have also been employed to macroscopically estimate the defect density of tubes. These investigations, however, demand severe treatment of tube samples and a high degree of technical expertise and/or are indirect. Herein, we propose a simple method to locate defect sites in SWNTs with an AFM technique by using a thermal oxidation strategy, based upon the assumption that the defect sites on SWNTs would be more chemically reactive than nondefect sites.[15] The structures of individual SWNTs deposited on a silicon surface changed a lot after thermal oxidation in air for some time, and almost all of the original SWNTs were fractured into short fragments. Such defect-induced damage along each individual SWNT could be clearly observed with AFM. In addition, we found that the density of defect sites on SWNTs was related to their length and growth time.

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The SWNT samples used here were synthesized by methane CVD using MgO-supported Fe catalysts as described in a previous study.[16] The purity of all SWNTs was higher than 90% after purification in 37% HCl. SWNTs used in the study were deposited from a dispersion in dichlorobenzene onto clean Si(111) surfaces and dried in air at room temperature. Thermal oxidation was carried out by heating the sample wafers in air for at least 30 min at 500 °C.

A thermal oxidation strategy has been employed as an effective method to purify carbon nanotube samples,[17−18] as disorder carbon deposits show lower thermal stability than tubular products that have perfect graphene structures. In a practical application of this method, however, amorphous carbon can be removed and a large quantity of tube samples are also burned out simultaneously. In addition, the rest of the SWNTs have a tendency to aggregate even worse. The situation will become different when this procedure was performed with well-dispersed individual SWNTs on surface. As in this case, oxygen molecules will have a better and sufficient contact with SWNTs, and the interaction among tubes arising from the presence of some dangling C−C bonds in the structures of SWNTs can be avoided, so we may have opportunities to investigate the structure variations before and after the thermal oxidation treatment.

As the length and quality of as-prepared SWNTs has been shown to be closely dependent upon the growth time.[16,20] the SWNTs used in the present study were deliberately synthesized using a relatively short growth time (<10 min), this is due to the fact that SWNTs tend to form micrometer-long entangled "ropes" when growth times exceed 10 min, which would lead to difficulties in obtaining well-dispersed individual SWNTs on surfaces for further investigations. Figure 1a shows a typical AFM image of SWNTs grown for 2 min and applied to heating treatment. The original tube structures are dramatically altered by the thermal oxidation step. Almost every tube appears to

10.1021/jp026512c CCC: $22.00
Published on Web 10/04/2002

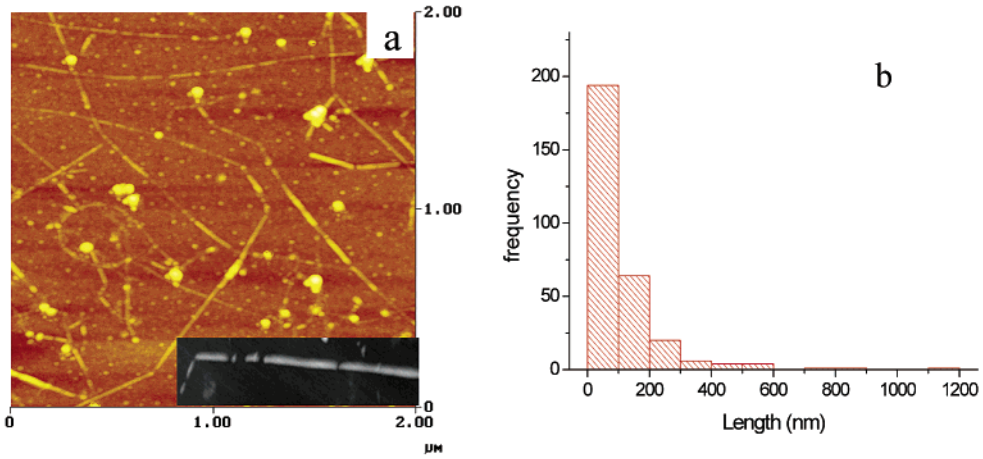

Figure 1. AFM image of SWNTs after thermal treatment in air at 500 °C (a) and histograms of the length distribution of disrupted tubes (b); insert is a typical rupturing of an individual tube.

have been ruptured into several short fragments. The sizes of the fragments in each individual tube are quite different, with the shortest fragments being only a few tens of nanometers in length while the longest ones remains at about 1 μm. For any given tube, the fracture event appears to preferentially occur at kink sites and on thinner and shorter tubes. Typically, a gap of the order of tens of nanometers would be seen between two fragments. Figure 1b shows the statistical results on the length distribution of fragments after the heating event. On the basis of the results from more than 300 tubes, 60% of the fractured tubes were shorter than 100 nm, 29% were in the range from 100 to 300 nm, and 10% in the range from 300 to 600 nm. The fragments with lengths greater than 600 nm comprised less than 1% of the total number.

Figure 2 shows the dependence of the structure deformation of individual SWNTs on the heating temperature. The rupture of SWNTs occurred around 500 °C. When the temperature was elevated above 520 °C, the structure of original tube would be seriously destroyed. If the heating temperature was set in a suitable range (490−510 °C), prolonging the heating time would not cause further damage to the structures of SWNTs. Since the thermal stability of the defective sites would be inferior to the thermal stability of the sites with perfect graphene structures, under a desired heating temperature, O_2 molecules in air will preferentially attack the defects on SWNTs, and be less likely to introduce other defects. The appearance of gaps between the two adjacent tube fragments after thermal treatments revealed that O_2 has eroded the defective sites on SWNTs.

To make sure that the damage of SWNTs was resulted from the presence of defects, HRTEM was carried out to characterize the SWNTs. As shown in Figure 3, the walls of SWNTs grown with short growth time were dirty and disintegrated, indicating that more defects formed on such tubes. On the contrary, when SWNTs were synthesized with longer growth time (>10 min), the resulting SWNTs generally show clean and whole walls with fewer adherent impurities. Furthermore, TGA results showed that the peak burning temperature of SWNTs slightly increased with growth times, for instance, the peak burning temperature for 1 min short tube was at 596 °C, it would go up to 604 °C when the growth time was kept for 10 min. This result implied that the increased thermal stability of tubes might be a result of their low defect densities. With these hints, a thermal oxidation experiment was further performed with the SWNT samples grown for different times. The results of AFM characterization revealed that increasing growth time favored the growth of

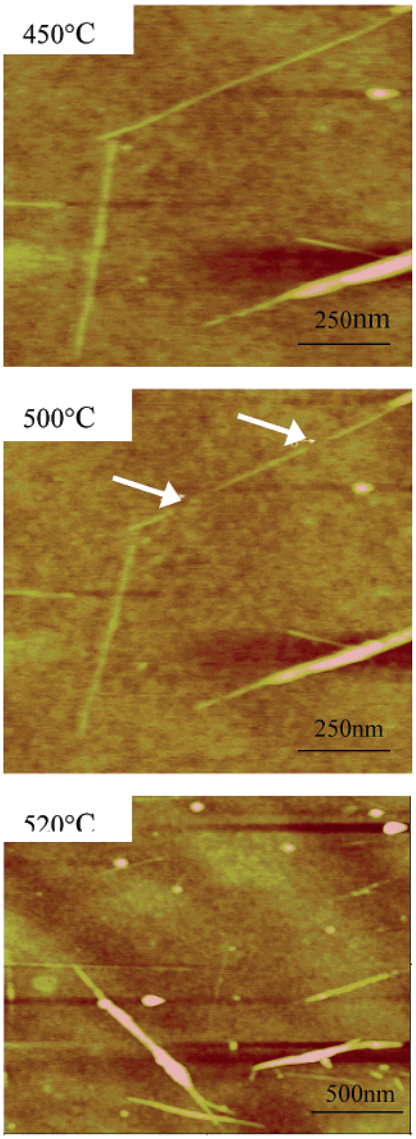

Figure 2. The effect of heating temperature on the structures of SWNTs.

SWNTs in greater length and larger bundles. The rupture of the tubes with longer growth time shown in Figure 4 became less severe just as we expected. These phenomena probably implied that during the initial stage of growth, the growth of

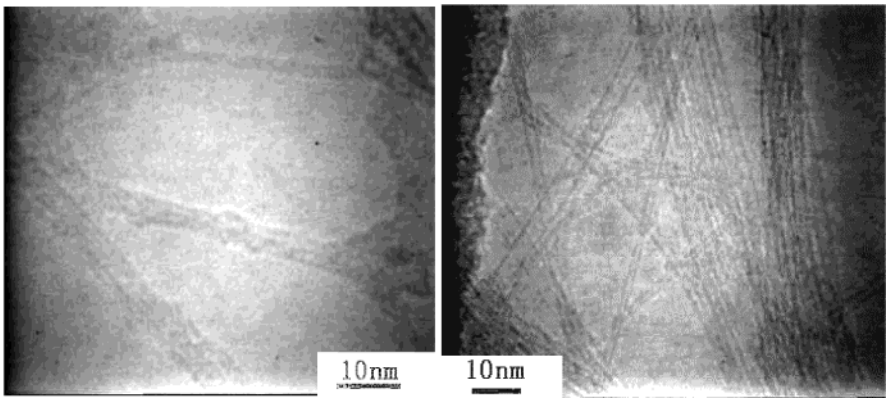

Figure 3. HRTEM images of SWNTs grown for 2 min (left) and 10 min (right).

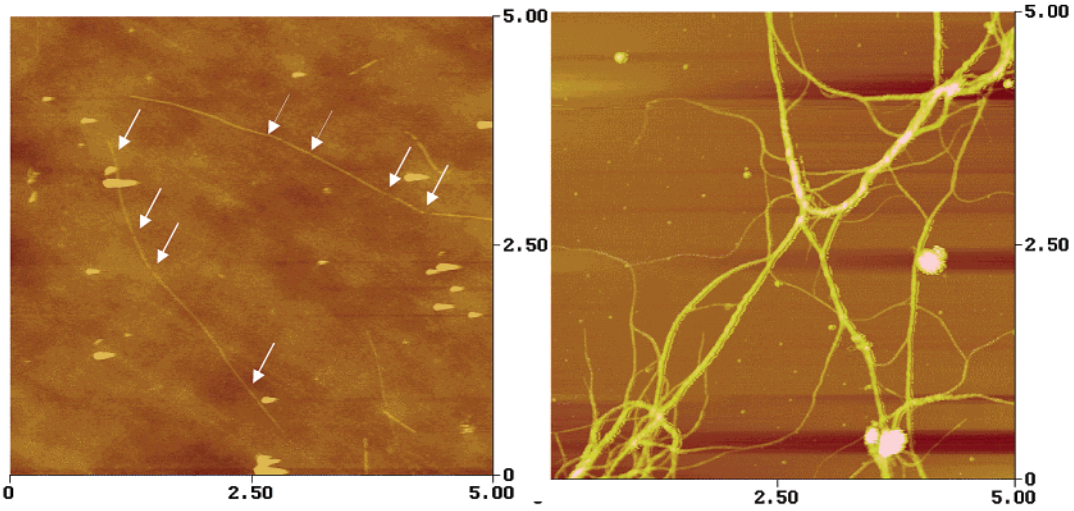

Figure 4. AFM images of SWNTs grown for 5 min (left) and 10 min (right) after thermal treatment in air at 500 °C (the ruptures in tubes are marked with arrows).

SWNTs might be a kinetically controlled process, in which rapid growth of SWNTs would be more likely to generate defects in their tubular structures. The growth of SWNTs in a later period would become thermodynamically controlled, the transformation into more ordered and stable graphene structures would be favored. In other words, longer growth times would favor the growth of tubes with smaller defect density and thus more perfect structures.

In previous work, rupturing of SWNTs into short fragments was also observed under high-energy electron beam irradiation during TEM characterization[10] or when high voltage pulses were applied during STM experiment.[20] As the foreign energy imposed upon an individual tube was so strong that it could break C−C bonds at any sites, not merely at defect sites, carbon nanotubes may be thus cut into short fragments with definite length. By contrast, the results presented here directly relate to defect sites themselves as we used a relatively mild method to disturb the pristine structures of SWNTs. Oxygen molecules in air may specifically erode the tubes at chemically active defect sites. The emergence of an absorbance peak at 1743 cm^{-1} in the IR spectra of heated SWNT samples clearly indicated the formation of carboxylic acid groups on tubes after oxidation in air, which presented further evidence to demonstrate that the damage of SWNTs was caused by the attack of oxygen molecules (see Figure 5a). As a result, this method was effective for locating the defect sites in tubes. In some sense, it would be more feasible than HRTEM and STM technique as it was rather simple and rapid. In addition, it may offer the possibility of assessing defect density on many individual tubes in each single experiment.

This method may also be developed as a potentially useful technique for the cutting of SWNTs. In our experiment, a certain amount of original micrometer-long SWNTs grown for 5 min were heated in air at 500 °C for half an hour, subsequent AFM characterization revealed that the SWNTs have been cut into short tubes, the general length of which was in the range of 200−600 nm (Figure 5b). It was thus obvious that thermal cutting of long tubes may provide several unique advantages over previous methods such as chemical etching and mechanical cutting [21,22] in that the process is simple, rapid, and labor saving. Given that thermal treatment was effective in removing amorphous carbon impurities, the shortened tubes obtained were quite clean. In addition, this method was apparently suitable for the large scale production of shortened and carboxylate functionalized SWNTs.

In summary, a simple thermal oxidation strategy was employed to investigate the defect distribution on individual nanotubes based on the high sensitivity of defect sites to thermal treatment. Defect density in SWNTs was found to be closely related to the growth process. An increase in the numbers of defect sites was observed on short tubes and tubes with greater kinks. The greater the defect density, the greater the possibility of generating shortened tubes through thermal cutting. Chemical functionality of the SWNTs could also be achieved successfully using this technique. In this regard, thermal treatment method

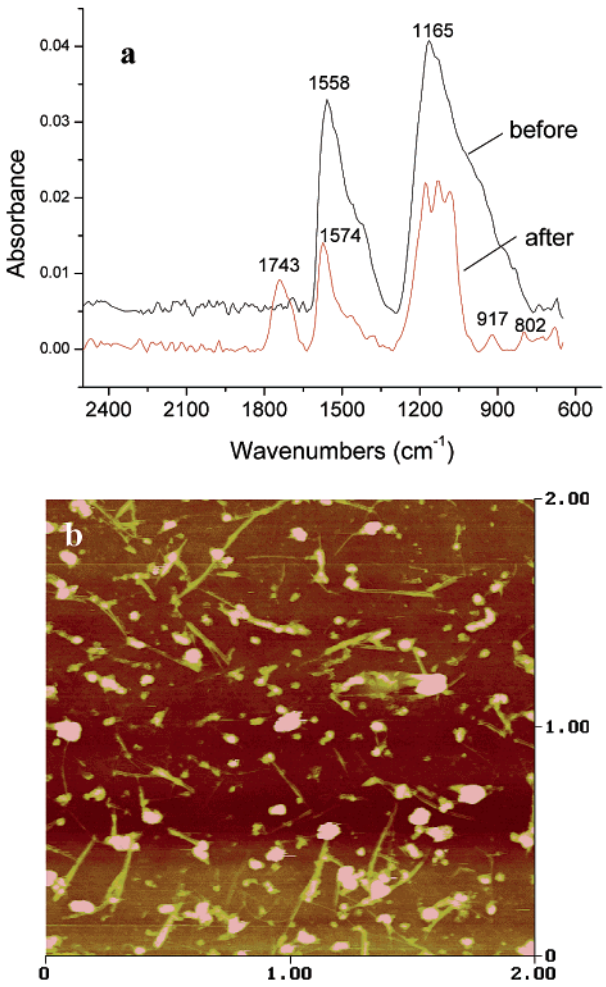

Figure 5. IR spectra of SWNTs before and after heating treatment (a) and AFM image of SWNTs prepared by thermal heating treatment (b).

would be employed as another useful cutting and functionalizing approach to tailor the chemical and physical properties of SWNTs.

Acknowledgment. We are grateful for the financial supports from National Natural Science Foundation of China (NSFC 6989022, 59910161982, 29973001, 30000044), Ministry of Science and Technology of China (2001CB6105), Postdoctoral fellowship, and SRF for ROCS, SEM. We are also grateful to Prof. J. Kirkham (University of LEEDS) for her kind help and useful discussion.

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