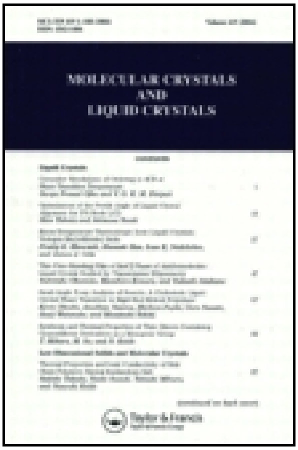

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Carbon nanotubes from camphor by catalytic cvd

Mukul Kumar [a], Xinluo Zhao [a], Yoshinori Ando [a], Sumio Iijima [a], Maheshwar Sharon [b] & Kaori Hirahara [c]

[a] Dept of Materials Science and Engineering, Meijo University, Nagoya, Japan

[b] Dept of Chemistry, Indian Institute of Technology, Mumbai, India

[c] Japan Science and Tech. Corp., c/o Meijo University, Nagoya, Japan

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Mukul Kumar, Xinluo Zhao, Yoshinori Ando, and Sumio Iijima
Dept of Materials Science and Engineering, Meijo University, Nagoya, Japan

Maheshwar Sharon
Dept of Chemistry, Indian Institute of Technology, Mumbai, India

Kaori Hirahara
Japan Science and Tech. Corp., c/o Meijo University, Nagoya, Japan

Multi-wall carbon nanotubes (MWNTs) have been grown from simple pyrolysis of camphor, a botanical hydrocarbon, at 900°C for 15 min in argon atmosphere at ambient pressure using ferrocene as a catalyst. The nanotube diameter is fairly uniform (20–40 nm) and the yield is extremely high (~90%). Structural characterization is done by SEM, TEM, HRTEM, EDX and Raman analyses. Good crystallinity, high purity, and absence of amorphous carbon and metal particles are the special features of camphor-pyrolyzed nanotubes.

Keywords: MWNT; CVD; camphor; pyrolysis

INTRODUCTION

There are many reports on synthesizing nanotubes from purified petroleum products such as methane [1], benzene [2,3], acetylene [4–6], etc. However, in view of the foreseen crisis of fossil fuels in the near future, it has become the time's prime demand to look for alternative sources for many kinds of useful application. Camphor ($C_{10}H_{16}O$), a botanical hydrocarbon, seems

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to be a promising precursor of carbon nanomaterials, viz. fullerenes [7], nanotubules [8], glassy carbon [9], diamond like carbon [10], nanobeads [11], semiconducting carbon films [12], etc. Being a plant-product, camphor is quite an eco-friendly source and can be easily cultivated in as much quantity as required. Abundantly found in Asian countries, camphor is very cheap and also user-friendly for pyrolysis due to its volatile and non-toxic nature. This is the first report of the growth of good quality, highly crystallized multi-wall nanotubes with a yield as high as 80–90%.

EXPERIMENTAL

A 900 mm long quartz tube (diameter 30 mm) serves as a CVD reactor kept horizontally inside two electrical furnaces. Appropriate quantities of camphor and ferrocene is taken in an alumina boat and kept inside the quartz tube in the centre of the first furnace. Argon is flown at the rate of 50 ml/min. Camphor and ferrocene vaporise within 4–5 min at 200°C in the first furnace and pyrolyse at 900°C in the second furnace. After 10 min of pyrolysis, both the furnaces are switched off. A thick deposit of carbon is observed on the inner wall of the quartz tube in the central region of the second furnace zone. As-obtained carbon powder was investigated on scanning electron microscope (Topcon: ABT-150F), transmission electron microscope (Hitachi: HU-12A) and high-resolution transmission electron microscope (JEOL: JEM-2010F). Micro-Raman spectra of these samples were taken on Raman spectrometer (Jobin Yvon: Ramanor T64000).

RESULTS AND DISCUSSION

Figure 1 shows an SEM micrograph of a thick mat of MWNTs grown at 900°C, which is a clear evidence of very high yield of MWNTs of diameter 20–40 nm. Figure 2 shows a TEM image of a similar bunch of MWNTs. Clear tubes of 20–40 nm diameter are seen without any trace of metal particles which are usually observed in general CVD or arc discharge method. Here the weight ratio of ferrocene to camphor plays an important role. When this ratio is higher than a critical value, depending upon the reactor geometry, more metal particles are observed in the specimen. When it is less than the critical value, more amorphous carbon is observed. In the present experimental conditions, this ratio was optimised to be 0.012, so that the metal particles are occasionally seen.

Figure 3 shows an HRTEM image of as-grown nanotubes, which suggests them to be multi-wall nanotubes having about 20–30 walls. The inner diameter varies from 10–15 nm while outer diameter is about 20–30 nm. The tube-ends are mostly closed having a pointed tip. Due to abundance

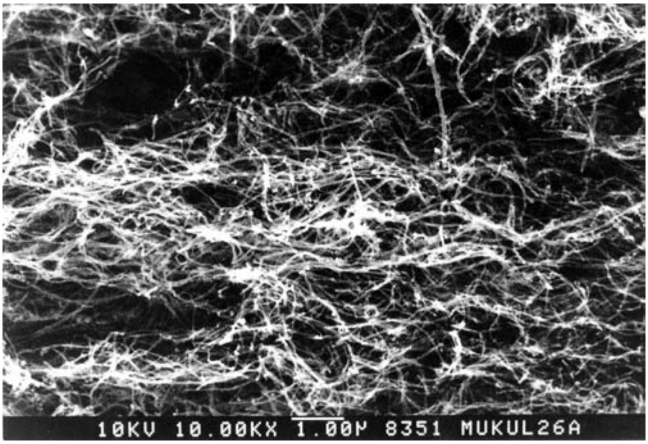

FIGURE 1 SEM image of a mat of MWNTs.

of pointed nanotips, as-grown MWNTs may be useful in field emission application, our next investigation in this series. The HRTEM image clearly shows that the tube layers are highly graphitised having a clear lattice fringe and without any trace of amorphous carbon. So we don't need any post-deposition heat treatment.

Raman spectra of these carbon nanotubes were taken by an Ar-laser of wavelength 514.5 nm at 20 mW power. A 100× objective lens was used to observe micro-Raman spectra with an illumination spot size of 1 μm and

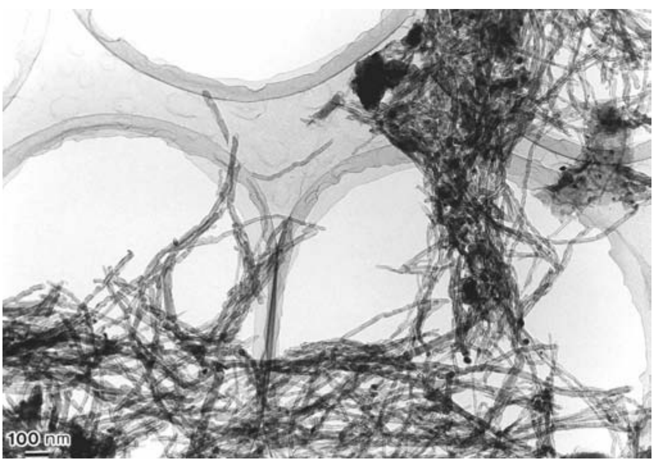

FIGURE 2 TEM image of a thin mat of MWNTs.

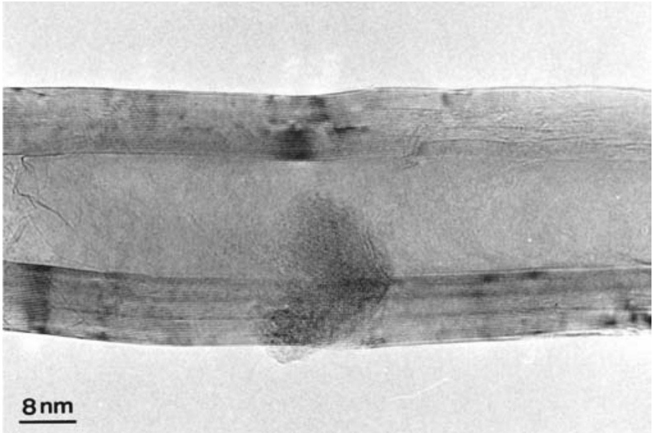

FIGURE 3 HRTEM image of an isolated MWNT.

acquisition time of 90 sec. As seen in Figure 4, two main peaks are observed at 1348 cm^{-1} and 1578 cm^{-1} corresponding to graphite's D- and G-lines respectively. The G-line corresponds to the E_{2g} mode of highly oriented pyrolytic graphite; and presence of high intensity G-line suggests the tubes to be composed of highly crystalline graphitic carbon. The D-line, at 1348 cm^{-1}, originates from disorder in the sp^2-hybridised carbon and indicates lattice distortions in the nanotubes formed. The relative intensity ratio (I_D/I_G), which is a measure of the amount of disorder in the

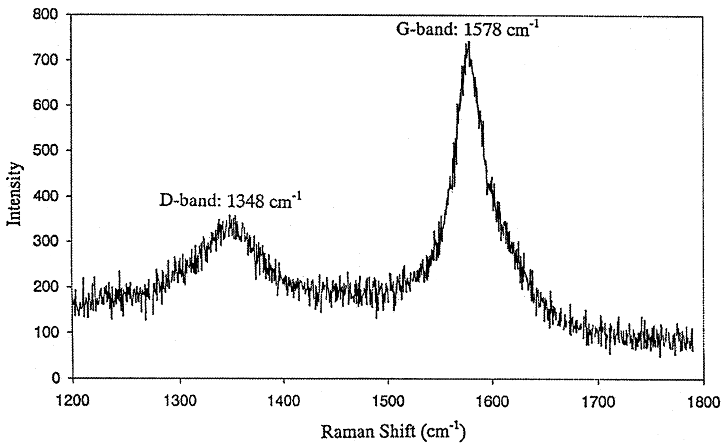

FIGURE 4 Micro-Raman spectra of as-grown MWNTs.

crystallinity, was measured to be 0.4. This is a much low and encouraging value as compared to MWNTs produced by similar thermal decomposition of acetylene on iron-plated silicon substrate in $Ar+H_2$ environment and showing $I_D/I_G = 0.85 \sim 1.3$ [13].

Our nanotubes are neither continuously hollow for a longer distance as produced from acetylene with iron-silica nanocomposite particles [4] nor bamboo type as produced from acetylene on iron-plated SiO_2 substrates [6]. Camphoric nanotubes have an intermediate structure in between the above two types; somewhat close to those prepared from benzene with ferrocene [2] and acetylene with $Fe(CO)_5$ [5]. But in terms of yield, purity and uniformity, the present nanotubes are much better than those. The energy dispersive X-ray (EDX) analysis has shown a molar C:Fe ratio of 99.63:0.37 and weight ratio of 98.3:1.7 in as-produced nanotubes, without any additional treatment.

CONCLUSION

Camphor, a very cheap botanical hydrocarbon, has the potential of growing high yield of well-crystallized MWNTs, free from amorphous carbon and metallic particles by simple CVD method, which is easy to scale-up. The work is in progress towards having more control on the tube diameter and getting single-wall nanotubes as well.

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