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Low Temperature Growth of Vertically Aligned Carbon Nanotubes by Spray Pyrolysis Method

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The aligned carbon nanotubes (ACNTs) have been synthesized using ferrocene as catalyst on silicon substrate from *Rosmarinus officinalis* oil as a carbon precursor at 650 °C by spray pyrolysis method in argon atmosphere. The ferrocene act an *in situ* Fe catalyst particle for the formation of vertically aligned CNTs on silicon substrate. The grown aligned CNTs were characterized by using HR-SEM, HR-TEM, XRD and Raman spectroscopy analysis. The average diameter of aligned CNTs was around 20nm. The advantage of this method is simple and use of low cost precursors to produce high purity aligned CNTs.

Keywords: Carbon nanotubes, Low temperature growth, Spray pyrolysis method.

INTRODUCTION

Carbon nanotubes (CNTs) have under scientific investigation more than 15 years since their unique properties predestined them for numerous potential applications. The field of nanotechnology and nanoscience push their investigation forward to produce CNTs with suitable parameters for future applications. It is evident that new approaches of their synthesis need to be developed and optimized. Vertically-aligned carbon nanotubes (ACNTs) were first reported by Thess *et al.*[1]. They were able to bundle 70 % of the volume of nanotubes in to crystalline ropes in 1996. In the same year, the Chinese Academy of Science reported that a 50 µm thick film of highly aligned nanotubes had successfully been grown by chemical vapor deposition (CVD)[2].

Vertically aligned CNTs are quasi-dimensional carbon cylinders that align perpendicular to a substrate. Vertically aligned CNTs with high aspect ratios and uniform tube length made it easy spinning into macroscopic fibers. The aligned CNTs have its own application in spintronic devices[3] microwave amplifiers[4], field emission devices in flat displays[5] *etc.* So the synthesis of aligned CNT with good alignment and purity is of great importance. Andrews *et al.*[6] obtained aligned CNTs by catalytic decomposition of ferrocene: xylene mixture. The ferrocene acts as an *in situ* Fe catalyst precursor and forms nanosized Fe particles for the growth of aligned CNTs[7]. Ren *et al.*[8] synthesized aligned CNTs by plasma enhanced hot filament chemical vapor deposition.

There are few reports on the synthesis of CNTs utilizing regenerative precursor such as camphor[9], turpentine oil[10], eucalyptus oil[11], coconut oil[12], pine oil[13], *Helianthus annus* oil[14], *Jatropha curcas* oil[15], *Glycine max* oil[16] and *Cymbopogen flexuous* oil[17]. For the synthesis of CNT arrays, several papers have been published and describe simple routine for synthesizing large- scale and low cost CNTs arrays from petroleum-based precursors like benzene, xylene, hexane[18] *etc.* In addition, the naturally occurring hydrocarbon precursors have generated some interest because of the possibility of production of aligned CNTs from bank of hydrocarbons. The significant advantages of these precursors are low cost, renewable, green and abundantly available.

In this paper, we report the synthesis of vertically aligned nanotubes from *Rosmarinus officinalis* oil as a carbon source by spray pyrolysis method (Fig. 1). Being a natural source which is renewable and low cost, *Rosmarinus officinalis* oil has the potential to be the green alternative for industrial scale production of ACNTs.

EXPERIMENTAL

Synthesis of vertically aligned carbon nanotubes: The synthesis of vertically aligned CNTs was carried out using the spray pyrolysis method. In this spray pyrolysis method, pyrolysis of the carbon precursor with catalyst take place followed by deposition of aligned CNT on silicon substrate. *Rosmarinus officinalis* oil was used as carbon precursor and ferrocene [$Fe(C_5H_5)_2$] (Sigma Aldrich, high purity 98 %) was used as a source of Fe which acts as a catalyst for the growth of ACNTs, n type silicon wafer (100) of size (1 cm × 1 cm) was used as a substrate. The spray pyrolysis setup is made up with consist of a nozzle (inner diameter 0.5 mm), attached to precursor solution supply used for spraying the solution into a quartz tube (500 mm long with an inner diameter of 30 mm). The outlet of the quartz tube was attached with a water bubbler. Before used, substrate was cleaned properly in acetone by ultrasonication followed by deionized water and finely dried using argon blower. The substrate was kept in a quartz boat which was then placed at the center of the quartz tube. In a typical experiment, the quartz tube was first flushed with argon in order to eliminate air from the quartz tube and then heated to a reaction temperature. The precursor solution was sonicated for 5 min to prepare the homogeneous mixture. The solution (*Rosmarinus officinalis* oil and ferrocene mixtures) was sprayed in to the quartz tube using argon. The concentration of ferrocene in *Rosmarinus officinalis* oil was 25 mg/mL. The flow rate of argon was 200 sccm/min. The experiments were conducted at 650 °C and 1 atmospheric pressure with reaction time of 45 min. After deposition, the furnace was switched off and allowed to cool down to room temperature under argon flow. A uniform black deposition on the silicon substrate at the reaction zone was observed. Finely, the substrate containing aligned CNTs was removed from the quartz tube for characterization.

The as-grown ACNTs materials were characterized using scanning electron microscope (SEM was performed by Hitachi-3000 H). For transition electron microscope (TEM was performed by JEOL-JEM-2010F) studies, the samples were prepared by sonication of products in isopropanol and few drops of resultant suspension was put on to holey carbon grid and dried. XRD and Raman spectroscopy of samples was performed by JASCO NRS-1500 w, green laser with excited on wave length 532 nm.

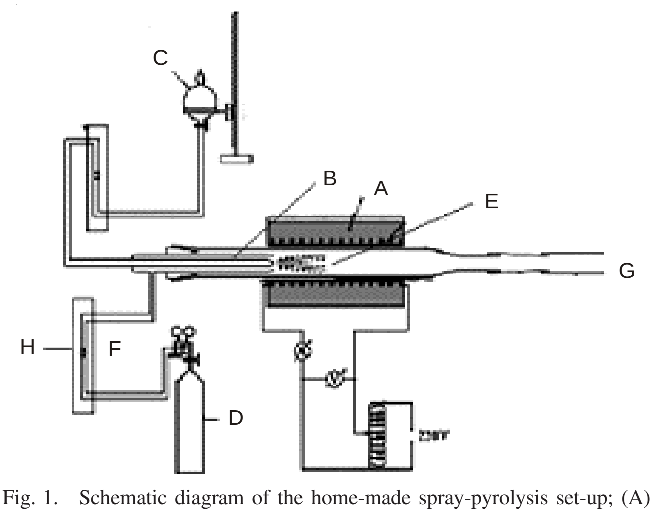

Fig. 1. Schematic diagram of the home-made spray-pyrolysis set-up; (A) furnace; (B) Spray nozzle; (C) Separating funnel containing carbon feed stock; (D) nitrogen gas cylinder; (E) quartz boat containing catalysts with supporting material, (F) rubber tube; (G) outlet; (H) flow meter

RESULTS AND DISCUSSION

Fig. 2a shows HR-SEM image of ACNTs array synthesized on the large surface of a silicon wafer. The whole substrate (1 cm × 1 cm) was covered by a black film of aligned CNTs and part of it has been peeled off for HR-SEM observation. The alignment of the nanotubes across the whole surface is uniform. An enlarged side view of the CNT array reveals that the majority of the CNTs are straight vertically aligned from the substrate surface Fig. 2b. The HR-TEM image Fig. 3a shows that the vertically aligned CNTs with hollow and multi-walled structure are well crystallized and little defects have been seen in the external walls. However defects in the wall structures can cause energy concentration points and lead to premature failure[19,20].

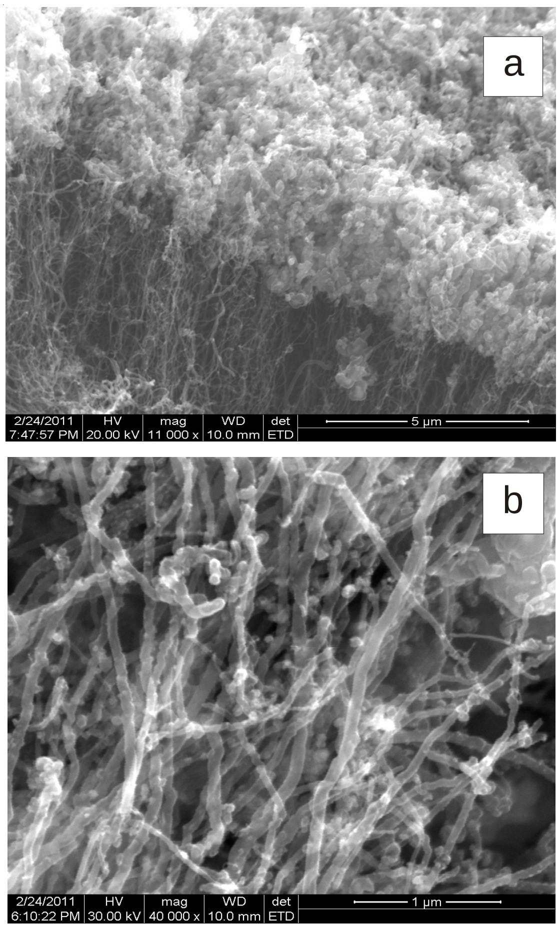

Fig. 2. SEM images of vertically aligned CNTs grown at 650 °C (a) as-grown CNTs on silicon wafer, the well-aligned CNTs thin film. (b) Zoom-in side view of the side structure of aligned CNTs

Higher temperature and increased residence time are expected to reduce defects and to increase the degree of graphitization[21,22]. Fig. 3b shows magnified view of aligned CNTs. The side wall of CNT was found to consist of 25 graphitic layers.

Raman spectra (Fig. 4) shows three peaks around 1357, 1591 and 2710 cm^{-1}, which are attributed to D,G and G' bands, respectively. The G-bands are related to stretching vibration in the basal plane of graphite crystal, which have been normalized to the same intensity. D bands are associated with disorder (or) detective planner graphite structure. G band is a second order two phonon process. The intensity ratio of D and G peaks is used to characterize the purity of CNTs. The ID/IG value of as-grown ACNTs is 0.72. The lower ID/IG value indicates a higher degree of graphitization[23].

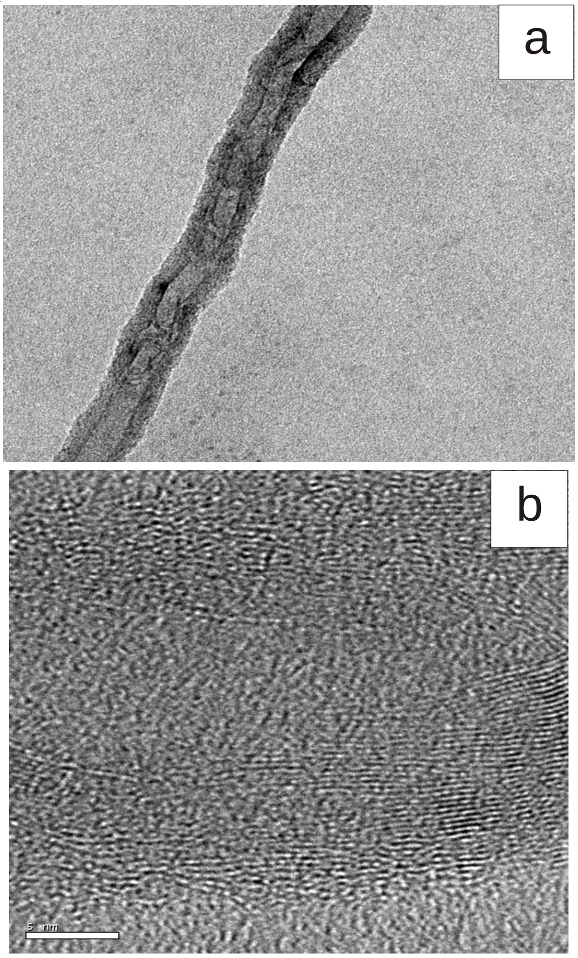

Fig. 3. TEM images of (a) as-grown vertically aligned CNTs (b) Magnified view of vertically aligned CNTs

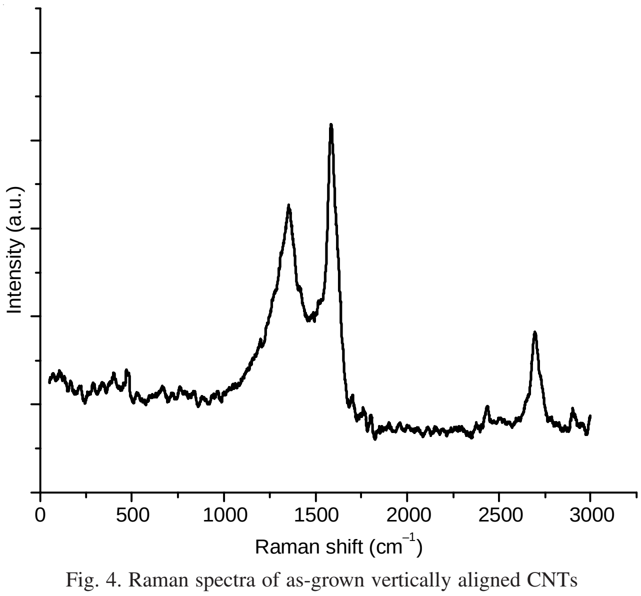

Fig. 4. Raman spectra of as-grown vertically aligned CNTs

The crystal structure of ACNTs was studied by X-ray diffraction. In Fig. 5, the intense peaks at 26.16 and 44.65 are indexed to be the (002) and (101) reflections of hexagonal graphite. The (002) peak indicates the graphitic structures of the ACNTs.

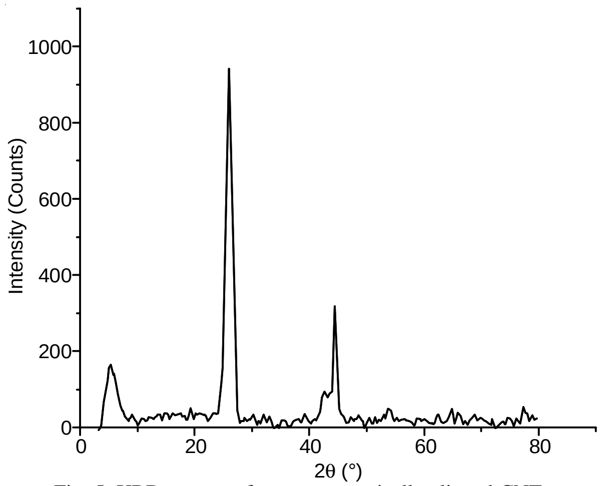

Fig. 5. XRD spectra of as-grown vertically aligned CNTs

Conclusion

Vertically aligned carbon nanotubes were obtained by spray pyrolysis from *Rosmarinus officinalis* oil using ferrocene catalyst at 650 °C on silicon substrate in argon atmosphere. The use of natural precursors gives sensible yield and makes the process natural world friendly as well. The as-grown vertically aligned CNTs have an outer diameter of 20-30 nm. Raman spectroscopy reveals that as grown vertically aligned carbon nanotubes are well graphitized.

REFERENCES

1. A. Thess, R. Lee, P. Nikolaev, H.J. Dai, P. Petit, J. Robert, C.H. 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).
2. W.Z. Li, S.S. Xie, L.X. Qian, B.H. Chang, B.S. Zou, W.Y. Zhou, R.A. Zhao and G. Wang, *Science*, **274**, 1701 (1996).
3. E. Titus, M.K. Singh, G. Cabral, V. Paserin, P.R. Babu, W.J. Blau, J. Ventura, J.P. Araujo and J. Gracio, *J. Mater. Chem*., **19**, 7216 (2009).
4. W.I. Milne, K.B.K. Teo, E. Minoux, O. Groening, L. Gangloff, L. Hudanski, J.-P. Schnell, D. Dieumegard, F. Peauger, I.Y.Y. Bu, M.S. Bell, P. Legagneux, G. Hasko and G.A.J. Amaratunga, *J. Vac. Sci. Technol*., **24**, 345 (2006).
5. M. Mauger and V.T. Binh, *J. Vac. Sci. Technol*., **24**, 997 (2006).
6. R. Andrews, D. Jacques, A.M. Rao, F. Derbyshire, D. Qian, X. Fan, E.C. Dickey and J. Chen, *J. Chem. Phys. Lett*., **303**, 467 (1999).
7. I. Gunjishima, T. Inoue, S. Yamamuro, K. Sumiyama and A. Okamoto, *Carbon,* **45**, 1193 (2007).
8. Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal and P.N. Provencio, *Science*, **282**, 1105 (1998).
9. M. Kumar and Y. Ando, *J. Chem. Phys. Lett*., **374**, 521 (2003).
10. A. Afre, T. Soga, T. Jimbo, M. Kumar, Y. Ando and M. Sharon, *Chem. Phys. Lett*., **414**, 6 (2005).
11. P. Ghosh, R.A. Afre, T. Soga and T. Jimbo, *Mater. Lett*., **61**, 3768 (2007).
12. S. Paul and S.K. Samdarshi, *New Carbon Mater*., **26**, 85 (2011).
13. S. Karthikeyan and P. Mahalingam, *Int. J. Nanotechnol. Appl*., **4**, 189 (2010).
14. S. Karthikeyan and V.S. Angulakshmi, *J. Environ. Nanotechnol*., **1**, 40 (2012).
15. S. Karthikeyan and P. Mahalingam, *Inter. J. Green Nanotechnol. Phys. Chem*., **2**, 39 (2010).
16. S. Karthikeyan, V.S. Angulakshmi, C. Sathishkumar and M. Karthik, *J. Environ. Nanotechnol*., **2**, 101 (2013).
17. S. Mageswari and S. Karthikeyan, *J. Environ. Nanotechnol*., **1**, 28 (2012).
18. Z. Sadeghian, *New Carbon Mater*., **24**, 33 (2009).
19. L.M. Cele and N.J. Coville, *Carbon*, **47**, 1824 (2009).
20. C. Pan, Y. Liu, F. Cao, J. Wang and Y. Ren, *Micron*, **35**, 461 (2004).
21. W. Huang, Y. Wang, G. Luo and F. Wei, *Carbon*, **41**, 2585 (2003).
22. B. Yi, R. Rajagopalan, C.L. Burket, H.C. Foley, X. Liu and P.C. Eklund, *Carbon*, **47**, 2303 (2009).
23. C. Singh, M.S.P. Shaffer and A.H. Windle, *Carbon*, **41**, 359 (2003).