Journal of Experimental Nanoscience
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t716100757

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To cite this Article Alonso-Nuñez, G. , Lara-Romero, J. , Paraguay-Delgado, F. , Sanchez-Castañeda, M. and Jiménez-Sandoval, S.(2010) 'Temperature optimisation of CNT synthesis by spray pyrolysis of alpha-pinene as the carbon source', Journal of Experimental Nanoscience, 5: 1, 52 — 60

To link to this Article: DOI: 10.1080/17458080903251786

URL: http://dx.doi.org/10.1080/17458080903251786

Journal of Experimental Nanoscience
Vol. 5, No. 1, February 2010, 52–60

Temperature optimisation of CNT synthesis by spray pyrolysis of alpha-pinene as the carbon source

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(*Received 15 January 2009; final version received 7 August 2009*)

Multi-wall carbon nanotubes (MWCNTs) were prepared by spray-pyrolysis of a botanical hydrocarbon, alpha-pinene and ferrocene as the catalyst at 700–1000°C. The MWCNTs were analysed by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and X-ray diffraction. The microscopy studies show the formation of carbon nanotubes with diameters between 20 and 30 nm and length greater than 100 µm. Raman spectroscopy revealed that the alpha-pinene-grown carbon nanotubes were graphitised showing both the D and G bands at 1330 and 1590 cm^{-1}, respectively, and that the corresponding intensity band ratio (I_D/I_G) varied with respect to temperature formation.

Keywords: carbon nanotubes; spray pyrolysis; microscopy

1. Introduction

Recently, carbon nanotubes (CNTs) and nanostructured materials have been extensively developed [1–3]. Since Iijima's landmark paper in 1991 [4], numerous papers have been published in this area; including, diameter and wall thickness evaluation (single or multiple) [5–7], growth mechanisms [8], alignment characteristics [9–11], electron emission properties [12–14], nanodevices [15,16], theoretical predictions [17] and potential applications [18]. Because of this enormous application potential, several methods have been reported for producing large quantities of quality CNTs at a low cost. Such methods include: arc discharge [19], laser evaporation [5] and chemical vapour deposition CVD [20]. Synthesis of CNTs by CVD methods have proved to be more controllable and cost efficient than arc discharge or laser evaporation methods [11]. Spray pyrolysis is a modification of the CVD method and is extensively used for the large-scale production of multi-wall carbon nanotubes (MWCNTs) at the lowest cost.

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ISSN 1745–8080 print/ISSN 1745–8099 online

DOI: 10.1080/17458080903251786
http://www.informaworld.com

The transition metals (e.g. Fe, Co and Ni) are the most common catalysts used as precursors for CNT growth [21]. Solid organometalocenes, such as ferrocene, cobaltocene and nickelocene are widely used as catalyst materials because they liberate metal particles *in situ*; therefore, enhance CNT growth [22].

By using CVD at temperatures between 625°C and 775°C, we find that ferrocene is a good catalyst for synthesising high-quality MWCNTs [23]. Ferrocene is also a good catalyst with the same method at 600°C under 12.4 MPa of pressure [24]. The carbon source materials are usually petrohydrocarbons such as acetylene [10], ethylene [25], toluene [26], benzene [27] and xylene [28]. Camphor has been successfully used as a botanical hydrocarbon in the synthesis of fullerenes [29], nanobeads [30], single-walled and multi-walled nanotubes [31] that are oriented towards photovoltaic applications [32]; and it has been used as secondary lithium batteries [33].

In this study, we used the spray pyrolysis method to investigate the influence of the temperature to optimise the production of the MWCN between 700 and 1000°C using alpha–pinene, a renewable biological carbon feedstock.

2. Experimental

The spray pyrolysis process used by us was described in an earlier paper [26]. A Vycor tube, used as a solution atomiser, was attached to a pneumatic system. The overall tube dimensions had an internal diameter of 0.9 cm and a length of 23 cm. A cylindrical furnace (Thermolyne 1200) with a high precision temperature controller (±1 K) heated the tubing. The solution feed time was kept constant for 15 min for all experiments. Twenty-five millilitres of alpha-pinene (Aldrich, 98.00%) and 1.00 g of ferrocene (Aldrich, 98.00%) were placed in a glass container. Argon (99.99%, Praxair) was used as the carrier gas; a mass flow controller at 83.33 cm^3/s regulated the flow rate. An argon/alpha-pinene/ferrocene mixture was fed into the Vycor tubing after the furnace temperature was set between 700 and 1000°C.

Afterwards, the black film of MWCNTs that formed at the inner surface of the Vycor tubing was mechanically removed with a brush and was analysed by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. Morphological analysis was carried out by a JEOL JSM5800 LV scanning electron microscope. The TEM micrographs were obtained by a Philips CM-200 analytical (TEM) operating at 200 kV. The TEM specimens were prepared by dispersing them in acetone and an ultrasonic bath for 2 min. A drop of suspension was put on a perforated carbon-coated Cu grid, and was allowed to dry. Raman spectroscopy was performed using a Labram system model Dilor micro-Raman equipped with a 20 mW He–Ne laser emitting at 632.8 nm and a holographic notch filter made by Kaiser Optical Systems, Inc. (model supertNotch-Plus) with a 256× q1024-pixel charge-coupled device (CCD) used as the detector; and a computer-controlled XY stage with a spatial resolution of 0.1 μm with two interchangeable gratings (600 and 1800 g/mm) and a confocal microscope with 10, 50, and 100× objectives. All measurements were carried out at room temperature with no special sample preparation. The XRD analyses were carried out using a Philips XPert MPD Diffractometer equipped with a curved graphite diffracted beam monochromator using a Cu-Kα radiation ($\lambda = 1.54184$ Å) at 43 kV and 30 mA.

3. Results and discussion

The growth temperature was varied between 700 and 1000°C. The SEM images taken from the middle section of the Vycor tube after the spray pyrolisis of alpha-pinene at different temperatures are shown in Figure 1 (a–d). At 700 and 800°C (Figure 1a and b), a large amount of nanotube films were obtained having a fibre-like morphology and were perpendicularly aligned with the Vycor tube. The lengths of the CNTs were estimated as being greater than 100 μm. When the temperature was increased to 900°C, the morphology of the nanotubes changed drastically as they became shorter in length and broadened in diameter. At 1000°C, the yield of carbon nanotubes was substantially decreased and the long fibre-like CNTs were hardly detected by SEM (Figure 1d).

The resulting films were also examined using TEM. Figure 2 (a–d) shows a sequence of TEM images of typical CNTs prepared by this method at different temperatures. At 700 and 800°C (Figure 2a and b), the formation of well defined and long MWCNTs is shown. The average diameter is about 40 nm at 700°C and 30 nm at 800°C. As the temperature was increased to 900°C, the diameter increased to about 250 nm and

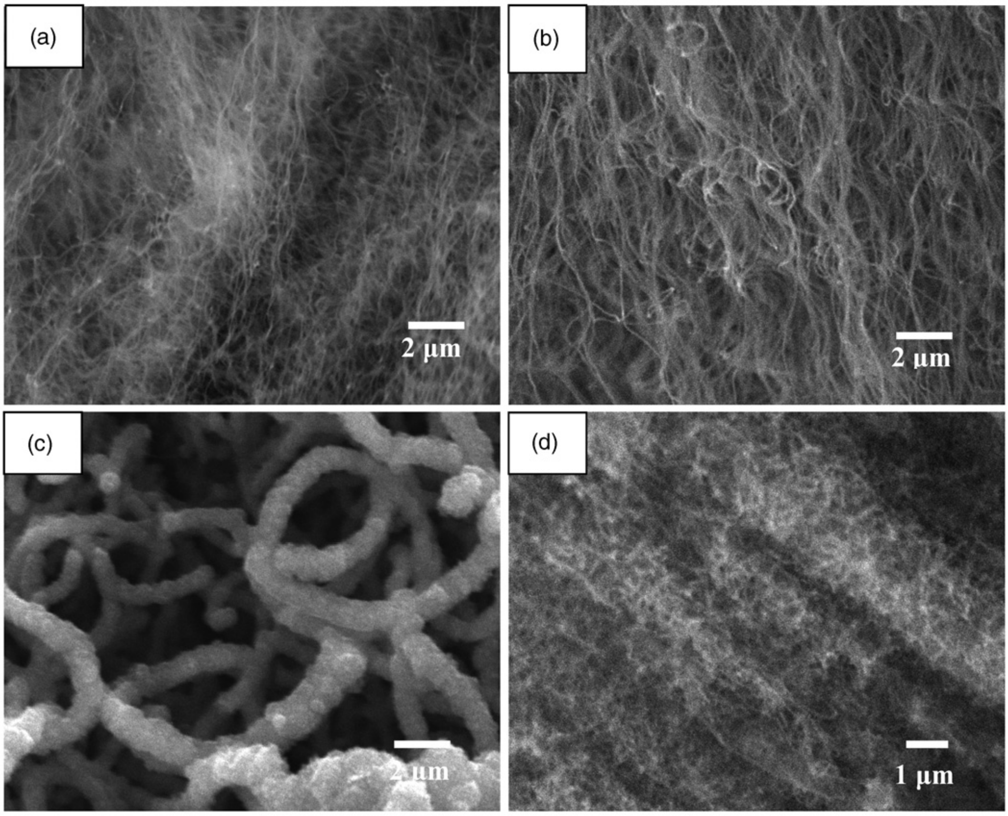

Figure 1. SEM images of nanotube films grown at different temperatures, (a) 700°C, (b) 800°C, (c) 900°C and (d) 1000°C, for 15 min and at a feed rate of 83.33 cm^3/seg of the solution.

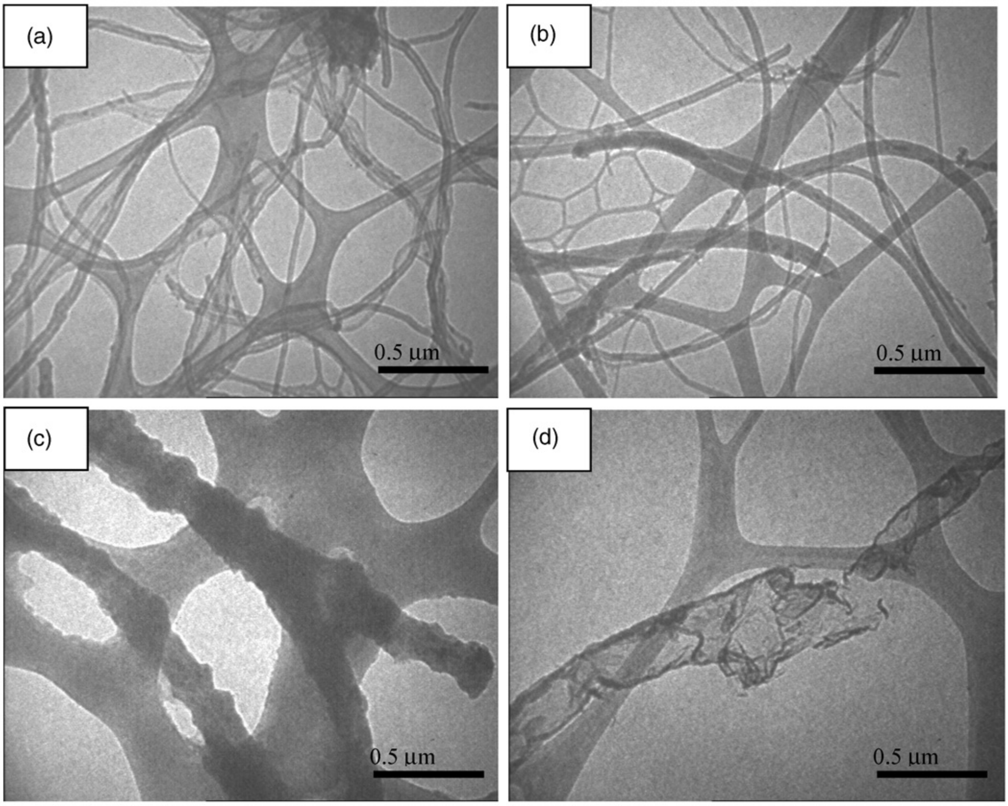

Figure 2. TEM images of nanotube films grown at different temperatures, (a) 700°C, (b) 800°C, (c) 900°C and (d) 1000°C, for 15 min and at a feed rate of 83.33 cm^3/seg of the solution.

the morphology changed. The grown nanotubes looked shorter and the walls seemed to lack continuity and had more defects.

More catalytic particles seemed to be present in the carbon nanotubes (Figure 2c). At 1000C (Figure 2d), the walls of the nanotubes were completely destroyed and more amorphous carbon was deposited. Both SEM and TEM analyses showed that the highest yield of well-structured carbon nanotubes took place at a temperature between 700 and 800°C. As the temperature increased above 900°C, more defects and amorphous carbon was detected.

Figure 3 shows the micro-Raman spectra of the MWCNTs grown at different temperatures observed under a He–Ne laser of wavelength 632.8 nm, 20 mW power, 1 µm illuminating spot size and 300 seconds acquisition time. The spectra revealed strong bands at 1350 and 1590 cm^{-1}which correspond to the D and G bands, respectively. The D band is the A_{1g} symmetrical stretch originating from crystallinity disorders and lattice imperfections in the MWCNTs. The G band was assigned to the tangential stretching mode of highly oriented graphite with E_{2g} symmetry [34]. The ratio of the intensities of the D band with respect to the G band (I_D/I_G) is often used as a measurement of the disorder

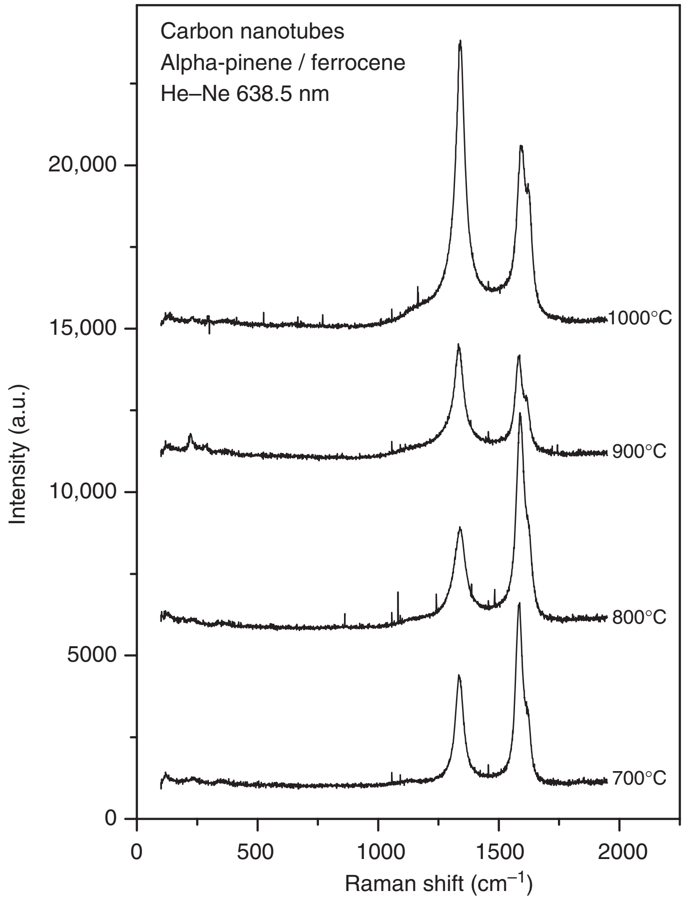

Figure 3. Raman spectra of carbon nanotubes grown from alpha-pinene/ferrocene at various temperatures.

of carbon nanotubes [35]. In this case, the average values of I_D/I_G as a function of temperature are given in Figure 4. A minimum of 0.43 was reached around 800°C, which corresponds to the optimal temperature required for procuring tubes with the least defects and highest yield. It is clear that the disorder increased as temperature increased, and is in agreement with the SEM and TEM observations.

XRD was used to determine the degree of graphitisation of the CNTs based on interlayer-spacing for ideal graphite (0.3354 nm) (JCPDS File 041-1487). The peaks at $2\theta = 26.1$ and 43.4° correspond to the graphite (002) and (100) planes, respectively. The results shown in Figure 5 indicate that the intensity of the graphite (002) peak changed with the reaction temperature and reached a maximum intensity at about 800°C. The calculated interlayer-spacing of graphite at this temperature was 0.3414 nm. This value is close to 0.3354 nm which is the value for an ideal graphite crystal with a high degree of graphitisation. At 900 and 1000°C, the intensity of the graphite (002) peak

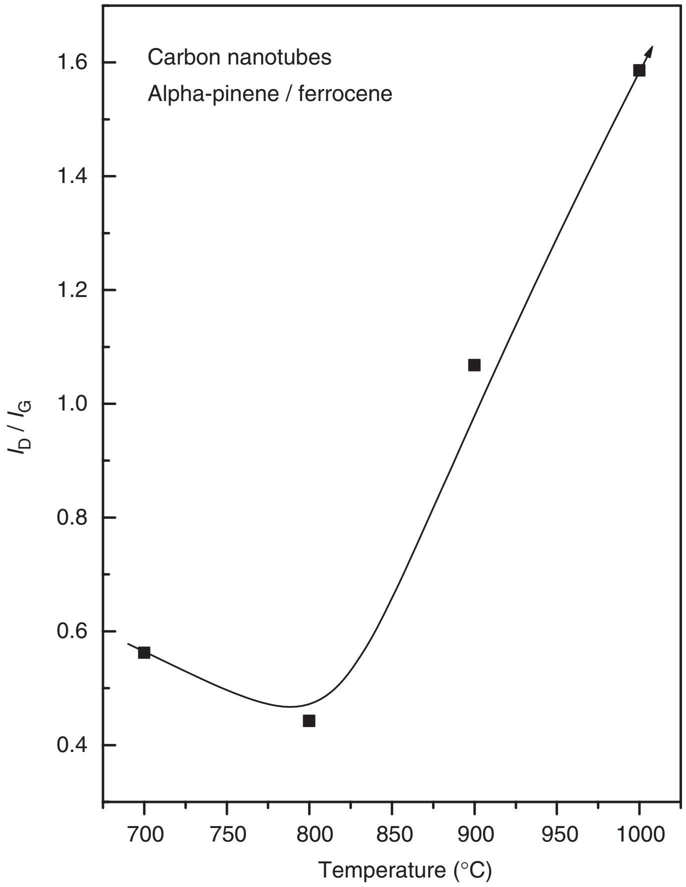

Figure 4. Average values of I_D/I_G showing the ratio of the D band to G band intensities for MWCNTs grown at various temperatures.

decreased substantially. This suggests that, at these temperatures, a less favourable process takes place for producing crystalline structures. At the same time, the intensity of the (100) peak increased which indicates that the distance between planes was reduced. These structures were thicker (~250 nm) and had a fibre-like shape.

4. Conclusions

Mixtures of alpha-pinene/ferrocene by nebulised spray pyrolysis were successfully used to produce MWCNTs inside Vycor tubing between 700 and 1000°C. SEM and TEM showed the formation of well-ordered carbon nanotubes at 800°C. XRD showed that, based on the intensities of the graphite (002) planes, the highest crystallisation yield took place at 800°C. Raman spectroscopy revealed that the lowest I_D/I_G ratio was at 800°C confirming the SEM, TEM and XRD results. The optimum temperature for procuring high-quality

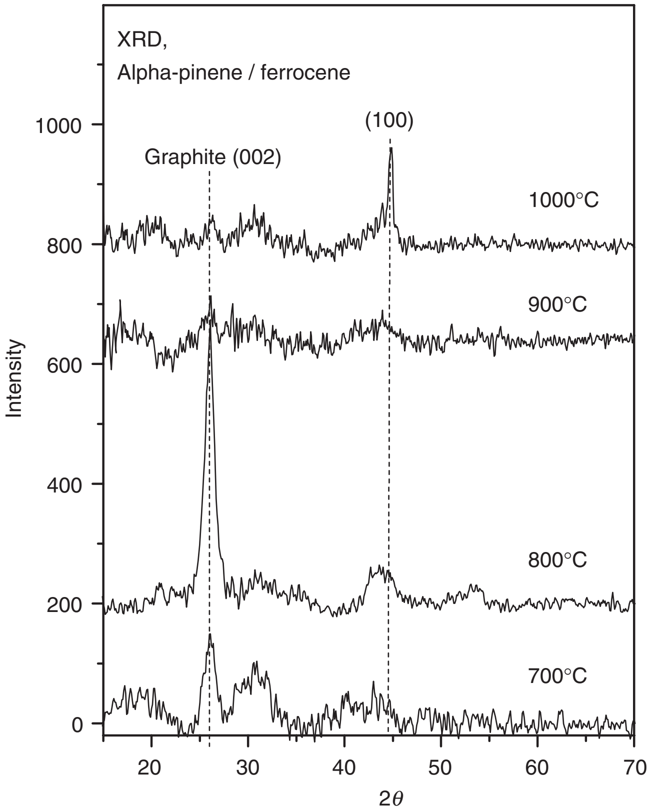

Figure 5. XRD results of MWCNTs grown at various temperatures.

MWCNTs using alpha-pinene as the natural carbon source and ferrocene as the catalyst by spray pyrolysis was at 800°C.

Acknowledgements

We would like to thank C. Ornelas, E. Torres, W. Antunez, I. Gradilla and D. Lardizabal for their valuable technical assistance. We also would like to acknowledge the support of CONACYT, Mexico; through grants 46871 and PAPIIT Project IN102509, UNAM.

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