Asian Journal of Chemistry; Vol. 30, No. 11 (2018), 2429-2432

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2018.21426

Preparation and Characterization of Carbon Nanotubes using Carbon Black by Electrochemical Technique with Anodic Aluminium Oxide

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Received: 5 May 2018; *Accepted*: 6 July 2018; *Published online*: 27 September 2018; AJC-19089

This study describes preparation and characterization of carbon nanotubes (CNTs) by anodic aluminium oxide (AAO) template assisted electrochemical deposition. A highly ordered array of cylindrical designed pores of anodic aluminium oxide was obtained from anodizing aluminum to use it as a template for deposition of carbon nanotubes. The fabrication of carbon nanotubes was done using moraine of micrometer sized carbon black with diameter range of 0.5-75 μm. The characterization of carbon nanotubes was done by FTIR, SEM and AFM indicating the formation of carbon nanotubes within anodic aluminium oxide template by electrodeposition at room temperature. FTIR spectrum indicated the presence of peaks of CH_x group associated with O-H, in addition to appear COOH group after functionalization of carbon nanotubes with (HNO_3-H_2SO_4) mixture to obtain functionalized carbon nanotubes (F-CNTs). The SEM morphology confirmed the fabrication of nanotube by appearing opened ends of tubes with nano dimensions. The atomic force microscopy analysis gave smother surface with more average diameters from 66.3 to 77.21 nm for F-CNTs compared with carbon nanotubes due to formation carboxylic groups.

Keywords: Carbon nanotubes, Carbon black, Anodized aluminum oxide, Electrochemical deposition.

INTRODUCTION

Carbon nanotubes were discovered in 1990s, they are like graphite sheets rolled up with fullerene end caps and there are two types of carbon nanotubes; single wall with a diameter of ≈ 1.4 nm and multiwall nanotubes with an outer diameter of 30-50 nm [1]. These nanotubes are strongest and hardest material due to the chemical bonding in their structure which based on sp^2 orbital bond [2] in addition to the flexible hexagonal network of carbon atoms [3,4], while their morphology is different and depended on the methods of preparation [5,6]. There are many used methods to prepare carbon nanotubes, among them is using anodic aluminum oxide (AAO) template to deposit carbon nanotubes in addition to nanodots, nanowires, nanopillars, *etc*. [7,8]. Other methods of preparation carried out by arc discharge [9,10], chemical vapor deposition (CVD) [11,12] and laser ablation [13,14].

This work aims to convert the micrometer sized material to nanostructured material by a simple method. Carbon nanotubes were fabricated by templates of anodized aluminum oxide (AAO) through simple electrochemical deposition using locally available materials (carbon black) at room temperature and then functionalized them for different applications. The present method represents simple way to synthesis with excellent uniformity of carbon nanotubes obtained and the short process time compared with the conventional carbon nanotube synthesis methods, where the synthesis of carbon nanotubes by Dadras and Faraji [15] needs high energy using microwave oven and the synthesis using Ni/AAO needs catalyst to prepare carbon nanotubes from waste plastics by Liu *et al*. [16] and the method of Hou *et al*. [17] by anodized aluminum oxide (AAO) is complex method includes several steps such as carbonize organic polymer within anodized aluminum oxide (AAO) and then deposit pyroltic carbon from gaseous hydrocarbons [17].

EXPERIMENTAL

Synthesis of anodized aluminum oxide (AAO): Aluminum foil with purity 99.99 % and area of (10 cm × 10 cm) and

thickness (0.3 mm) was used as an anode in the electrochemical cell, while stainless steel 306 L used as a cathode in 0.3 M oxalic acid. Ethanol, acetone, 3M NaOH, a mixture of (H_3PO_4 + H_2CrO_4) acids and 5 % H_3PO_4 were used as a cleaning and treating reagents in addition to electrolytes for dissolving the template after deposition of carbon nanotubes. The anodization of aluminum was done with two steps according to the literature [18,19].

Deposition of carbon nanotubes: Carbon electrode with a length of 12 cm and diameter of 1 cm was used as an anode in the electrochemical cell using prepared anodized aluminum oxide as a cathode with carbon nanopowder in 30 g/L of boric acid. After deposition at 1.5 volt for 30 min, deposited carbon nanotubes were filtered and washed with deionized water at room temperature. Carbon black (50 g) obtained from Babylon Tires factory was milled by planetary mill with balls for a period time 30 h.

Functionalization of carbon nanotubes: Carbon nanotubes (0.5 g) as nanopowder was added to 250 mL of conc. H_2SO_4/HNO_3 with a ratio of 3:1. The mixture solution was then cooled and ultrasonicated for 30 min at 25-30 ºC using ultrasonic mixing liquid (MTI corporation: USA) and then centrifuged at 2500 rpm for 20 min. Then, MWCNTs were washed with deionized water and centrifuged for several times. The additional step was purification the mixture by qualitative filter paper with (0.1 μ). Finally, carbon nanotubes were collected and dried in air for one week.

RESULTS AND DISCUSSION

Analysis of particle size of the started material (carbon black) is shown in Fig. 1, which indicates that the particle size is within micrometer. Fig. 2 shows the XRD pattern of carbon black which is a good agreement with JCPDS card No. 03-0401 for carbon as graphite with strongest peaks at 2θ = 25.9225º (002), 43.6464º (101) and 77.5845º (110). The FTIR of fabricated carbon nanotubes with two dominant peaks: 1649 and 3468 cm^{-1} (O-H). Several peaks (Fig. 3) in the range of 3000 cm^{-1} are attributed to CH_x groups. The vibration at near 1593 cm^{-1} indicated the presence of cylinder like carbon structure (rolled graphene sheet). Several bands near 1580 cm^{-1} is referred to active modes in infrared spectrum and depending on the geometry of the carbon nanotube and its diameter as observed by Jishi *et al*. [20].

In the FTIR spectrum of functionalized carbon nanotubes, there are two dominant peaks *viz*., 3483 & 1652 cm^{-1} and another

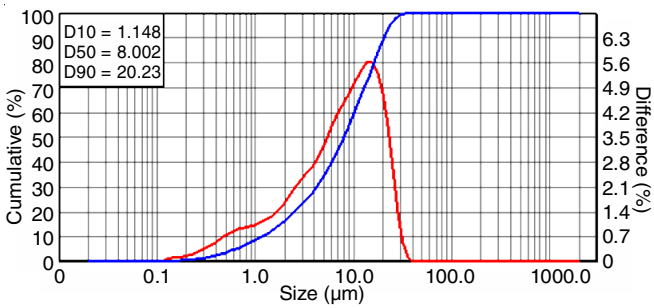

Fig. 1. Particle size analysis of carbon black

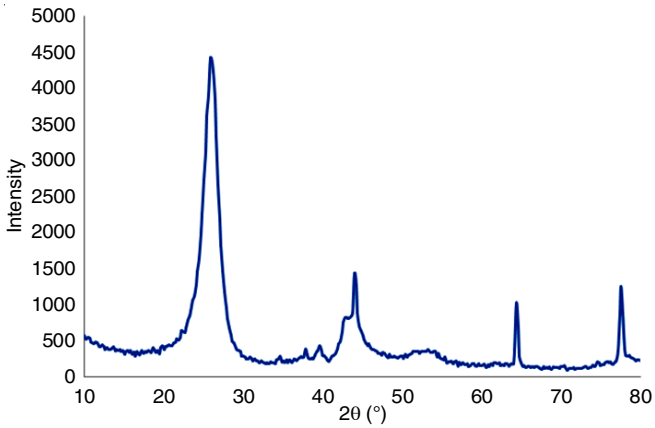

Fig. 2. XRD of carbon black

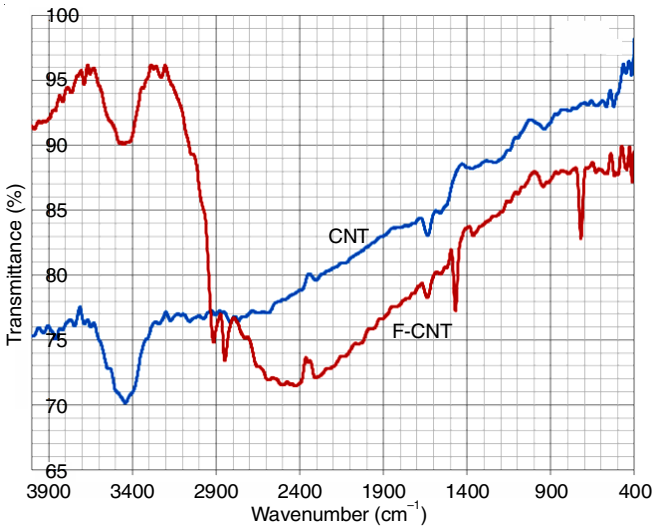

Fig. 3. FTIR spectra of CNTs and F-CNTs

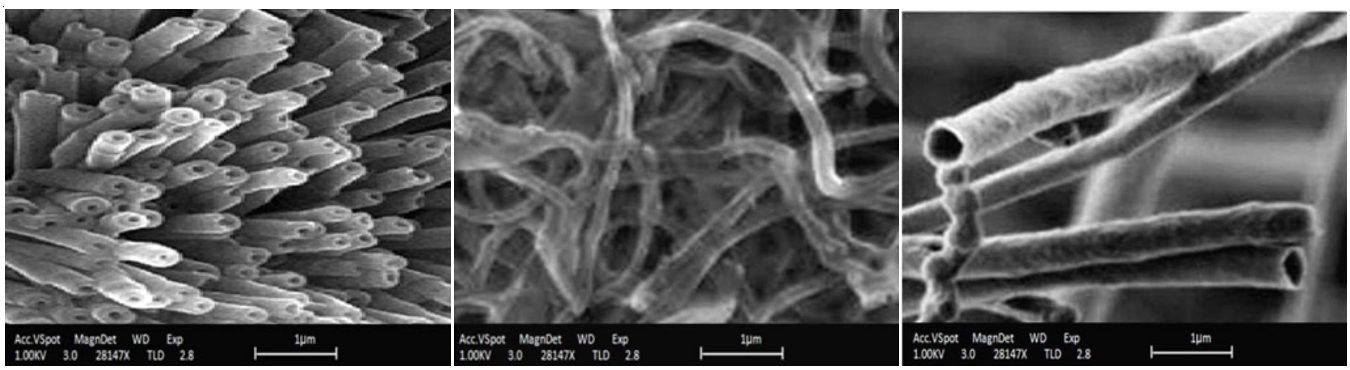

Fig. 4. SEM of carbon nanotubes

peak at 1472 cm^{-1} agreed with the observation of Misra *et al.* [21]. The peak presented at 1450 cm^{-1} is a unique to MWCNTs as referred by Kouklin *et al.* [22]. The broader band at 3400 cm^{-1} is attributed to COOH groups, while several peaks in the range of 3000 cm^{-1} range are attributed to CH_x groups [22].

SEM images of functionalized carbon nanotubes are shown in Fig. 4. These morphologies indicated the nanotubes after partially dissolved of AAO template which appeared as multi arrays (MWCNTs) having an outer diameter of 30-80 nm and inner diameter ranged between 8-15 nm. After complete dissolution of AAO, the nanotubes as associated here with a length of 10-20 μm. While the morphology of single nanotubes confirm the obtaining tubes with opened end not nanowires or nanorods. The EDS analysis of carbon nanotubes is shown in Fig. 5 confirmed the generation of the carbon nanotubes under experimental conditions.

AFM images for CNTs and F-CNTs are shown in Figs. 6 and 7, respectively. These figures show 2D and 3D images for fabricated tubes, AFM gives information only about the length of nanotubes and approximate value of the bundles diameter. The functionalization gives more order in a carbon nanotube with less valley depth. Also, the functionalization of carbon

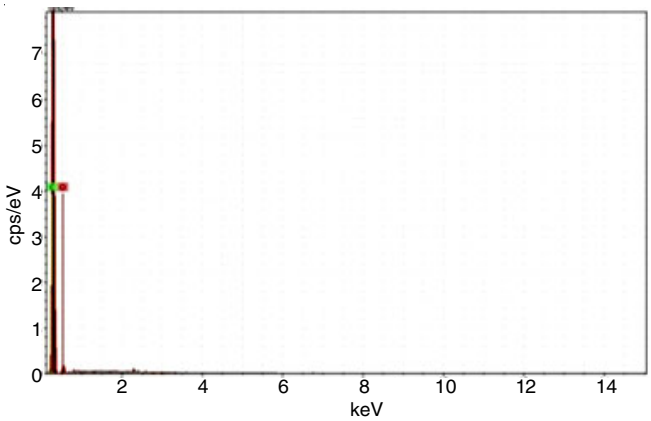

Fig. 5. EDS of carbon nanotubes

nanotubes gave a reduction in roughness average from 2.26 to 0.162 nm due to carboxylic groups which appeared due to functionalization and by formation H-bonding, henceforth smoother surface obtained. Formed carboxylic groups gave more average diameters (Fig. 8), where average diameter was increased from 66.3 to 77.21 nm. The diameters having less than 10 % were decreased, while the diameters that more than 10-90 % were increased.

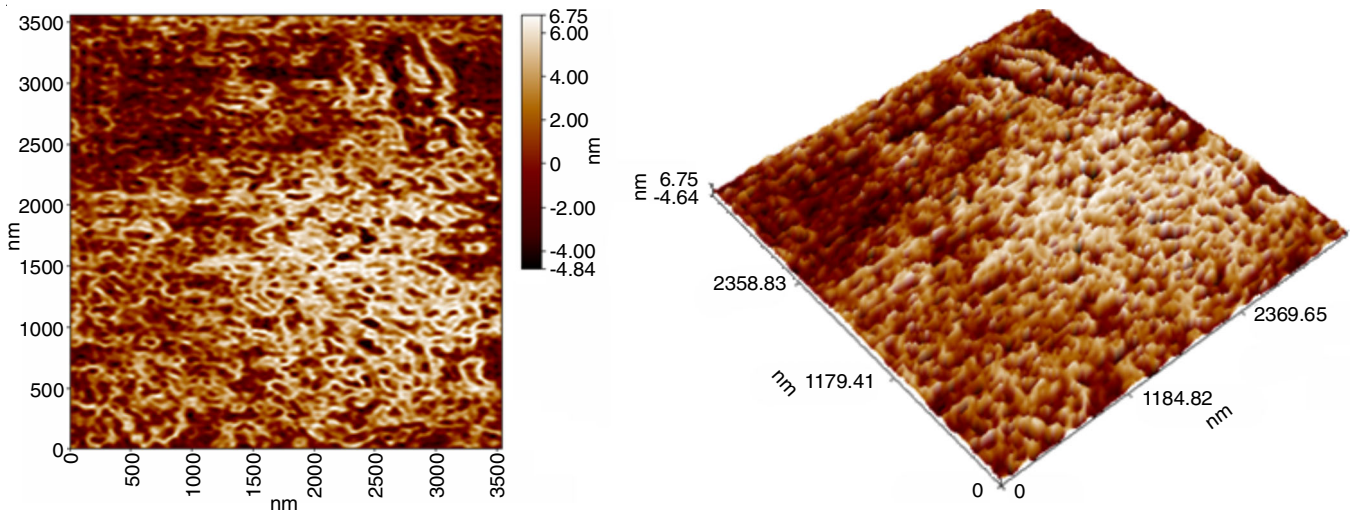

Fig. 6. AFM images of carbon nanotubes

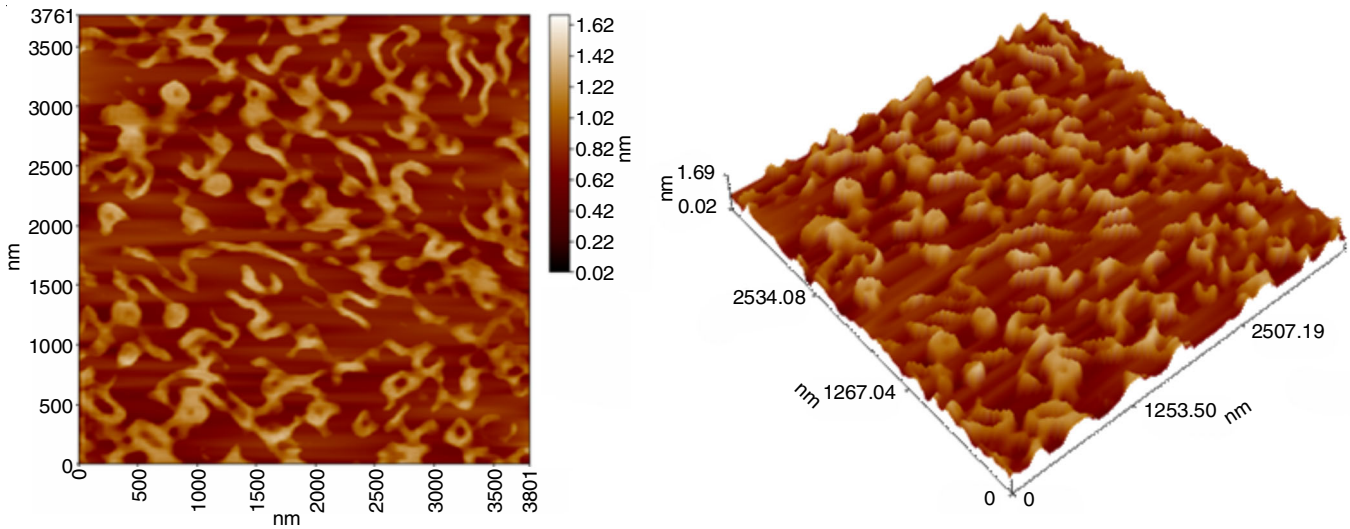

Fig. 7. AFM images of functionalized carbon nanotubes

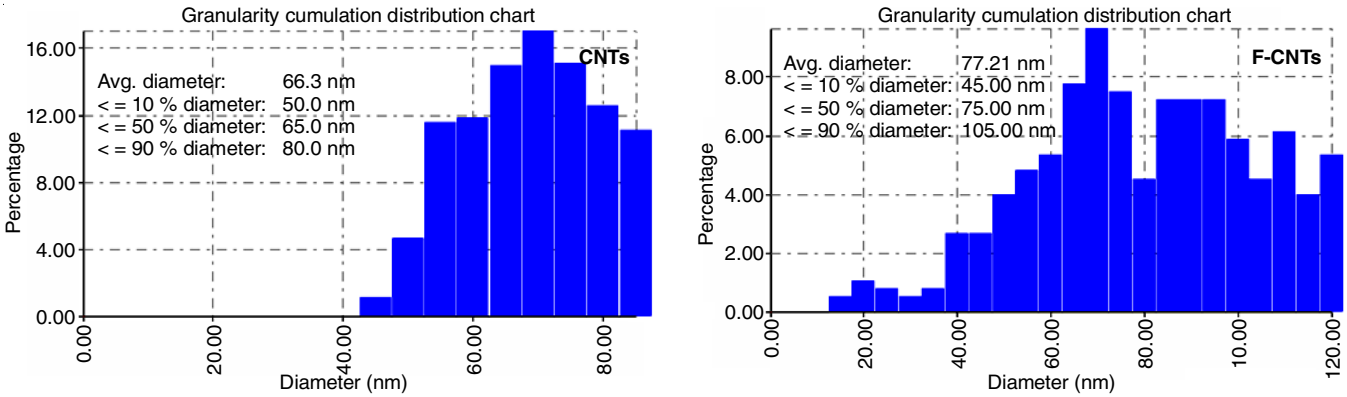

Fig. 8. Granularity accumulation distribution for CNTs and F-CNTs

Conclusion

In this research, carbon black was converted to carbon nanotube by a simple method at room temperature. The fabricated carbon nanotubes were characterized by SEM, EDS, FTIR and AFM. These characterization results confirmed the formation of carbon nanotubes. Then, functionalization of these carbon nanotubes was done to be used in many fields as reinforcement.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. F. Luisa and S. Duncan, Nanotechnologies: Principles, Applications, Implications and Hands-On Activities, European Commission (2013).
2. B. Peng, M. Locascio, P. Zapol, S. Li, S.L. Mielke, G.C. Schatz and H.D. Espinosa, *Nat. Nanotechnol.*, **3**, 626 (2008); https://doi.org/10.1038/nnano.2008.211.
3. D. Qian, G.J. Wagner, W.K. Liu, M.-F. Yu and R.S. Ruoff, *Appl. Mech. Rev.*, **55**, 495 (2002); https://doi.org/10.1115/1.1490129.
4. K. Bordo, Ph.D. Thesis, Nanoporous Thin Film Templates for the Fabrication of Nanowires and Nanotubes, NanoSYD, Mads Clausen Institute University of Southern Denmark (2011).
5. S. Iijima, C. Brabec, A. Maiti and J. Bernholc, *J. Chem. Phys.*, **104**, 2089 (1996); https://doi.org/10.1063/1.470966.
6. P.M. Chaudhari, S.C. Daswadkar and P.V. Kasture, *J. Pharm. Res.*, **2**, 1179 (2009).
7. H. He, L.A. Pham-Huy, P. Dramou, D. Xiao, P. Zuo and C. Pham-Huy, *BioMed. Res. Int.*, **Article ID 578290** (2013); https://doi.org/10.1155/2013/578290.
8. G.D. Sulka, ed.: A. Eftekhari, Highly Ordered Anodic Porous Alumina, Formation, by Self-Organized Anodzing, section 1.2.1 Types of Anodic Oxide Film, In: Nanostructured Materials in Electrochemistry, Wiley-VCH Verlag GmbH & Co. KGaA, Chap. 1 (2008).
9. D.S. Bethune, C.H. Kiang, M.S. de Vries, G. Gorman, R. Savoy, J. Vazquez and R. Beyers, *Nature*, **363**, 605 (1993); https://doi.org/10.1038/363605a0.
10. S. Iijima, *Nature*, **354**, 56 (1991); https://doi.org/10.1038/354056a0.
11. R. Fu, M.S. Dresselhaus, G. Dresselhaus, B. Zheng, J. Liu, J. Satcher Jr. and T.F. Baumann, *J. Non-Crystalline Solids*, **318**, 223 (2003); https://doi.org/10.1016/S0022-3093(02)01903-8.
12. G. Che, B.B. Lakshmi, C.R. Martin, E.R. Fisher and R.S. Ruoff, *Chem. Mater.*, **10**, 260 (1998); https://doi.org/10.1021/cm970412f.
13. A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y.H. Lee, S.G. Kim, A.G. Rinzler, D.T. Colbert, G.E. Scuseria, D. Tomanek, J.E. Fischer and R.E. Smalley, *Science*, **273**, 483 (1996); https://doi.org/10.1126/science.273.5274.483.
14. T. Guo, P. Nikolaev, A.G. Rinzler, D. Tomanek, D.T. Colbert and R.E. Smalley, *J. Phys. Chem.*, **99**, 10694 (1995); https://doi.org/10.1021/j100027a002.
15. S. Dadras and M. Faraji, *J. Phys. Chem. Solids*, **116**, 203 (2018); https://doi.org/10.1016/j.jpcs.2018.01.039.
16. X. Liu, B. Shen, P. Yuan, D. Patel and C. Wu, *Energy Procedia*, **142**, 525 (2017); https://doi.org/10.1016/j.egypro.2017.12.082.
17. P.X. Hou, C. Liu, C. Shi and H.M. Cheng, *Chin. Sci. Bull.*, **57**, 187 (2012); https://doi.org/10.1007/s11434-011-4892-2.
18. R.A. Anaee, A.H. Ali and A.R. Hassan, *Asian J. Chem.*, **28**, 2529 (2016); https://doi.org/10.14233/ajchem.2016.20078.
19. R.A. Anaee, A.H. Ali and A.R. Hasan, *Int. J. Adv. Sci. Eng. Technol.*, **5**, 29 (2017).
20. R.A. Jishi, L. Venkataraman, M.S. Dresselhaus and G. Dresselhaus, *Chem. Phys. Lett.*, **209**, 77 (1993); https://doi.org/10.1016/0009-2614(93)87205-H.
21. A. Misra, P.K. Tyagi, P. Rai and D.S. Misra, *J. Nanosci. Nanotechnol.*, **7**, 1820 (2007); https://doi.org/10.1166/jnn.2007.723.
22. N. Kouklin, M. Tzolov, D. Straus, A. Yin and J.M. Xu, *Appl. Phys. Lett.*, **85**, 4463 (2004); https://doi.org/10.1063/1.1812837.