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Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor

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ABSTRACT

Vertically aligned carbon nanotubes (VACNTs) have been synthesized on silicon substrates in a thermal catalytic chemical vapor reactor using natural palm oil as the carbon source. Field Emission Scanning Electron Microscopy (FESEM) and microraman analysis revealed dense bundles of mixed multi-walled and single-walled carbon nanotubes (CNTs). The diameters of the single-walled carbon nanotubes (SWCNTs) were estimated to be between 0.6 nm and 1.2 nm. Thermogravimetric analysis (TGA) results showed that 90% purity was achieved at the expense of 4% weight catalyst material.

1. Introduction

The chemical vapor deposition technique is arguably the most efficient method for the synthesis of carbon nanotubes. It afforded the growth of bulk as well as aligned CNTs on substrates. Conventionally, fossil based carbon precursors such as methane, acetylene, ethanol or xylene were used. There have been reports on the use of natural precursors such as camphor powder [1–5], turpentine oil [6–9] and eucalyptus oil [10] to produce CNTs in CVD reactors. The main motivation of utilizing these sources was to provide "green" alternatives of cheap and renewable raw materials for industrial volume CNT production.

Another promising green source for the production of CNT is palm oil. Known scientifically as hexaeconoic acid, palm oil is obtained from the fibrous exocarp and mesocarp of the fruits of palm tree. The main components of palm oil are hydrocarbon containing oxygen for example $C_{67}H_{127}O_8$ which provided the precursor species in catalytic CVD growth of CNTs.

In this paper, we report the synthesis of vertically aligned CNT nanotubes using palm oil as the carbon source using the thermal chemical vapor deposition technique. To the best of our knowledge, there has not been any report on the use of this bio-hydrocarbon in producing vertically aligned CNT. Being a natural source which is renewable and cheap, palm oil has the potential to be the green alternative for industrial scale production of CNT.

2. Materials and methods

The synthesis was done using a two stage tube furnace system equipped with a single alumina tube. 5.33 wt.% of ferrocene was thoroughly mixed in palm oil sample and 3 ml of the mixture was placed in an alumina boat. Then the boat was placed at the centre of furnace 1. Silicon substrates of dimension 1 cm × 1 cm were ultrasonically cleaned in acetone. Excess oxide layers were etched using HF solution before rinsing in DI water. Air dried substrates were placed at the centre of furnace 2. The substrates were stacked on another piece of silicon substrate where CNTs were grown on limited space between them. Such an arrangement resulted in significant efficiency in the CNTs growth as a comparison with other report elsewhere [11]. Prior to the synthesis process, the tube was flushed with Ar gas through the tube end of furnace 1 for 10 min. In a typical deposition process, the temperature of the deposition furnace (furnace 2) was increased to 750 °C before increasing the temperature of the precursor furnace (furnace 1) to 450 °C. After the synthesis process which took 30 min, both furnaces were allowed to cool to room temperature under continuous Ar flow. The samples were characterized by FESEM (ZEISS Supra 40VP), TGA (Perkin Elmer Pyris 1 TGA), FTIR (Thermo Scientific Nicolet 6700) and microraman spectroscopy (Horiba Jobin Yvon-DU420A-OE-325).

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3. Results and discussions

Fig. 1 shows the FESEM images of densely packed VACNTs grown on a silicon substrate, which was a typical product obtained at argon flow rate of 150 sccm, furnace temperature 750 °C and 30 min deposition time. The image in Fig. 1(a) shows a bundle of VACNTs that was peeled off from the substrate. The length of the nanotubes was estimated to be about 110 μm, giving an approximate growth rate of 4 μm min^{-1}. The side view of the aligned bundle of CNT (Fig. 1(b)) consisted of wriggly individual CNTs. A closer inspection revealed the bundle consisted of entwined individual CNTs.

Vibrational spectroscopic analysis of the sample was achieved using microraman spectroscopy and FTIR spectroscopy. From microraman analysis (Fig. 2(a)), it was evident that the sample consisted of a mixture of SWNT and MWNT. The carbon G and D peaks were prominent at 1583 cm^{-1} and 1346 cm^{-1} respectively. The ratio of the intensities of these peaks, I_D/I_G was found to be 0.52. The presence of the lower frequency radial breathing modes at 214.9 cm^{-1}, 277.2 cm^{-1} and a faint peak at 395.5 cm^{-1} indicated the presence of SWNTs as shown in Fig. 2(b). The diameter, d, of the SWNTs can be estimated from the RBM peak position, ω, as $d = 248\ (cm^{-1}\ nm)/\omega(cm^{-1})$ [14], which yielded diameters of about 1.2 nm, 1 nm and 0.6 nm respectively.

The results of TGA analysis on the sample is shown in Fig. 3. Initial weight loss at about 110 °C and 210 °C could be due to the decomposition of trace hydrocarbon impurities which constituted about 1% of the total weight. Gradual weight loss from 250 °C to about 550 °C may be attributed to the decomposition of amorphous carbon materials [12–14] which make up about 5% weight. Significant weight loss occurs between 650 °C to 730 °C which was due to the decomposition of carbon nanotubes. From the analysis, it was estimated that the carbon nanotubes produced was 90% pure. Notice that the metal catalysts in the sample constituted about 4% of the total weight, which oxidized as evident by the weight gain beyond 800 °C.

It has been demonstrated that natural palm oil is an efficient source for the production of high purity carbon nanotubes with minimal amorphous carbon impurities. The small amount of amorphous carbon can be attributed to the presence of hydrogen and oxygen atoms which aided its removal by forming volatile species such as CH_x ($x = 1$ to 4) and CO_y ($y = 1,2$). The key parameter for the production of CNTs using natural palm oil using the thermal catalytic CVD technique seems to be the synthesis temperature. Based on our experiment, no growth or very inefficient growth was obtained at temperatures less than 600 °C.

Speculating on the mechanism of the synthesis process, heating the furnace containing the palm oil source to 450 °C essentially decomposes the ferrocene molecules to nanosized Fe particles. At the same time, palm oil molecules decompose into a rich concoction of hydrocarbons containing C, H and O molecules. The hydrocarbon vapor mixed with nanosized Fe particles settled on the Si substrate in the synthesis region where the temperature was 750 °C. Here, catalytic decomposition of the hydrocarbon occurred resulting in the dissolution of carbon into the Fe particles and the release of hydrogen and oxygen. Minute temperature fluctuations due to the Ar gas flow resulted in the condensation of the dissolved carbon to nanotubes at the nanosized Fe particles. For this reason, the optimum percentage of ferrocene in the mixture was 5.33 wt.%, giving the eventual 4% wt. Fe in the synthesized CNTs.

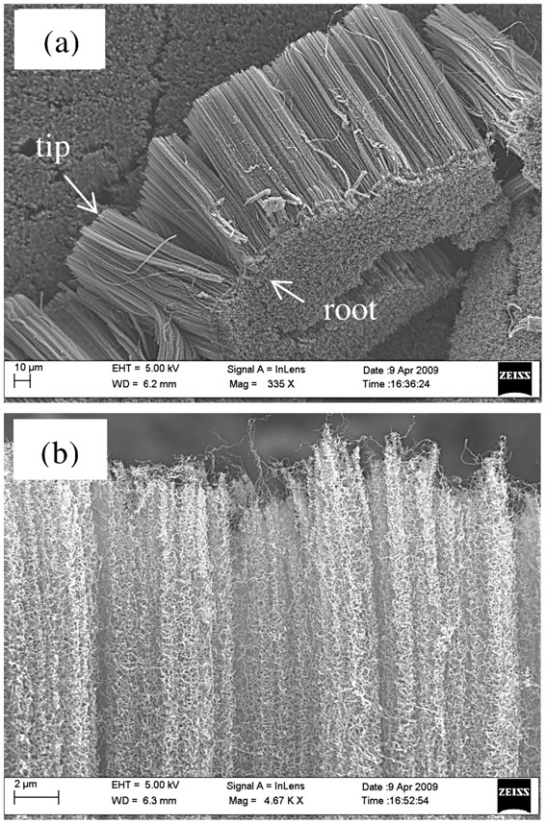

Fig. 1. FESEM images of VACNT grown on a Si substrate, (a) peeled off bundle of dense CNT, (b) side view of the aligned CNTs.

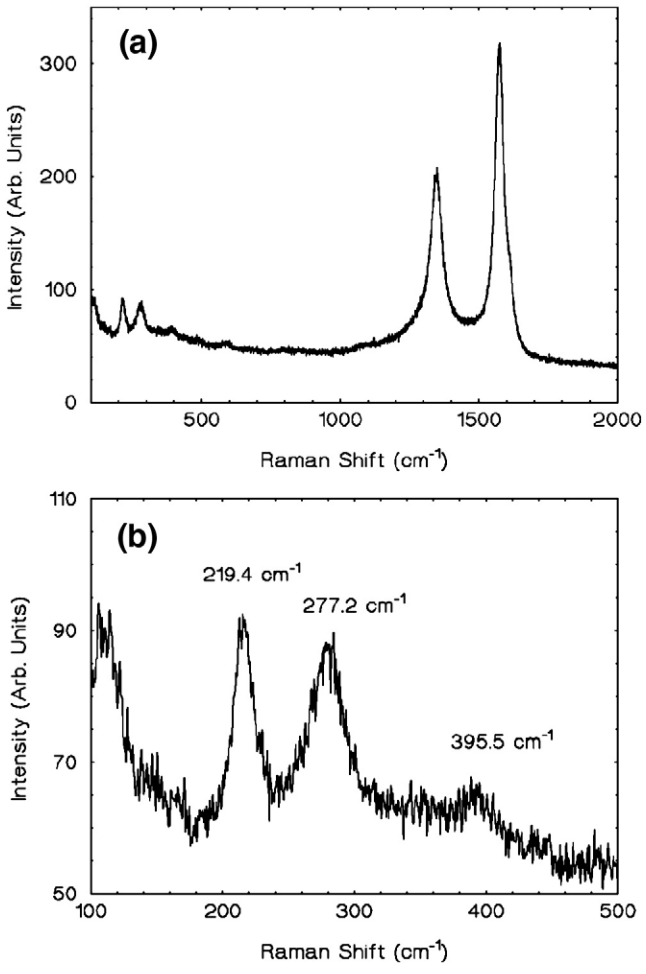

Fig. 2. Vibrational spectroscopy of VACNT grown with natural palm oil. (a) Microraman spectrum showing the RBM modes, the D line and the G line of CNTs. (b) Microraman spectrum showing the RBM modes of SWNT.

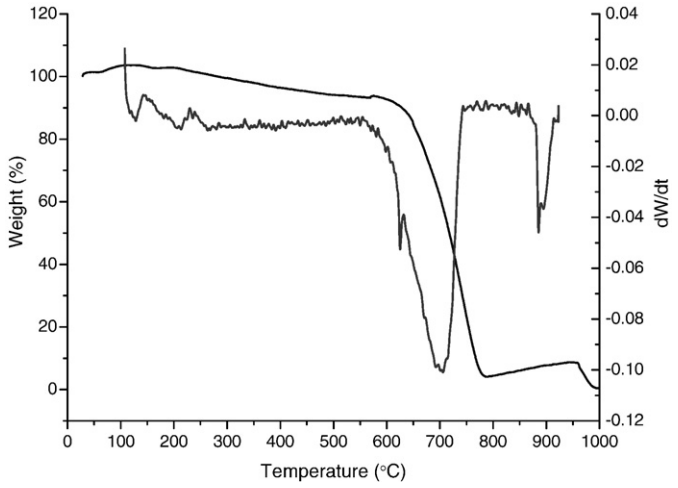

Fig. 3. TGA and DTGA curves of CNTs grown with natural palm oil.

4. Conclusions

The synthesis of vertically aligned carbon nanotubes have been demonstrated using natural palm oil as the carbon source and Fe nanoparticles derived from the decomposition of ferrocene as the catalyst. The technique was capable of producing CNTs of about 90% purity with minimal amorphous carbon content. Selective synthesis of SWNT or MWCNT is possible by tuning the deposition parameters such as the amount of catalyst materials, gas flow rates and synthesis temperature. Furthermore, this technique can be easily adopted for the synthesis of bulk CNTs. The simplicity of incorporating the catalyst material into the carbon source material and the economy of utilizing a readily available, renewable green source renders this technique a significant potential for large scale commercial production of CNTs.

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References

[1] Kumar M, Ando Y. Chem Phys Lett 2003;374:521.
[2] Kumar M, Ando Y. Diamond Relat Mater 2003;12:1845.
[3] Kumar M, Kakamu K, Okazak T, Ando Y. Chem Phys Lett 2004;385:161.
[4] Kumar M, Ando Y. Carbon 2005;43:533.
[5] Ghosh K, Kumar M, Maruyama T, Ando Y. Carbon 2009;47:1565.
[6] Ghosh P, Soga T, Afre RA, Jimbo T. J Alloys Compd 2008;462:289.
[7] Ghosh P, Soga T, Ghosh K, Afre RA, Jimbo T, Ando Y. J Non-Cryst Solids 2008;354:4101.
[8] Afre RA, Soga T, Jimbo T, Kumar M, Ando Y, Sharon M. Chem Phys Lett 2005;414:6.
[9] Afre RA, Soga T, Jimbo T, Kumar M, Ando Y, Sharon M, et al. Microporous Mesoporous Mater 2006;96:184.
[10] Ghosh P, Afre RA, Soga T, Jimbo T. Mater Lett 2007;61:3768.
[11] Isrihetty S, Azira AA, Rusop M. AIP Conf Proc 2009;1136:705.
[12] Saito R, Dresselhaus G, Dresselhaus MS. Phys Rev B 2000;61:2981.
[13] Huang W, Wang Y, Luo G, Wei F. Carbon 2003;41:2585.
[14] Chen CM, Chen M, Leu FC, Hsu SY, Wang SC, Shi SC, et al. Diamond Relat Mater 2004;13:1182.