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Thermal stability of functionalized carbon nanotubes studied by *in-situ* transmission electron microscopy

Zhiping Luo^{a,*}, Aderemi Oki^b, Laura Carson^c, Luqman Adams^b, Gururaj Neelgund^b, Nathaniel Soboyejo^b, Gloria Regisford^d, Melisa Stewart^c, Kemar Hibbert^c, Gavannie Beharie^c, Cordella Kelly-Brown^c, and Pasakorn Traisawatwong^c

^aMicroscopy and Imaging Center and Materials Science and Engineering Program, Texas A&M University, College Station, TX 77843-2257, USA

^bDepartment of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA

^cCooperative Agricultural Research Center, Prairie View A&M University, Prairie View, TX 77446, USA

^dDepartment of Biology, Prairie View A&M University, Prairie View, TX 77446, USA

Abstract

The thermal stability of functionalized carbon nanotubes (CNTs) has been studied experimentally by direct *in-situ* observations using a heating stage in a transmission electron microscope, from room temperature (RT) to about 1000 °C. It was found that the thermal stability of the functionalized CNTs was significantly reduced during the *in-situ* heating process. Their average diameter dramatically expanded from RT to about 500 °C, and then tended to be stable until about 1000 °C. The X-ray energy dispersive spectroscopy analysis suggested that the diameter expansion was associated with coalescence of the carbon structure instead of deposition with additional foreign elements during the heating process.

Keywords

Carbon nanotubes; functionalization; *in-situ*; thermal stability; transmission electron microscopy

1. Introduction

Carbon nanotubes (CNTs) are cylindrical nanostructures composed of carbon layers. Their diameter ranges from few nanometers for single-walled CNTs (SWCNTs) to up to several hundred nanometers for multi-walled CNTs (MWCNTs), while their length can be very long, normally from nanometer to micrometer scales or even longer. Due to their unique structure features, they possess extraordinary mechanical, thermal and electrical properties, which make them promising materials for wide range applications in nanotechnology.

However, the hydrophobicity and chemical inertness of CNTs cause tangling or poor dispersion, which limit their commercial applications [1,2]. To solve this technical issue, the

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*Corresponding author. Tel.: +1-979-845-1129, FAX.: +1-979-847-8933, luo@mic.tamu.edu.

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CNTs have been tailored with surface covalent modifications using chemical reactions [3–7]. Lin et al. [3] proposed an approach to achieve homogeneous dispersion of exfoliated CNTs in nanocomposites using functional polymers that are structurally identical or similar to the matrix polymers. McIntosh et al. [4] used the benzoyl peroxide initiated functionalization of CNTs in order to improve their interfacial adhesion and to some degree their alignment, and thus improved their mechanical properties that were dominated by the CNT dispersion degrees [8–10]. Various acids [5–7] and plasma [11] methods have been introduced to modify the CNT surface structures. For example, Wepasnick et al. [6] modified these structures using six common wet chemical oxidants (HNO_3 , KMnO_4 , $\text{H}_2\text{SO}_4/\text{HNO}_3$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 , and O_3). From X-ray photoelectron spectroscopy (XPS), they found that MWCNTs treated with $(\text{NH}_4)_2\text{S}_2\text{O}_8$, H_2O_2 and O_3 yielded higher concentrations of carbonyl and hydroxyl functional groups, while more aggressive oxidants (HNO_3 and KMnO_4) formed higher fractional concentrations of carboxyl groups. Saleh [7] treated the MWCNTs with HNO_3 and a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$ at different temperatures. The acidity was found to increase with increasing the treatment temperature, which was accompanied by an increase with the oxygen content as determined from X-ray energy dispersive spectroscopy (EDS) measurements in a scanning electron microscope.

The thermal stability of both functionalized and unfunctionalized CNTs is an important issue to be studied for their high-temperature applications. Previous work on the thermal stability of SWCNTs demonstrated that thermal treatments performed from 1600 – 2800 °C under argon have a dramatic influence on the SWCNTs structures [12]. At 1800 °C, coalescence of SWCNTs was observed, which led to smaller bundles but with increased tube diameters, as well as significantly decreased crystalline order. From 2200 °C, SWCNTs progressively disappear to form MWNTs with two to three carbon layers. Thermal stability on the double-walled CNTs (DWCNTs) indicated that they are more stable up to 2000 °C [13]. Above 2100 °C, the outer walls of adjacent DWNTs started coalescing into large diameter tubes. However, less research has been done on the thermal stability of functionalized CNTs. Kundu et al. [14] studied the thermal stability of nitric acid-treated MWCNTs using XPS at temperatures up to 720 °C. They found that the acid treatment introduced carboxyl, carbonyl and phenol groups on the CNT surface, and ether-type oxygen between the two adjacent graphite layers, which decreased the thermal stability. After heating to 720 °C in an ultrahigh vacuum, the concentration of surface oxygen atoms was found to decrease from 10.7 to 4.3%.

Transmission electron microscopy (TEM) has been utilized to directly visualize the morphology as well as the structure of functionalized CNTs [2,6,13,15–17]. The goal of this work is to provide an experimental study of the thermal stability of functionalized MWCNTs through direct TEM observations. An unfunctionalized CNT sample was also used for comparison. We performed the *in-situ* heating inside the microscope to monitor their thermal stability from room temperature (RT) up to about 1000 °C, and, surprisingly, found that all three functionalized CNTs we studied demonstrated very reduced thermal stability.

2. Experimental details

The experimental MWCNTs with commercial purity were obtained from Helix Materials Solutions, and all chemicals utilized were obtained from Sigma Aldrich. The MWCNTs first reacted with mixed sulfuric and nitric acids (1:1 ratio) to derive CNT-COOH. Some of the CNT-COOH sample (1.0 g) was further reacted with thionyl chloride SOCl_2 (10 mL) to derive CNT-COCl. On the other hand, the original MWCNTs were also reacted with hydrofluoric acid to derive CNT-F. The TEM samples were deposited on Cu grids coated with holly carbon support film for conventional characterization, as well as silicon nitride

support film with a 50 nm thickness through a 0.25×0.25 mm size window on a Si frame (Ted Pella, Inc., Prod. No. 21502–10) for *in-situ* heating. The TEM work was performed using a JEOL 2010 TEM at 200 kV, equipped with a Gatan heating stage, Oxford Instruments INCA EDS system and a Gatan SC1000 ORIUS CCD camera. The heating rate was about $10^\circ\text{C}/\text{min}$ with a dwell time of ~ 5 min or even longer to ensure the sample stability at each temperature. In order to minimize the electron beam damage, observations were made using reduced dose illumination and the view area was moved away from the electron beam during the heating process. Each heating experiment was done at a fixed magnification to avoid the magnetic hysteresis of the microscope used. Any necessary refocusing was mainly made by adjusting the specimen Z-height mechanically, with the minimum usage of the electrical focus knob that interferes with the optical focus length f and thus may introduce magnification error. In order to make accurate size measurement, magnifications were carefully calibrated using SiC lattice fringes [18]. The size measurements were made using Gatan DigitalMicrograph program after zooming in to reach sufficiently high screen magnification. These samples were also tested for chemical compositions using EDS on 3–8 different spots before and after heating.

3. Results and discussion

Figure 1 shows representative images of CNTs studied, with an enlargement of each image at the lower-right corner. As shown in Figure 1(a), the untreated CNTs exhibit almost clean surface, although there are also few attachments on their outer surfaces. However, the samples CNT-COOH, CNT-COCl, and CNT-F presented evidence of reactants on their surfaces, as shown in Figure 1(b – d), respectively. In the CNT-COOH sample (b), the CNT with three layers is coated over about half of the total surface area. In the CNT-COCl sample (c), the black particles are identified as Co nanoparticles. In the CNT-F sample in (d), the CNTs are almost entirely coated with thin layers. EDS analysis shows that the CNT-COOH sample contains N, O and S, CNT-COCl contains N, O, S and Cl, and CNT-F contains N, O and F.

In-situ heating was performed on the four CNT samples from RT up to about 1000°C inside the TEM. Figure 2 shows the TEM images of the untreated CNT sample. As shown in Figure 2(a), the diameter variations of 14 nanotubes are monitored at different temperatures. Figure 2(b) shows the image at 1000°C , and the images at other temperatures can be found in the Supplementary information. After cooling down to RT, a magnified image from the framed area in (b) is shown in (c), where it is seen that carbon layer fringes are still visible after heating, although some areas have become amorphous, possibly due to the heating as well as electron beam damage [19]. Quantitative measurements of the diameter of selected nanotube at different temperatures are plotted in (d), and the average diameter values are given in Table 1. It is seen that their size basically remains unchanged within the precision level of the measurement, although there are size fluctuations that are due to experimental error. It is known that the coefficient of thermal expansion (CTE) α is defined as

$$\alpha = \frac{dl}{l_0 dT}$$

where dl and dT are the changes in length and temperature, respectively, and l_0 is the original length. Suppose the sample radial CTE $\alpha = 2.9 \times 10^{-5} \text{ K}^{-1}$ [20], a nanotube with 3.6 nm diameter at 17°C would expand to 3.703 nm at 1000°C . Such a small change may not be accurately recorded, since the nanotubes may move or rotate during the heating process, as well as the sample drift and refocusing that may introduce magnification error.

The measurement error is estimated as $\pm (0.2\text{--}0.3)$ nm from the measurement results (Table 1). Therefore, no attempt is made to measure the thermal expansions from the TEM images.

The images of the functionalized CNT-COOH sample during the *in-situ* heating are shown in Figure 3, where size variations of 12 nanotubes are monitored. Completed images are presented in the Supplementary information. Surprisingly, it is found that even at a lower temperature (253 °C), most of the nanotubes are significantly expanded, such as 4, 6–10 and 12, indicating that the coalescence happens even at the lower temperature. As mentioned previously, unfunctionalized SWCNTs started to coalesce at 1800 °C, leading to a diameter increase from 1.4 nm to 3 nm mean diameter [12], and the DWCNTs showed even higher thermal stability, starting to coalesce at 2100 °C [13]. Therefore, the thermal stability of functionalized CNTs is very reduced. In the following heating process, their diameters continue to grow, while at about 500 °C their diameters keep almost the same size to 1007 °C (c and d). An image after cooling down to the RT is shown in (e), where it is seen that the nanotubes completely transform to an amorphous state. The measured size variations of selected nanotubes are shown in (f). It is seen that size expansion is inhomogeneous. For example, the nanotubes 1 and 2 have less variation as compared with others. Their average diameter is increased from 4.5 nm at RT to 7.9 nm at 500 °C, and finally 8.6 nm at 1007 °C (Table 1), with the final expansion of about 91%. It is apparent that such size expansion cannot be attributed to the measurement error.

In the CNT-COCl sample, it is also observed that the CNTs are unstable exhibiting similar unusual expansion during heating, as shown in Figure 4. The images at RT and 1000 °C are shown in (a) and (b), while other images at different temperatures are included in the Supplemental information. After cooling down to RT, the nanotubes are seen in an amorphous state (c). The size variations of selected nanotubes are plotted in (d). It is seen that their size largely increases, with averaged diameter (Table 1) from 3.6 nm (RT) to 7.2 nm (500 °C), and then tends to stabilize until 1000 °C (7.2 nm) so that the final averaged size has doubled.

The images of the CNT-F sample during heating are shown in the Figure 5, as well as in the Supplementary information. Similarly, the nanotubes largely expand from RT to 1000 °C (a and b). After cooling down to RT, the nanotubes are seen as amorphous structures (c). The size variations are shown in (d). The average size (Table 1) is 5.0 nm at RT, 8.6 nm at 500 °C, and 9.4 nm at 1000 °C, with final 88% expansion.

After heating, the samples are examined with EDS, and some typical EDS spectra from these three samples before and after heating are shown Figure 6. The Si signal mainly comes from the Si frame, as well as the silicon nitride support film that also contributes a nitrogen source. Therefore in the composition quantification, N is not counted. The results from multiple spots are listed in Table 2 (measurement standard deviations are also given). Despite the systematic error of the EDS especially for the light elements, by comparison of the EDS data before and after heating, it is found that the chemical elements are slightly reduced after heating, indicating that they partially evaporated during the heating process. Among them, S and F are evident in Figure 6. This is consistent with the results of a previous work that after heating to 720 °C in an ultrahigh vacuum, the concentration of surface oxygen atoms was found to decrease [14]. Therefore, the observed expansion of the functionalized CNT during the heating process is associated with the coalescence of the carbon structure, rather than a coating of additional foreign elements on their surfaces. The coalescence has been extensively observed in the past [12,13,21,22] and theoretically modeled [21–25]. In this work, the coalescence happens at low temperatures for those functionalized samples. It is apparent that the surface defects induced in the functionalization, as shown in Figure 1(b–d), are responsible for the reduced stability. In the

case of nanotube bundles, the coalescence was explicated through merging models of adjacent nanotubes as proposed previously [21–25]; however in the case of single nanotubes, the coalescence may be related to the carbon disordering and vacancies within the carbon multi-walls, forming amorphous structure as experimentally observed in Figures 3–5.

4. Conclusions

We have performed *in-situ* TEM observations of the functionalized CNTs to examine their thermal stability. The CNTs were functionalized with sulfuric and nitric acids, and some of them were further treated with thionyl chloride SOCl_2 , and with hydrofluoric acid as well. Untreated CNTs were also used for comparison, which were stable during the heating process, resulting in no detectable size variations by the TEM observation. However in all three types of functionalized CNTs, it was surprisingly found that their stability was significantly reduced as compared with the unfunctionalized CNTs. Quantitative measurement of the nanotube diameter indicated that the average size of functionalized CNTs was dramatically increased from RT to about 500 °C, and then it tended to be stable until about 1000 °C. The EDS analysis suggested the increase in size was due to the coalescence of the carbon structure, instead of coating of additional foreign elements on their surfaces.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Representative TEM images of the samples CNT (a), CNT-COOH (b), CNT-COCl (c) and CNT-F (d). An enlargement is inserted at the lower-right corner of each image.

Figure 2. TEM images of the unfunctionalized CNT sample during *in-situ* heating at RT (a), 1000 °C (b), and then cooled down to RT (c). The measured diameters of selected CNTs at different temperatures are plotted in (d).

Figure 3. TEM images of the functionalized CNT-COOH sample during *in-situ* heating at RT (a), 253 °C (b), 500 °C (c), 1007 °C (d), and then cooled down to RT (e). The measured diameters of selected CNTs at different temperatures are plotted in (f).

Figure 4. TEM images of the functionalized CNT-COCl sample during *in-situ* heating at RT (a), 1000 °C (b), and then cooled down to RT (c). The measured diameters of selected CNTs at different temperatures are plotted in (d).

Figure 5. TEM images of the functionalized CNT-F sample during *in-situ* heating at RT (a), 1000 °C (b), and then cooled down to RT (c). The measured diameters of selected CNTs at different temperatures are plotted in (d).

Figure 6. EDS spectra from samples CNT-COOH (a), CNT-COCl (b), and CNT-F (c) before and after heating.

Table 1

Average diameter d at different temperature T during *in-situ* heating.

T (°C)	d (nm)	CNT-COOH		CNT-COCl		CNT-F	
		T (°C)	d (nm)	T (°C)	d (nm)	T (°C)	d (nm)
17	3.6	17	4.4	16	3.6	17	5.0
130	3.6	263	7.6	105	5.0	125	5.7
250	3.4	500	7.9	255	6.8	250	7.6
500	3.6	590	8.3	500	7.2	500	8.6
750	3.5	730	8.6	750	7.2	750	9.1
900	3.5	830	8.6	1000	7.2	1000	9.4
1000	3.5	910	8.6				
		1007	8.6				

Table 2

Chemical composition of functionalized samples measured by EDS before and after heating (all at%).

Sample		C	O	S	Cl	F
CNT-COOH	Before heating	92.6 ± 1.5	6.5 ± 1.3	0.9 ± 0.5	N/A	N/A
	After heating	94.9 ± 0.4	4.4 ± 0.6	0.7 ± 0.4	N/A	N/A
CNT-COCl	Before heating	92.7 ± 3.3	5.9 ± 3.2	1.0 ± 0.2	0.4 ± 0.2	N/A
	After heating	94.3 ± 2.6	5.0 ± 2.4	0.4 ± 0.3	0.2 ± 0.2	N/A
CNT-F	Before heating	92.1 ± 2.0	2.7 ± 0.2	N/A	N/A	5.2 ± 1.8
	After heating	97.3 ± 0.9	2.2 ± 1.2	N/A	N/A	0.5 ± 0.3