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A Comparative Study of the Oxidation and Wet Chemical Methods for Uncapping the Multi-Walled Carbon Nanotubes

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Carbon nanotubes (CNTs) are generally capped at either end with a half of a fullerene. Hence, for storing different materials into the hollow space of CNTs, their caps need to be removed in the first step. In this study, we studied both the oxidation and wet chemical (acid-based) methods for opening the multi-walled carbon nanotubes (MWCNTs). In The oxidation method, 250 mg of CNTs were heated at 810 °C for 15 minutes in the air, and yielded about 56 % opened CNTs, while 78 % weight loss was recorded. The second sample with the same weight of the sample 1 was treated at 780 °C for 15 min. The weight loss and yielded uncapped CNTs were recorded 36 % and 47 %, respectively. The 780 °C was observed to be more appropriate than the higher temperature. In the acid-based method, the CNTs were refluxed in boiling nitric acid (65 % analar grade) at 110 °C for 12 h. In this case, about 80 % of the CNTs were thoroughly opened without any weight loss. The acid-based method was finally deduced to be more economical and efficient than the oxidation method.

Keywords: Carbon nanotube, Uncapping, Oxidation, Wet chemical.

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1. INTRODUCTION

Carbon nanotubes (CNTs) have attracted a lot of attention due to their excellent mechanical, thermal and electrical properties coming from their unique structure. CNTs possess high flexibility, low mass density, and large aspect ratio (typically > 1000), whereas predictions and some experimental data have indicated extremely high tensile moduli and strengths for these materials [1]. Since the documented discovery of the CNTs in 1991 by Iijima [2], and the realization of their unique properties, many investigators have endeavored to fabricate advanced composite materials using the CNTs.

Another fascinating aspect of carbon nanotubes is their hollow space, which can be used to incorporate different materials such as metals [3, 4], metal salts [5], hydrogen [6-10], water [11], and C60, CH4 and Ne [12] to generate novel compounds or nanostructured materials. Furthermore, carbon nanotubes can be modified to be used as nanoreservoirs of healing agent in self-healing nanocomposite. Since the CNTs are generally closed at either end, they need to be uncapped before storing the materials into their hollow space. Such closure is made possible by the presence of five-membered rings of the half a fullerene [13].

The carbon nanotubes can be uncapped by two methods: (i) oxidation at elevated temperatures [14], (ii) boiling CNTs in concentrated acids such as HNO_3 and H_2SO_4, known as wet chemical or acid-based method [15]. Tips of the CNTs are more reactive than their side walls. Subsequently, the tips of CNTs react prior to the side walls. Hence, by controlling the rate of oxidation and erosion, respectively in the oxidation and wet chemical methods, the side walls of the CNTs could be kept unchanged, while the tips are eliminated.

The oxidation method is simpler than the wet chemical method. In this method, the heating of the CNTs in the air at temperatures above 700 °C results in the etching away of the caps [14]. The side walls of the nanotubes are also observed to be attacked by the oxygen, but they seem to be much more resistant than the caps. In fact, the CNTs are attacked specifically at points where the curvature of the tube implies the presence of non-six-membered (probably five-membered) carbon rings [13]. High rate of weight loss in the CNTs is the main drawback of the oxidation method, in the spite of its simplicity. Therefore, the time and temperature conditions of the experiments need to be optimized in order to prevent the side walls damaging, while achieving desirable quantities of uncapped CNTs.

The second method is refluxing the carbon nanotubes in the boiling acid leading to removal of the caps rather than the side walls of the CNTs.

In this study, we conducted some experiments to study and compare the oxidation and acid-based methods.

2. EXPERIMENTS AND MATERIALS

The multi-walled carbon nanotubes (MWCNT) with the averaged internal diameter of about 5-10 nm, were purchased from Research Institute of Petroleum Industry (RIPI) of Iran [16].

2.1 The Oxidation Method

At temperatures below 700 °C, the CNTs exhibit high resistance against oxidation in air, but with increasing the temperature above 700 °C, the oxidation process takes place quickly [14].

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Two samples including 250 mg of the CNTs were prepared and oxidized in two temperature conditions, 780 °C and 810 °C, for 15 minutes in the air.

2.2 The Wet Chemical Method

250 mg of MWCNTs were refluxed in 10 ml of concentrated nitric acid (65 % analar grade) at 110 °C for 12 h. Then the temperature was gradually decreased down to the room temperature and the sample was kept at this condition for 4 h. Finally, the sample was dried at 150 °C for 30 minutes.

3. RESULTS AND DISCUSSION

In the oxidation method, heating the CNTs at about 810 °C in the air for 15 min, resulted in the etching away of the tube caps and also erosion of the side walls of CNTs, and subsequently, the high weight loss of the sample 1 (78 %wt). Using the images of Transmission Electron Microscopy (TEM), the approximate percentage of the opened nanotubes in sample 1 was estimated to be 56%. TEM images of the sample 1 revealed serious damage in the side walls of the CNTs. To avoid this, the temperature of the experiment for the sample 2 was decreased to 780 ° to reduce the reaction intensity and erosion of the side walls. After 15 min of oxidation of the sample 2, the approximate percentage of opened nanotubes and weight loss were estimated to be 47% and 36 %, respectively. The conditions of experiments and the results for two samples are summarized in Table 1.

The resulted TEM images of the sample 1 are represented in Fig. 1. Obviously that the oxidation reaction has caused the removal of the tips and also erosion of the side walls of the CNTs.

For the sample 2 (heated at 780 °C for 15 minutes), the tips were again opened successfully, while much less damaged side walls were detected from TEM images. It means that for sample 2, the oxidation reaction occurs preferentially at the tubes ends instead of the outer layers of side walls. Hence, the recorded weight loss of the sample 2 was less than that of sample 1.

The TEM images of the treated nanotubes in sample 2 are shown in Fig. 2. It is evident from Fig. 2 that the nanotubes have been effectively opened without any serious damage in the side walls. From the results it is clear that by decreasing the temperature from 810 °C to 780 °C, the erosion of the side walls and also the weight loss percentage can be greatly decreased.

In the wet chemical method, the weight of the treated CNTs was interestingly recorded to be about 290 mg, i.e. 40 mg more than the primary value. It is probably due to little amounts of nitric acid remained in the treated sample, either attached to the side walls or absorbed into of CNTs. Fig. 3 shows TEM images of CNTs treated by nitric acid. Remained nitric acid can be recognized from the figure.

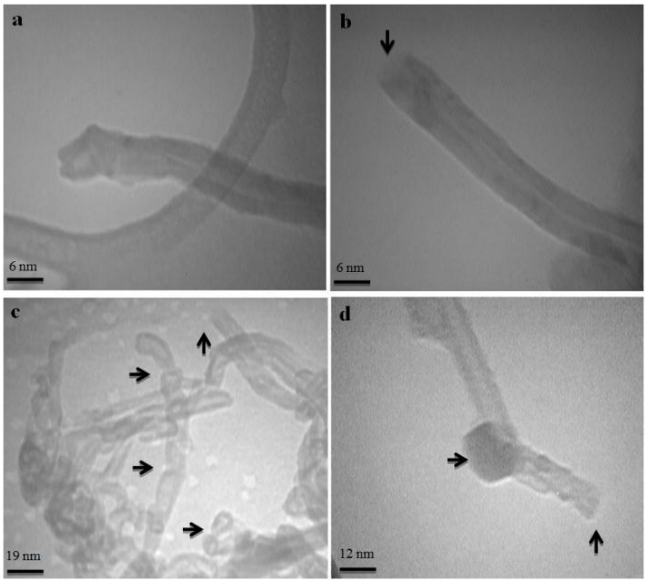

Fig. 1 – TEM images of carbon nanotubes in sample 1 before any treatment (a), completely uncapped CNT heated at 810 °C (b), and the CNTs with damaged side walls heated at 810 °C (c, d). The vertical and horizontal arrows show the opened tips and damaged side walls of the CNTs, respectively

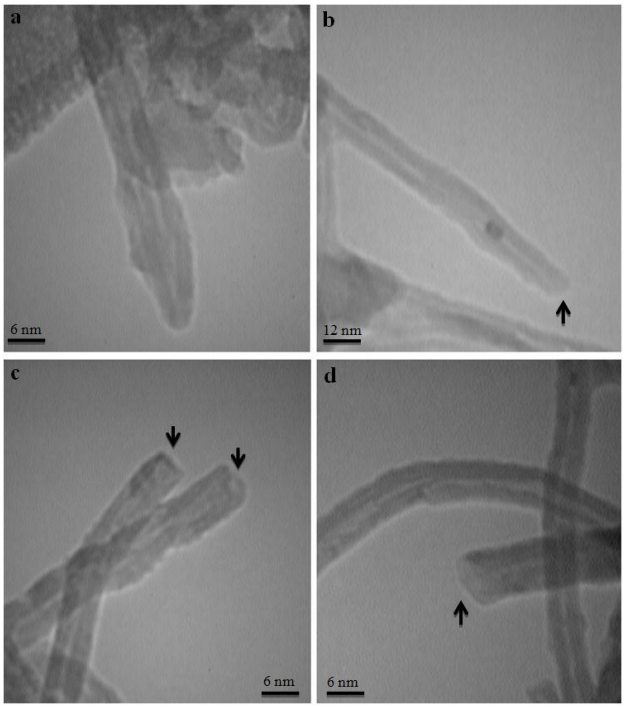

Fig. 2 – TEM images of carbon nanotubes in sample 2 before any treatment (a), completely uncapped CNT with undamaged side walls, heated at 780 °C (b, c, d). The arrows show the opened tips of the CNTs

Table 1 – The approximate percentage of the opened CNTs and the weight losing percentage for two samples that was opened by Oxidation method

Sample Number	Temperature (°C)	Primary Weight (mg)	Final Weight (mg)	Weight loss (% wt)	Estimated Opened CNTs (%)
1	810	250	55	78	56
2	780	250	160	36	47

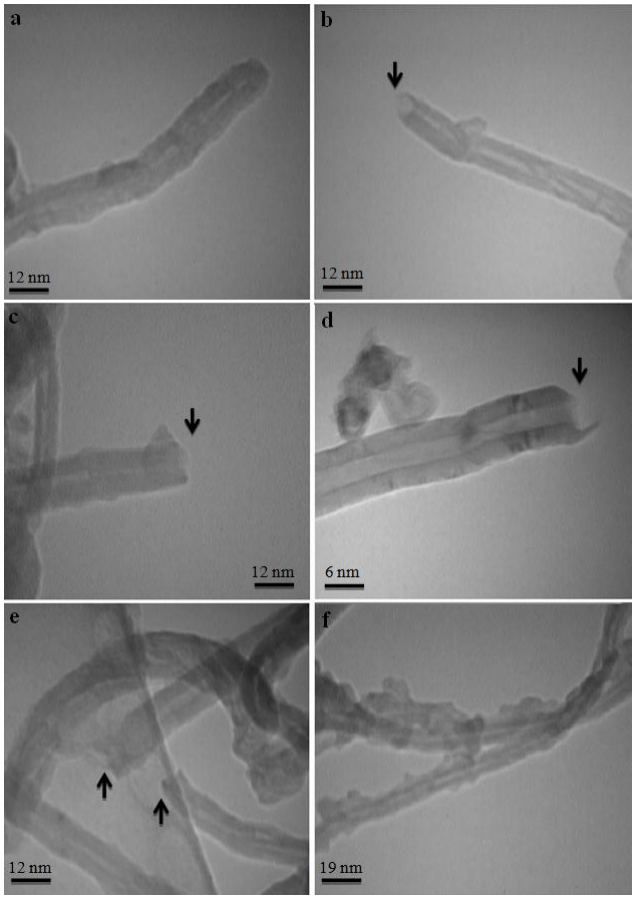

Fig. 3 – TEM images of CNTs before any treatment (a), and after treatment using the wet chemical method (b, c, d, e, f). The remained nitric acid can be distinguished. The arrows show the opened tips of nanotubes

Analyzing the TEM images revealed that the wet chemical method yielded about 80 % successfully uncapped CNTs. This method was observed to be more economical and effective than the oxidation method. The percentage of opened CNTs for acid-based method was about 30 % more than that of oxidation method. This percentage for oxidation method was recorded about 47 % at the optimal condition (heating the CNTs at 780 °C for 15 min in air atmosphere). Almost no damage was detected in the side walls of the CNTs treated with nitric acid. The achieved results from both the oxidation and wet chemical methods are summarized in Table 2.

4. CONCLUSIONS

In this study, both oxidation and wet chemical (acid-based) methods were employed for uncapping the closed multi-walled carbon nanotubes. In the oxidation method, two samples with the weight of 250 mg were prepared and heated at 810 °C and 780 °C for 15 min in the air atmosphere. At 810 °C, about 56 % of CNTs were opened, while substantial portion of the CNTs were damaged in their side walls, and the measured weight loss was considerable. Treating the sample 2 at 780 °C significantly reduced the erosion of the outer layers of the side walls.

The wet chemical method (refluxing CNTs in boiling nitric acid at 110 °C for 12 h) observed to be more effective than the oxidation method. About 80 % of the treated carbon nanotubes were opened without any weight loss. Furthermore, the weight of the sample was increased about 40 mg, due to existence of little amounts of the nitric acid. The main drawback of the acid-based method is the long process time. Increasing the temperature can reduce the process time; however, it may lead to dissipation of the nitric acid without yielding desirable amounts of uncapped nanotubes.

Table 2 – Comparison of the conditions and results of the wet chemical and oxidation methods

Method		Weight (mg)			Temperature (°C)	Time	Opened CNTs (%)
		primary	final	loss (% wt)			
Wet chemical		250	290	0	110	~ 16 h	80
Oxidation	Sample 1	250	55	78	810	15 min	56
	Sample 2	250	160	36	780	15 min	47

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