

Uncapping Multi-Walled Carbon Nanotubes Using Wet Chemical and Oxidation Methods

Behrouz Arab*, Ali Shokuhfar, Mahdi Valinejad, Ashkan Zolriasatein

*Advanced Materials and Nanotechnology Research Lab, Faculty of Mechanical Engineering,
K. N. Toosi University of Technology, Tehran, Iran*

(Received 27 June 2012; published online 08 August 2012)

Different materials can be introduced into hollow space of carbon nanotubes and result in very useful nanostructures for different applications such as energy storage, self-healing materials, nanocomposites, etc. In this study, the multi-walled carbon nanotubes were uncapped using two methods, oxidation with carbon dioxide or oxygen at elevated temperatures, and boiling carbon nanotubes in concentrated nitric acid (wet chemical method). In the oxidation method, the carbon nanotubes were heated at about 830 °C in air atmosphere for 15 minutes. In the second method, the CNTs were refluxed in boiling HNO₃. The chemical method was found to be more effective than the oxidation method, since the number of opened nanotubes was about 60 % more than that in oxidation method. Furthermore, unlike the oxidation method, no weight loss was observed in the chemical method.

Keywords: Carbon nanotube; Wet chemical method; Oxidation method; Capillarity of CNTs; Uncapping.

PACS number: 61.48.De

1. INTRODUCTION

Carbon nanotubes (CNTs) have superior properties, making them attractive materials for a wide range of industries from household appliances to aerospace. CNTs possess high flexibility, low mass density, and large aspect ratio (typically >1000), whereas predicted and some experimental data indicate extremely high tensile moduli and strengths for these materials [1].

Since the discovery of carbon nanotubes in 1991 by Iijima [2], considerable amount of research activities has been focused on using CNTs in different fields due to their unique physical, mechanical, thermal, and electrical properties. For instance, they can be used as reinforcement in composite materials, because the CNT-reinforced composites have been observed to have more strength than the other types of nanocomposites.

Another fascinating aspect of carbon nanotubes is their hollow space, which can be used to incorporate different organic and inorganic materials and generate novel compounds or nanostructured materials. Although carbon nanotubes are generally closed at either end due to presence of five-membered rings [3], they can be modified into nano composite fibers by simultaneous opening of the caps and filling the interior space with an organic or inorganic phase. Since the carbon nanotubes have a high capillary rise, considerable amounts of liquids and solids can be stored inside them.

Using CNTs as nanoreservoirs in self-healing materials is one of newly emerged ideas in the field of smart materials. In practice, there are three challenging issues related to this concept: (i) opening capped CNTs, (ii) storing the healing agent into the hollow space of the CNTs, and (iii) rupturing the walls of CNTs when facing the crack, followed by release of the healing agent. These challenges are dealt with, to some extent, in some research studies. Some of them developed approaches to open the end-capped CNTs [4-8]. Some others investigated the storage of metals [9, 10], metal salts [11], hydrogen [12-16], water molecules [17], DNA [18], C₆₀, CH₄ and Ne [19], noble gases [20], and car-

bides [10]. Some others focused on fracture behavior of the CNTs under different loading conditions [21-24]. It seems that in presence of a perfect cohesive interface between the matrix and CNTs, and regarding the high stress intensity at the crack tip, the rupture of the CNTs walls is likely to occur when facing a propagating crack. The third challenge was investigated by Lanzara et al. [25] through the molecular dynamic simulations. It was concluded that the healing agent can be released from the ruptured CNT at a reasonable time interval.

In this study we tried to deal with the first challenge. The oxidation and wet chemical methods have been used separately in individual studies [4, 8]. We conducted some experiments based on the opening of multi-walled carbon nanotubes using both the oxidation and wet chemical methods, in order to compare the results in terms of efficiency, productivity, time length, etc.

2. MATERIALS AND EXPERIMENTS

The multi-walled CNTs with an averaged internal diameter of about 5 nm, were purchased from Research Institute of Petroleum Industry (RIPI) of Iran [26].

2.1 Oxidation

Carbon nanotubes show a fairly high resistance to oxidation (negligible weight loss) up to some critical temperature (700 °C in air atmosphere), above which the oxidation proceeds rapidly [4].

In the first experiment, 250 mg of the Multi-Walled carbon nanotubes was heated at about 830 °C and air atmosphere for 15 minutes.

2.2 Wet Chemical Method

In the second method, 250 mg of multi-walled carbon nanotubes was refluxed in 10 ml of concentrated nitric acid (65% analar grade) and heated at 110 °C for 12h. Then the temperature was reduced down to the room temperature and the sample was kept at this condition for 4h. Eventually the sample was dried at 150 °C for 30 min and the excess of the acid was removed.

* arab@dena.kntu.ac.ir

3. RESULTS AND DISCUSSION

In the oxidation method, the heating of the CNTs resulted in the etching away of the tube caps and the weight loss. The weight of CNTs after the experiment was 120mg. A weight loss of %52 was recorded here. The TEM images of the nanotubes opened through the oxidation method is depicted in Fig. 1.

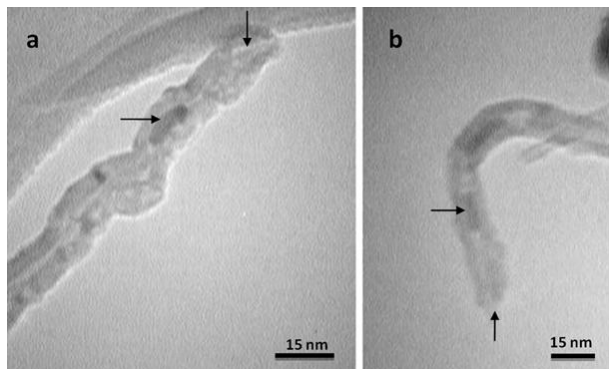


Fig. 1 – TEM images of carbon nanotubes opened by oxidation in air atmosphere at 830 °C for 15 min. the vertical arrows show the tube tips opened during heating. The horizontal arrows show the impurities inside the CNT after uncapping

From the figure, it is evident that the oxidation reaction occurs preferentially at the tips of nanotubes. More than 35% of the nanotubes were completely opened. By increasing the time duration and temperature, this percentage can be increased. However, the weight loss of CNTs will be increased too. Also, it worth mentioning that by decreasing the temperature down to 750 °C - 800 °C, the weight loss will be reduced, while the percentage of the opened nanotubes would be same as the previous value.

The Chemical method (refluxing CNTs in boiling acid) is the best method for the opening of CNTs that is reported so far. This method was applied here and about 80% of nanotubes were successfully opened after being refluxed in the boiling acid nitric for the 16h at 110 °C. No weight loss was observed here. The TEM images of the treated nanotubes are shown in Fig. 2.

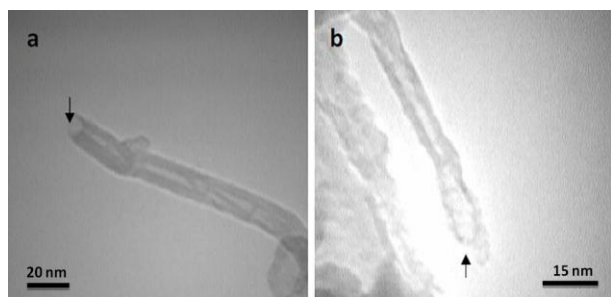


Fig. 2 – TEM images of carbon nanotubes opened by wet chemical method. The arrows show the uncapped tubes

The weight of treated CNTs after the experiment was 290 mg, i.e. 40 mg more than the primary amount, mainly due to the fact that the CNTs were filled with little amounts of nitrate compounds. Fig. 3 shows the TEM images of opened CNTs.

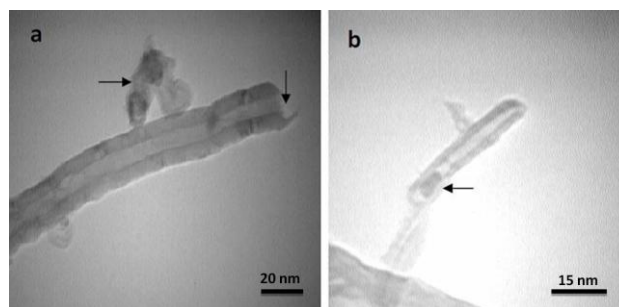


Fig. 3 – The nitrate compounds, (a) on the outer wall of the CNTs, and (b) inside the opened CNTs.

The obtained nitrate compounds located inside and outside the CNTs are depicted by horizontal arrows. The results are summarized in Table 1.

Table 2 – Comparison of the results of chemical and oxidation methods.

Method	Weight (mg)			Temperature (°C)	Time	Opened CNTs (%)
	Primary	Final	Loss (%)			
Wet Chemical	250	290	0	110	12h	>80
Oxidation	250	120	52	830	15 min	>40

4. CONCLUSIONS

In this study, both oxidation and wet chemical methods were employed for uncapping the closed multi-walled carbon nanotubes. In the oxidation method, the carbon nano tubes was heated at about 830 °C in the air atmosphere for 15 min, and more than 25% of the tubes was completely opened. In the second method, the CNTs were refluxed in boiling nitric acid and about 80% of carbon nanotubes was opened at their ends.

As was mentioned, both the oxidation and chemical methods led to the opening of the nanotubes. But the chemical method was observed to be more effective than the oxidation method. In the chemical method, the amount of opened nanotubes was about 60% more than that achieved by oxidation method. Furthermore, the chemical method caused no weight loss, while in the oxidation method, up to 52% weight loss was observed, at temperatures more than 750°C. Actually, both the efficiency and weight loss are temperature-dependent in the oxidation method, and thus, there should be a trade-off between these two factors so that an appropriate temperature could be applied to the experiments.

In the chemical method, on the other hand, negligible amounts of impurities and nitrate compounds are inevitable. In order to reduce the time of experiments in chemical method, the temperature can be increased up to about 120°C, above which, the acid will be dissipated without yielding remarkable amounts of uncapped nanotubes.

ACKNOWLEDGEMENTS

The authors would like to thank the supports from K. N. Toosi University of Technology and Iran Nanotechnology Initiative Council (INIC).

REFERENCES

1. Z. Spitalsky, D. Tasis, K. Papagelis, C. Galiotis, *Prog. Polym. Sci.* **35**(3), 357 (2010).
2. S. Iijima, *Nature* **354**(6348), 56 (2010).
3. B. Satishkumar, A. Govindaraj, J. Mofokeng, G. Subbanna, C. Rao, *J. Phys. B: At. Mol. Opt. Phys.* **29**, 4925 (2010).
4. P. Ajayan, T. Ebbesen, T. Ichihashi, S. Iijima, K. Tanigaki, H. Hiura, *Nature* **362**(6420), 522 (2010).
5. R.S. Ruoff, D.C. Lorents, B. Chan, R. Malhotra, S. Subramoney, *Science* **259**(5093), 346 (2010).
6. S. Seraphin, D. Zhou, J. Jiao, J.C. Withers, R. Loutfy, *Appl. Phys. Lett.* **63**(15), 2073 (2010).
7. S. Seraphin, D. Zhou, J. Jiao, J.C. Withers, R. Loutfy, *Nature* **362**(6420), 503 (2010).
8. S.C. Tsang, Y.K. Chen, P.J.F. Harris, M.L.H. Green, *Nature* **372**(6502), 159 (2010).
9. N. Demoncey, O. Stephan, N. Brun, C. Colliex, A. Loiseau, H. Pascard, *Eur. Phys. J. B: Condens. Matter Complex Syst.* **4**(2), 147 (2010).
10. Y. Saito, T. Yoshikawa, M. Okuda, N. Fujimoto, K. Sumiyama, K. Suzuki, *J. Phys. Chem. Solids* **54**(12), 1849 (2010).
11. D. Ugarte, T. Stöckli, J. Bonard, A. Chatelain, W. De Heer, *Appl Phys A: Mater. Sci. Process* **67**(1), 101 (2010).
12. H. Dodziuk, G. Dolgonos, *Chem. Phys. Lett.* **356**(1), 79 (2010).
13. Z. Zhou, J. Zhao, Z. Chen, X. Gao, T. Yan, B. Wen, *J. Phys. Chem. B* **110**(27), 13363 (2010).
14. Cheng, A.C. Cooper, G.P. Pez, M.K. Kostov, P. Piotrowski, S.J. Stuart, *J. Phys. Chem. B.* **109**(9), 3780 (2010).
15. M. Hirscher, M. Becher, *J. Nanosci. Nanotechnol.* **3**(1-2), 3 (2010).
16. C. Liu, Y.Y. Fan, M. Liu, H.T. Cong, H.M. Cheng, M.S. Dresselhaus, *Science* **286**(5442), 1127 (2010).
17. A. Berezhtskii, G. Hummer, *Phys. Rev. Lett.* **89**(6): 64503 (2010).
18. H. Gao, Y. Kong, D. Cui, C.S. Ozkan, *Nano Lett.* **3**(4): 471 (2010).
19. B. Ni, S.B. Sinnott, P.T. Mikulski, J.A. Harrison, *Phys. Rev. Lett.* **88**(20): 205505 (2010).
20. M.K. Kostov, M.W. Cole, J.C. Lewis, P. Diep, J.K. Johnson, *Chem. Phys. Lett.* **332**(1), 26 (2010).
21. T. Dumitrică, T. Belytschko, B.I. Yakobson, *J. Chem. Phys.* **118**, 9485 (2010).
22. T. Belytschko, S. Xiao, G. Schatz, R. Ruoff, *Phys. Rev. B* **65**, 235430 (2010).
23. A.H. Barber, S.R. Cohen, A. Eitan, L.S. Schadler, H.D. Wagner, *Adv. Mater.* **18**(1), 83 (2010).
24. J.M. Wernik, S.A. Meguid, *Acta Mech.* **212**(1), 167 (2010).
25. G. Lanzara, Y. Yoon, H. Liu, S. Peng, W. Lee, *Nanotechnology* **20**, 335704 (2010).
26. Research Institute of Petroleum Industry (RIPI) of Iran, <http://www.ripi.ir/index.php>.