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Economic growth of vertically aligned multiwalled carbon nanotubes in nitrogen atmosphere

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ABSTRACT

Vertically aligned carbon nanotube (VACNT) arrays are widely studied because of their immense potential in a wide range of applications. In order to tailor the properties of carbon nanotubes (CNTs) for a particular application, vertical alignment in the form of sheet is a major breakthrough. Herein we report an economic and effective strategy developed to synthesise aligned multiwalled carbon nanotube sheets using Al powder as buffer layer. We achieved easy growth of VACNTs sheets using toluene/ferrocene solution in a two-zone furnace by chemical vapor deposition method. First zone was set at temperature 200 °C and other zone was set at temperature 750 °C for the synthesis of VACNTs. Almost 500 µm long VACNT sheet was grown. We observed the significant growth of VACNT sheet on Al powdered quartz substrate in nitrogen medium. Uniform length of CNTs was maintained all over the sheet and additionally nitrogen is an economical alternative rather than other inert gases. Copyright © 2015 VBRI Press.

Keywords: Chemical vapor deposition; vertically aligned CNT; buffer layer; synthesis.

Introduction

In early 1950's tubular carbon filaments were produced by two Russian scientists Radushkevich and Lykynovich **[1]**. Potential of carbon nanotubes (CNTs) was felt tremendous after the work of Iijima *et al.* **[2]** and Bethune in 1993 **[3]**. CNTs have marvellous electrical **[4, 5]**, thermal **[6]**, optical **[7]**, hydrophobic **[8]** and mechanical**[9]** properties. Almost every field of technology like Biomedical **[10]**, Electronic **[5]**, Bio Sensors **[11,12]**, super-capacitors **[13]**, Industrial area**[14, 15]** etc. have applied these properties e.g. replacing copper in interconnected circuits with CNTs. The advantage of CNTs is that they can be grown in high aspect ratio.

Various methods have been discovered to synthesise CNTs but chemical vapor deposition (CVD) **[16]** method is the most economic and effective method because of better control over parameters like precursor flow rate, composition, temperature, catalyst **[17]**. CVD method can be used for both liquid and gaseous precursors. Aligned CNT arrays provide more advanced properties rather than random oriented CNT powder. Mechanical properties **[18]** can be increased by using aligned CNTs. Well aligned CNT arrays have been synthesized by chemical vapor deposition method **[19, 20]**. In CVD method precursor flows along with carrier gases like hydrogen or argon into the reactor. The reactor is heated over 660 °C - 800 °C and at that point solution decomposes and forms CNTs in the presence of catalyst or structure directing matrix. Water assisted growth of CNTs has been reported by Shenghua *et al.* **[21-23]**. The catalyst is deposited on the substrate and the substrate is placed inside the reactor and at 750 °C hydrocarbon solution is flown. Floating catalyst method is also used to synthesise vertically aligned carbon nano tubes (VACNTs). In floating catalyst method, carbon and catalyst source are mixed together and flown into the reactor. Carrier gases like hydrogen **[24, 25]** argon **[26, 27]** are generally used as reported earlier. Much work has been done on the deposition of catalyst and buffer layer on the substrate **[28].** Buffer layer **[29]** is also an important parameter for preventing agglomeration of catalyst into substrate. Qingwen **[30]** *et al.* reported a dense Al_2O_3 buffer layer (10 nm) deposited on a Si substrate using ion-beam assisted deposition (IBAD), and a Fe film (1 nm) was deposited on the buffer layer. Xuemei **[31]** and Yang **[32]** *et al.* reported deposition of buffer layer and catalyst layer by electron beam evaporation and also used Ar and H_2 as carrier gases. Predisposition methods like e-beam **[33, 34]**, sputtering **[35]**, thermal deposition are used to prepare buffer layer and catalyst layer on substrate. These methods are expensive and mostly not feasible and a very few researchers have worked to solve these issues.

Here, we present a better economic technique to produce VACNTs by using aluminium powder as buffer layer and nitrogen as the carrier gas at 750 °C. We successfully synthesized VACNTs of high quality by CVD method, without using any complex predisposition method for buffer layer and catalyst as described earlier or any special treatment. Nitrogen gas has not yet been explored as an inert medium for growing VACNTs to the best of our knowledge; therefore, we report this novel methodology using nitrogen as the carrier gas. Nitrogen has major advantage over other inert gases, as it is an easily available alternative at low cost. Apart from that, toluene has been used as the carbon source and ferrocene as the catalyst. This synthesis procedure can be used easily for economic growth of VACNTs, with further scope for mass production with just few modifications.

Experimental

CVD method **[20]** is generally used for the growth of multi walled carbon nanotubes (MWCNTs). We used a two-zone furnace (shown in **Fig. 1**) for the synthesis of VACNT sheets using CVD procedure. Temperature of the first zone was maintained at 200 °C and that of second zone was maintained at 750 °C.

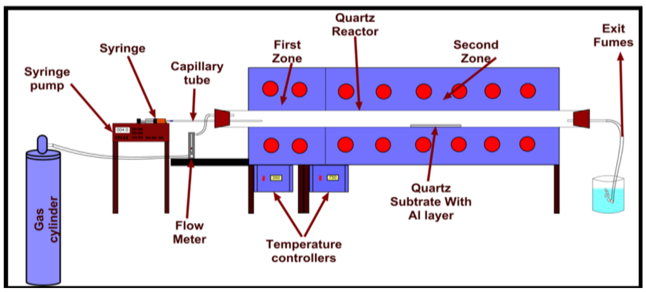

Fig. 1. Schematic of the two zone CVD furnace setup with syringe pump system.

Acetone and DI water were used to clean the quartz substrate and then dipped into hydrofluoric acid for the etching process. Etching process was completed in approximately five minutes and the substrate was again washed with DI water. As shown in **Fig. 2**, quartz substrate was coated with aluminium powder (25 µm) by simply dipping the substrate into the powder. Then that substrate was placed into the reactor at the second zone as shown in the **Fig. 1**. At the same time the hydrocarbon -catalyst solution was prepared using 3.2gm of ferrocene and 40ml of toluene and ultra sonicated for one hour. When the reactor reached a temperature of 750 °C, this prepared solution was injected using a syringe mounted on the syringe pump connected with the capillary tube in first zone.

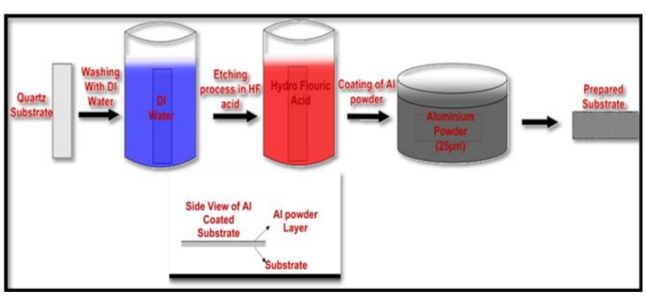

Fig. 2. Schematics of various steps in substrate preparation.

The flow rate was maintained at 4 ml/hr. In the complete process, nitrogen gas was used to maintain inert medium as well as acted as the carrier for the precursor vapours to be carried into the reaction zone. Solution was converted into vapours in the first zone and decomposed in the second zone. Hence, after the scheduled experimental time, VACNTs were grown on the substrate, which was peeled off in the form of sheets.

Characterization

Morphology of sheets, alignment and length was observed by Scanning Electron Microscope (SEM) model EVO-MA10 ZIESS. The morphology of sheet was observed perpendicularly to the growth of VACNT sheet after cutting a small piece of sample from sheet by razor blade. Raman Spectrum was recorded by Renishaw in-Via Raman spectrometer, UK, with an excitation wavelength 514 nm. Sheet was also characterized by X-ray diffractometer (XRD, RIGAKU Tokyo) to understand the structural formation. The weight percentage of catalyst in sheet was evaluated by a thermo gravimetric analyzer (TGA, Mettler Toledo). The sample was heated to 1000 °C in an air atmosphere; during heat treatment carbon would oxidized completely and residue remained. The detailed structures of the sample was studied using transmission electron microscopy (TEM) images taken by Tecnai G20 stwin, operated at 300 kV and having a point resolution of 0.2 Å. For detailed structural observation the sample was ultra-sonication in ethanol for 30 min and TEM grid was dipped into that solution then observed into the system.

Results and discussion

Optical image of the VACNT sheet formed on quartz substrate is shown in **Fig. 3(b)**. These VACNTs were peeled out in the form of sheet same as the size of substrate because of etching process. Al powder has a melting temperature of about 660 °C, so during the reaction when the surrounding temperature reached 750 °C the powder melts, and eventually falls out of the substrate. Therefore to avoid such limitations, the substrate is etched using HF acid. HF acid results in formation of pores on the substrate thereby holding the aluminium powder intact as well demonstrated in the **Fig. 3(a)**. Additionally agglomeration effect is also shunned out due to which the catalyst does not come in direct contact with the substrate. SEM characterization revealed that the sheet contained mostly aligned CNTs with a little amount of amorphous carbon.

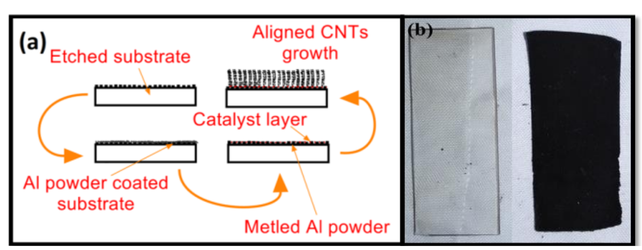

Fig. 3. (a) Schematics of the process of Al powder coating on etched surface for aligned CNTs growth and (b) Optical image of VACNT sheet.

SEM images clearly show the growth of densely aligned CNTs on the substrate at 750 °C in nitrogen medium. The thickness of the films was determined from edge-on SEM images of cleaved samples. **Fig. 4(a)** shows a typical image of almost half millimetre (500 µm) grown VACNTs and **Fig. 4(b)** and **(c)** show the high magnification images of aligned nanotubes. **Fig. 4(b)** shows the bundled pillars of aligned tubes and **Fig. 4(c)** shows the densely grown MWCNTs. Further characterization was done using RAMAN, XRD, and TEM for in depth studies.

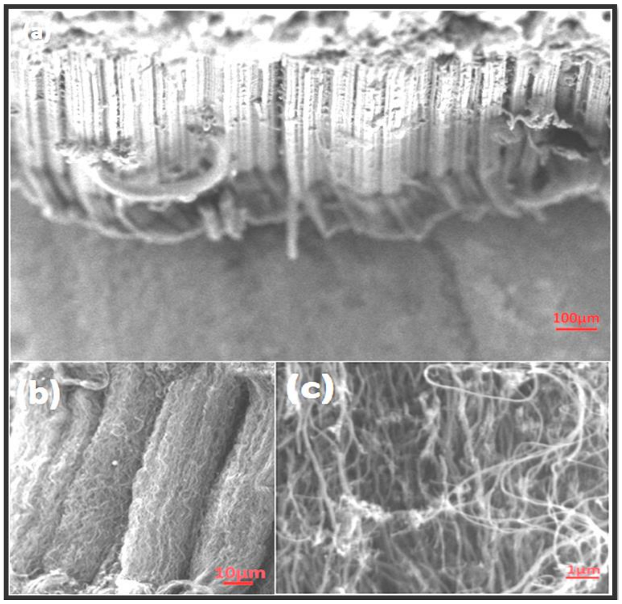

Fig. 4. Various SEM image of the as grownVACNTs.

Fig. 5 depicts the Raman spectrum of the side walls of the VACNTs. The expected D and G bands are obtained at 1350 and 1574 cm^{-1}, respectively. Ratio of intensity of D band(I_D) and G band(I_G) gives the quality factor which is obtained as 0.85 thereby confirming the synthesis of good quality CNT.

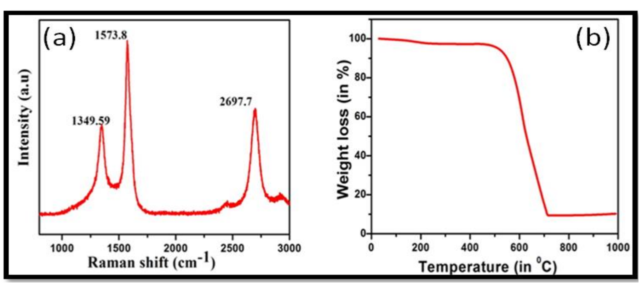

Fig. 5. (a) Raman spectrum of MWCNTs and (b) TGA curve of MWCNTs.

Thermo gravimetric analysis (TGA) was done to study the weight loss with increase in temperature. Sample was heated from 30 °C to 1000 °C in the air and the residual mass was studied. The result showed that only 9.4 % of catalyst was left behind, which proves good purity of the MWCNTs.

Structural and compositional studies were performed by using XRD. It is a non-destructive technique which reveals information about crystallographic structure, chemical composition and physical properties of the material. XRD pattern of VACNT is shown in **Fig. 6** in which, a sharp peak determined at 2θ value of 25.8° is obtained which corresponds to the (0 0 2) planes of graphitic structure. Due to (1 1 0) and (1 0 0) graphitic planes humps in around 43° are obtained confirming the successful growth of CNTs.

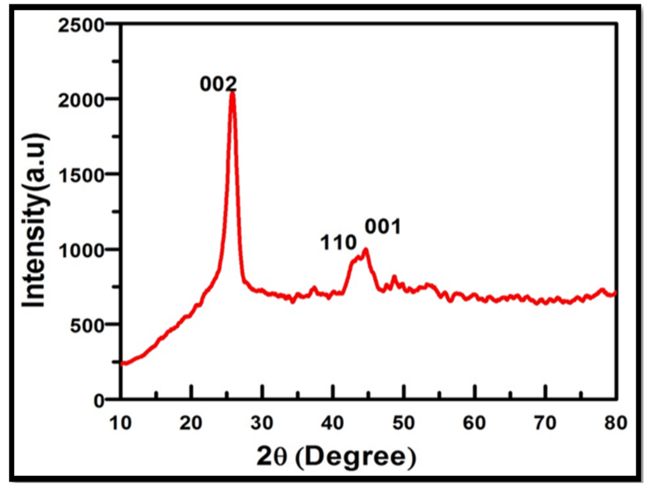

Fig. 6. XRD image of nitrogen grown VACNTs.

In order to carry out fine structural analysis of the as obtained CNTs, TEM images were thoroughly studied. **Fig. 7(a)** show the varied diameter CNTs as peeled out from the substrate. Similarly **Fig. 7(b)** shows the HRTEM image of very few-walled CNTs where number of walls obtained is three as calculated and **Fig. 7(c)** shows the HRTEM image of multi walled CNTs with 15 walls. Small amount of catalyst particles encapsulated within the walls of the MWCNTs are also portrayed as visible in **Fig. 7(a)**.

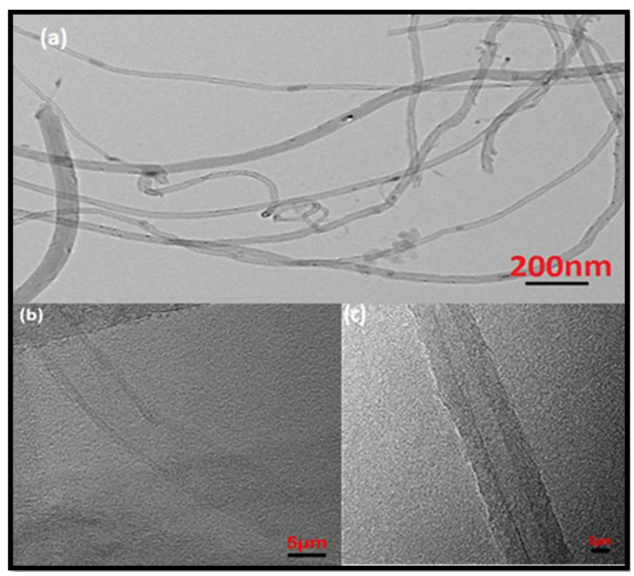

Fig. 7. (a) TEM images of the MWCNTs (b) and (c) HRTEM images of the MWCNTs.

Hence from the various TEM images it was confirmed that clean and good quality of graphitic layers were observed in the walls of the VACNTs grown. These various characterizations confirmed the successful growth of VACNT sheets in a much economical methodology. We intend to grow these sheets commercially and further investigate the mechanism for length-dependent parameters of the growth of VACNT sheets.

Conclusion

VACNT sheets were successfully synthesized by CVD method using a two-zone furnace using nitrogen as the carrier gas. Etching of the substrate creates pores and Al powder used as buffer layer on the quartz substrate is soaked into these pores that results in the alignment of the CNTs. Use of Al powder prevents agglomeration of catalyst on the substrate. Factors like choice of the carrier gas, buffer layer, and catalyst contributed to the sustained and efficient growth of VACNT sheets. This report presents the novel economic method to synthesise VACNTs that is way more efficient than the other costlier alternative techniques like e-beam evaporation, sputtering. VACNTs of 500µm in length were achieved which were spread throughout the sheet, grown at temperature 750°C with good alignment. This structural feature allows for processing tailored VACNT sheets for a variety of applications.

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Reference

1. Radushkevich, L.; Lukyanovich, V. *Zurn Fisic Chim* **1952,** *26(1)*, 88.
2. Iijima, S; Ichihashi, T. **1993**.
   DOI: 10.1038/363603a0
3. Bethune, D.; Klang, C.; De Vries, M.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R.; **1993**.
   DOI: 10.1038/363605a0
4. Odom, T. W.; Huang, J.L.; Kim, P.; Lieber, C. M.; *Nature*, **1998**, *391 (6662)*, 62.
   DOI: 10.1038/34145
5. Li, J.; Stevens, R.; Delzeit, L.; Ng, H. T.; Cassell, A.; Han, J.; Meyyappan, M. *Appl.Phys. Lett.* **2002,** *81(5)*, 910.
   DOI: 10.1021/nl0340677
6. Poncharal, P.; Berger, C.; Yi, Y.; Wang, Z.; de Heer, W. A. *The Journal of Physical Chemistry B*, **2002,** *106(47)*, 12104.
   DOI: 10.1021/jp021271u
7. Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezu, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. *Synthetic metals*, **1999,** *103(1)*, 2555.
   DOI: 10.1016/S0379-6779(98)00278-1
8. Lau, K. K.; Bico, J.; Teo, K. B.; Chhowalla, M.; Amaratunga, G. A.; Milne, W. I.; McKinley, G. H.; Gleason, K. K.; *Nano Letters*, **2003,** *3(12)*, 1701.
   DOI: 10.1021/nl034704t
9. Salvetat, J.-P.; Bonard, J.-M.; Thomson, N.; Kulik, A.; Forro, L.; Benoit, W.; Zuppiroli, L. *Applied Physics A*, **1999,** *69(3)*, 255.
   DOI: 10.1007/s003390050999
10. Bianco, A.; Kostarelos, K.; Prato, M. *Current opinion in chemical biology*, **2005,** *9(6)*, 674.
   DOI:10.1016/j.cbpa.2005.10.005
11. Wang, J.; *Electroanalysis*, **2005,** *17(1)*, 7.
   DOI: 10.1002/elan.200403113
12. Narang, J.; Jain, U.; Malhotra, N.; Singh, S.; Chauhan, N.
   DOI: 10.5185/amlett.2015.5735
13. Mahore, R. P.; Burghate, D. K.; Kondawar, S. B.; *Adv. Mat. Lett*, **2014,** *5(7)*, 400.
   DOI: 10.5185/amlett.2015.5735
14. Singh B.P., V. C., Satish Teotia, T.K. Gupta, V.N. Singh, S.R. Dhakate, R.B.Mathur. *Advanced Material Letter* **2015,** *6(2)*, 104.
   DOI: 10.5185/amlett.2015.5612
15. Sambyal, P.; Singh, A. P.; Verma, M.; Gupta, A.; Singh, B. P.; Dhawan, S. *Advanced Material Letter* **2015**.
   DOI: 10.5185/amlett.2015.5807
16. Cassell, A. M.; Raymakers, J. A.; Kong, J.; Dai, H. *The Journal of Physical Chemistry B*, **1999,** *103(31)*, 6484.
   DOI: 10.1021/jp990957s
17. Kathyayini, H.; Nagaraju, N. D.; *Advanced Materials Letters*, **2012**, *3(4)*, 309.
   DOI: 10.5185/amlett.2011.8291
18. Gouda, P. S.; Kulkarni, R.; Kurbet, S.; Jawali, D.; *Advanced Materials Letters*, **2013,** *4(4)*, 261.
   DOI: 10.5185/amlett.2012.9419
19. Zhang, X.; Cao, A.; Wei, B.; Li, Y.; Wei, J.; Xu, C.; Wu, D.; *Chemical Physics Letters*, **2002,** *362 (3)*, 285.
   DOI: 10.1016/S0009-2614(02)01025-4
20. Wei, B.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, R.; Ramanath, G.; Ajayan, P.; *Nature*, **2002,** *416 (6880)*, 495.
   DOI: 10.1038/416495a
21. Liu, S.; Zhang, Y.; Lin, Y.; Zhao, Z.; Li, Q.; *Carbon*, **2014,** *69*, 247.
   DOI: 10.1016/j.carbon.2013.12.023
22. Cho, W.; Schulz, M.; Shanov, V. *Carbon* **2014,** *69*, 609.
   DOI: 10.1016/j.carbon.2013.12.088
23. Zhang, L.; Zhao, B.; Wang, X.; Liang, Y.; Qiu, H.; Zheng, G.; Yang, J.; *Carbon*, **2014,** *66*, 11.
   DOI: 10.1016/j.carbon.2013.08.007
24. Scardamaglia, M.; Amati, M.; Llorente, B.; Mudimela, P.; Colomer, J. F.; Ghijsen, J.; Ewels, C.; Snyders, R.; Gregoratti, L.; Bittencourt, C.; *Carbon*, **2014,** *77*, 319.
   DOI: 10.1016/j.carbon.2014.05.035
25. Deng, J. H.; Cheng, G. A.; Zheng, R.-T.; Yu, B.; Li, G. Z.; Hou, X. G.; Zhao, M. L.; Li, D. J. *Carbon*, **2014,** *67*, 525.
   DOI: 10.1016/j.carbon.2013.10.025
26. Zhu, L.; Xu, J.; Xiu, Y.; Sun, Y.; Hess, D. W.; Wong, C. *Carbon* **2006,** *44(2)*, 253.
   DOI: 10.1016/j.carbon.2005.07.037
27. Grinet, M. A.; Zanin, H.; Granato, A. E. C.; Porcionatto, M.; Marciano, F. R.; Lobo, A.; O. *Journal of Materials Chemistry B;* **2014,** *2(9)*, 1196.
   DOI: 10.1039/C3TB21525C
28. Dupuis, A. C. *Progress in Materials Science*, **2005,** *50(8)*, 929.
   DOI: 10.1016/j.pmatsci.2005.04.003
29. de los Arcos, T.; Garnier, M. G.; Oelhafen, P.; Mathys, D.; Seo, J. W.; Domingo, C.; Garcıa-Ramos, J. V.; Sánchez-Cortés, S. *Carbon* **2004,** *42(1)*, 187.
   DOI: 10.1016/j.carbon.2003.10.020
30. Li, Q.; Zhang, X.; DePaula, R. F.; Zheng, L.; Zhao, Y.; Stan, L.; Holesinger, T. G.; Arendt, P. N.; Peterson, D. E.; Zhu, Y. T.; *Advanced Materials*, **2006,** *18(23)*, 3160.
   DOI: 10.1002/adma.200601344
31. Sun, X.; Lu, X.; Qiu, L.; Peng, H. *Journal of Materials Chemistry C*, **2015,** *3(11)*, 2642.
   DOI: 10.1039/C5TC00011D\
32. Li, Y.; Xu, G.; Zhang, H.; Li, T.; Yao, Y.; Li, Q.; Dai, Z.; *Carbon*, **2015,** *91*, 45.
   DOI:10.1016/j.carbon.2015.04.035
33. Hart, A. J.; Slocum, A. H.; Royer, L.; *Carbon*, **2006,** *44(2)*, 348.
   DOI: 10.1016/j.carbon.2005.07.008
34. Gao, Z.; Zhang, X.; Zhang, K.; Yuen, M. M.; *The Journal of Physical Chemistry C*, **2015,** *119(27)*, 15636.
   DOI: 10.1021/acs.jpcc.5b01564
35. Yamada, T.; Namai, T.; Hata, K.; Futaba, D. N.; Mizuno, K.; Fan, J.; Yudasaka, M.; Yumura, M.; Iijima, S.; *Nature nanotechnology*, **2006,** *1(2)*, 131.
   DOI: 10.1038/nnano.2006.95