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Gigas Growth of Carbon Nanotubes

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ABSTRACT

An exceptionally high yield of carbon nanotubes (CNTs) has been achieved by chemical vapour deposition (CVD) of camphor over zeolite support. A simple 30 min CVD of 12 g camphor over *Fe-Co*-impregnated zeolite at 650 °C in an academic laboratory setup, yields 6 g multiwalled CNTs of dia ~10 nm with an as-grown purity of ~88 per cent. Owing to the enormous CNT growth, the zeolite bed inflates by 1000 wt per cent and 10,000 vol per cent. Camphor-to-CNT production efficiency is 50 per cent and net carbon-to-CNT conversion efficiency is 61per cent. These figures are incomparably higher than that of any CNT precursor by any method. Hence it is called 'gigas growth'. The technique greatly complies with the principles of green chemistry, and thus sets an example of an environment-friendly nanotechnology.

Keywords: Carbon nanotubes, camphor, chemical vapour deposition, green nanotechnology, gigas growth

1. INTRODUCTION

Nanotechnology is attracting scientists, industrialists, journalists, governments, and even common people alike. Carbon nanotubes (CNTs) are supposed to be a key component of this nanotechnology. It is the authors' pride privilege that the first CNT was discovered in the experimental specimen of Y. Ando[1]. Although CNTs are just 17 years old, having realised its tremendous application potential in nanotechnology, a huge amount of efforts and energy is invested in CNT projects worldwide. Nevertheless, till date, the art of CNT synthesis lies in the optimisation of the preparative parameters for a selected group of materials (carbon source, catalyst and support) on a particular experimental setup. And by any method, the CNT produced is not more than 10–20 per cent of the raw material used. In other words, 80–90 per cent of the feed stock goes waste and contributes to the environmental load. Therefore, it is high time to evaluate the existing CNT techniques on both economy and ecology perspectives.

Three most commonly used methods of CNT synthesis are: (i) arc discharge, (ii) laser vaporisation, and (iii) chemical vapour deposition (CVD). Arc-discharge method, in which the first CNT was discovered[1], employs evaporation of graphite electrodes in electric arcs that involves very high temperatures (~ 4000 °C). Although arc-grown CNTs are well crystallised, they are highly impure[2]. Laser vapourisation technique employs evaporation of high-purity graphite target by high-power lasers in conjunction with high-temperature furnaces[3]. Although laser-grown CNTs are of high purity, their production yield is extremely low[4]. Thus it is obvious that these two methods score too low on account of efficient use of energy and resources. The CVD method, incorporating catalyst-assisted thermal decomposition of hydrocarbons, is the most popular method of

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producing CNTs, and it is truly a low-cost and scalable technique for mass production of CNTs[5,6]. However, there are two weak points of the existing CVD-CNT technique: (i) it is a natural resource-dependent technique, because till date only purified petroleum products such as methane, ethylene, acetylene, benzene, xylene are in practice for synthesising CNTs and it is important to note that petrol cannot be generated but can only be exploited from the earth, and (ii) the CNT yield from these conventional precursors is not more than 25 per cent of the raw material used. That is, the feedstock-to-CNT conversion efficiency is still poor.

According to the principle of green chemistry, the feedstock of any industrial process must be renewable, rather than depleting a natural resource. Moreover, the process must be designed to achieve maximum incorporation of the constituent atoms (of the feedstock) into the final product. Hence, it is the time's prime demand to explore regenerative materials for CNT synthesis with high efficiency.

Success has been achieved in growing gram quantities of CNTs (on authors' academic laboratory setup) from camphor, a botanical product. Camphor is simply extracted from the latex of cinnamomum camphora tree of lauracea family. It is a white crystalline solid ($C_{10}H_{16}O$), comprising a cage-like molecular structure (Fig. 1).

Camphor has long been valued for its great medicinal usage in Asia but remained less-known in Europe and America. Its modern applications include its use as a plasticiser. Being a green-plant product, camphor is quite an environment-friendly source and can be easily cultivated in as much quantity as required. Unlike any fossil fuel or petroleum product, there is no fear of its ultimate shortage

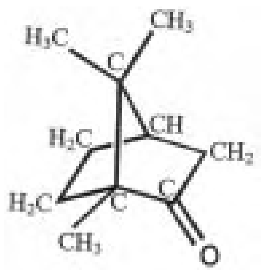

Figure 1. Molecular structure of camphor.

as it is a regenerative, reproducible source. Abundantly found in Asian countries, camphor is extremely cheap and also user-friendly for CVD due to its volatile and non-toxic nature.

This well-valued material of biotechnology research was first launched in nanotechnology research by Sharon's Group at IIT Bombay, Mumbai, who reported the syntheses of fullerene[7], semiconducting carbon tubules[8] and spongy carbon beads from camphor[9]. Inspired with those novel reports, camphor was chosen as a CNT precursor; however, it was not possible until 2001 that a systematic, reproducible and high-yield growth of CNTs from camphor was achieved[10]. Since then, extensive research was carried out with this environment-friendly source of CNTs and optimum conditions were established for growing multiwall nanotubes (MWNTs)[11,12], single-wall nanotubes (SWNTs)[13], and vertically aligned MWNTs on quartz and silicon plates[14] by a simple and inexpensive CVD technique. As-grown CNTs have shown appreciable field emission properties[15,16]. Recently, using a zeolite powder as the catalyst support, MWNTs were grown at a temperature as low as 550 °C, whereas SWNTs could be grown at relatively high (900 °C) temperature[17]. Using the same materials and method, now the relative concentrations of camphor, catalyst and support material in the reactor have been optimised to achieve an exceptionally high growth of MWNTs at 650 °C at atmospheric pressure.

2. EXPERIMENTAL

In an ordinary CVD reactor (a horizontal quartz tube in a split furnace), a desired quantity of camphor is vapourised at 150–170 °C and is pyrolysed over a calculated quantity of *Fe*-*Co*-impregnated zeolite support at 650 °C for 30 min at atmospheric pressure. The experimental setup and the catalyst preparation method is the same as reported earlier[17]. However, the metal concentration in zeolite, CVD time, and camphor vaporisation rate were changed in a wide range and optimised for the highest CNT yield[18]. Typically, the weight of the metal-supported zeolite powder taken is 10 wt per cent of camphor. Structural characterisations were done by scanning electron microscopy (SEM, Topcon: ABT-150F), transmission electron microscope (TEM, Hitachi: H7000) and

CNT purity was determined on the basis of thermogravimetry analysis (TGA, Shimadzu: TA-60 WS).

3. RESULTS AND DISCUSSION

The simple process described above is extremely effective towards CNT production. In the best optimised condition, 30 min CVD of 12 g camphor yields about 6 g CNTs. Figure 2 shows the photographs of the zeolite bed before and after CVD, which evidences a gigantic inflation as a consequence of camphor CVD. The 1.2 g *Fe-Co*-impregnated zeolite bed, which occupies a space of 1.5 ml before CVD, becomes 6.6 g after CVD and occupies a space of nearly 150 ml. Here it is important to note that there is a significant amount of moisture in the zeolite bed at room temperature. During the heating process of the reactor from room temperature to the CVD temperature (650 °C), this moisture and volatile acetate content of the catalyst are evaporated. To get an exact idea of such a weight loss in the zeolite bed, several blank experiments were carried out with the catalyst-impregnated zeolite alone in the reactor, maintaining all CVD conditions the same but without camphor. These experiments evidenced a significant weight loss of 45-50 per cent in the zeolite bed. This suggests that 1.2 g zeolite catalyst first reduces to ~0.6 g as a consequence of heating, and then gains ~6 g as a consequence of camphor CVD. That is, owing to a gigantic CNT growth, the zeolite bed inflates by 1000 wt per cent and 10,000 vol per cent. Hence, it is called 'gigas growth'. In this process, camphor-to-CNT production efficiency is 50 per cent, which is incomparably higher than that of any CNT precursor by any method. Another important point to note here is that camphor is not 100 per cent carbon. Calculated from its molecular weight, the carbon content of camphor is approximately 79 per cent. So, wrt the carbon content in the feedstock, net carbon-to-CNT conversion efficiency is 61 per cent. This figure is also amazingly high. Most efficient ways of MWNT production by CVD have a feedstock carbon-to-CNT conversion efficiency around 20-30 per cent.

It is important to note here that the percentage increase in the zeolite bed is a function of the amount of camphor evaporated during CVD. Initially the CNT deposit on the zeolite increased with the increase in the camphor feed. However, it got saturated when the camphor feed exceeded 12 g. It was experienced that, this factor is limited by the reactor size. Higher amounts of camphor evaporation, and hence, higher CNT yields should be possible in bigger-sized CVD reactors.

(a)

(b)

Figure 2. Photographs of the zeolite bed: (a) before CVD and (b) after CVD.

Figure 3 shows a typical SEM image of camphor-grown CNTs. The CNT growth is so huge that it is hard to locate a zeolite particle in the as-grown CNT bunches. Figure 4 shows a typical TEM image of camphor-grown CNTs. It clearly illustrates that as-grown samples are multiwall nanotubes of fairly uniform diameter. Careful diameter measurement from several TEM images showed a diameter distribution from 5 nm to 15 nm with a peak at ~10 nm. Presence of amorphous carbon or graphite particles was negligible. However, the CNTs were not very straight or of high crystallinity like those grown at high temperatures; typical surface defects of low-temperature CVD-grown CNTs were prevalent.

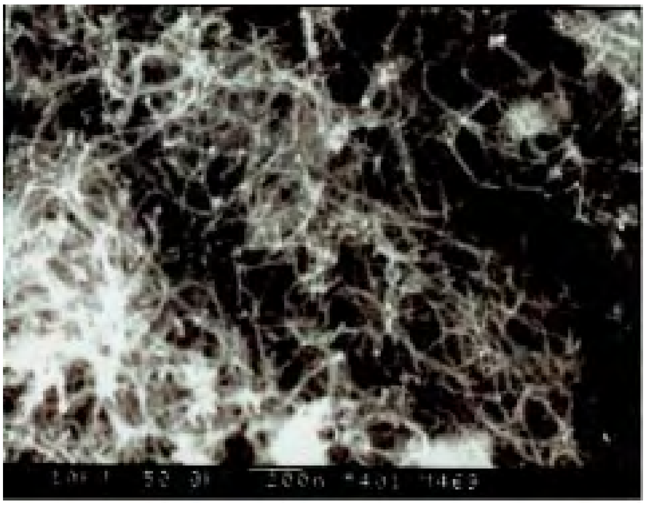

Figure 3. SEM image of as-grown CNTs.

The CNT purity was determined based on thermogravimetric analysis. Figure 5 shows typical DTA and TGA plots of an as-grown sample from room temperature to 800 °C @ 10 °C/min in the presence of dry air. A single DTA peak at 568 °C shows that there is a single burning material in the specimen, i.e., CNTs only. There is no peak corresponding to amorphous carbon (usually appearing around 400 °C) or graphite particles (usually appearing around 750 °C). The TGA weight loss, on the other hand, suggests the as-grown CNT purity of >88 per cent. Such a CNT specimen may directly be used for many applications without further purification. Nevertheless, for high-purity applications, the zeolite content of the as-grown specimen can easily be removed by 6M *NaOH* treatment[19] and the CNT purity can be increased over 99 per cent.

What's the most important factor for the gigas growth? To answer this question one has to consider what is new in this growth process. Carrier gas (*Ar*), catalyst (*Fe*-*Co*), catalyst support (zeolite), growth temperature (650 °C) and growth pressure (atmospheric): all have been attempted by thousands of CVD researchers for the last 10-15 years for several hydrocarbons (methane, ethylene, acetylene,

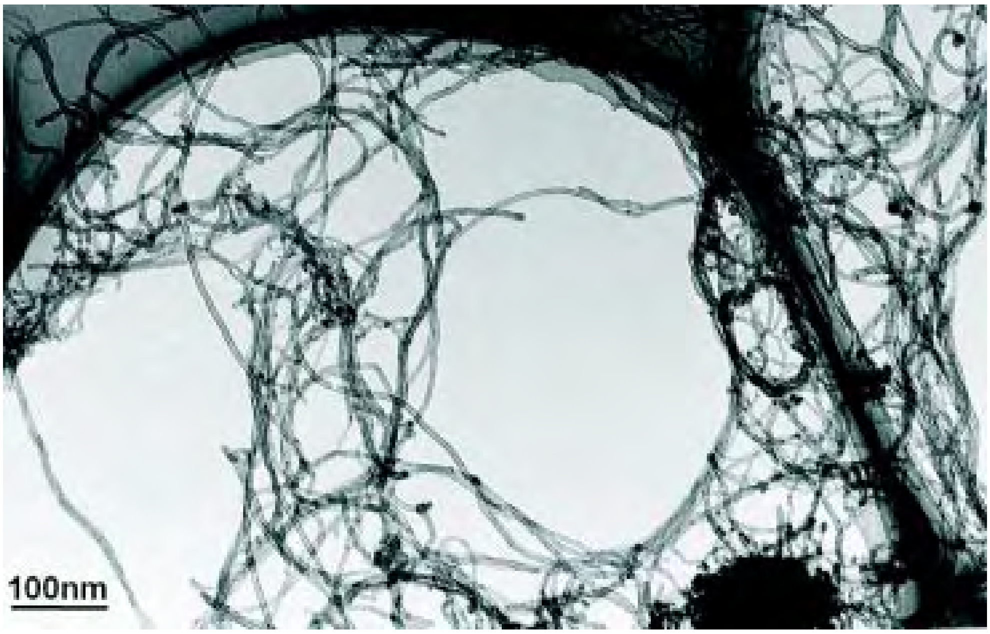

Figure 4. TEM image of as-grown CNTs.

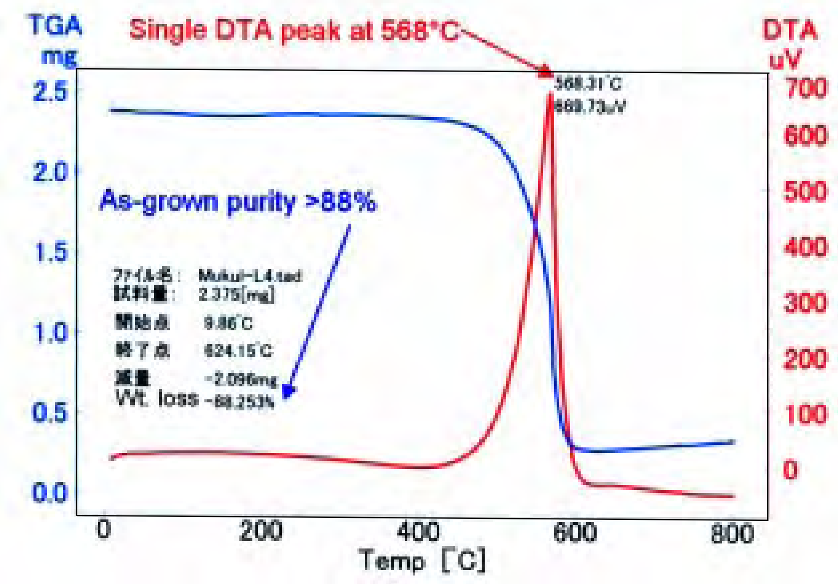

Figure 5. TGA and DTA curves of as-grown CNTs.

benzene, xylene, etc.) worldwide. But there is no report of such a gigantic growth ever. What's new here is the source material camphor which can straightforward be held responsible for the gigas growth. Now, to find a reason why camphor is so efficient towards CNT formation, the structure of the camphor molecule is needed to be considered (Fig. 1). As compared to the conventional CNT precursors such as CH_4, C_2H_4, C_2H_2, C_6H_6, camphor ($C_{10}H_{16}O$) is carbon-rich, hydrogen-rich, and oxygen-present. The bicyclic cage-structure of camphor plays a vital role in such an efficient CNT growth. Most probably, the hexagonal and pentagonal carbon rings of camphor construct CNTs as a basic building block: without breaking into atomic carbon. Moreover, CVD-CNT researchers usually mix a small amount of hydrogen gas in the carrier gas to reduce the metal oxide into pure metal catalyst. It was experimentally observed that the abundance of hydrogen in camphor serves this purpose to a great extent, and eliminates the need of additional hydrogen mixing into the carrier gas. And it was believed that the oxygen atom present in the camphor molecule helps oxidising amorphous carbon *in-situ*, as proposed by Maruyama[20,21], *et al*. Thus, every atom of camphor has a positive role towards CNT synthesis. The authors have described a probable growth mechanism of CNTs from camphor in an earlier report[13]. Recently, a chinese group[22] carried out *in-situ* mass spectroscopy of benzene CVD and supported the ring-based CNT growth hypothesis reported by the present authors[13].

Apart from camphor, the second important factor in gigas growth lies in the uniform impregnation of catalyst in the zeolite. Uniform growth of CNTs from all around the zeolite particles suggests that the catalyst is uniformly distributed in the zeolite pores. This fact is also supported by the narrow dia distribution of as-grown CNTs (~10 nm) which further suggests the uniformity of the particle size of the metal catalyst. The third important factor, then, is well-controlled influx of camphor vapour over the zeolite bed, which is controlled by the optimised argon flow rate of 200 sccm. It is very important that the camphor vapour gets decomposed catalytically on the zeolite surface only, not thermally above the zeolite. Here comes the role of low reactor temperature. Low CVD temperature (650 °C) greatly reduces the possibility of spontaneous (uncatalysed) decomposition of camphor vapour in the reactor. After completion of CVD, the quartz tube and ceramic boat are absolutely clear and clean, and it is only the zeolite bed which gets blackened and inflated gigantically. Gigas growth is therefore a consequence of so many factors controlled altogether. Recently high CNT-production efficiency of camphor and camphor-like materials has been reported by some other research groups as well[23,24]. It may be debatable whether the key of gigas growth lies in the source material–camphor, or in the optimisation of the control parameters, or in both (most probably); however, there is no doubt that this is a breakthrough in the utmost utilisation of a carbon source for CNT growth.

4. ENVIRONMENT-FRIENDLINESS

The United States Environmental Protection Agency (USEPA) has formulated 12 principles of green chemistry that explain what green chemistry means in actual practice[25]. Waste prevention, atom economy, energy efficiency and renewable feedstock are most vital points for an industrial process to be environmentally benign. Using those principles as a protocol, the authors have made an effort to evaluate how environment-friendly this technique is.

It is straightforward that the higher is the yield, the lesser is the waste. Giving the highest CNT-production efficiency, camphor complies with the waste-prevention rule significantly. Moreover, as explained above, every atom of camphor plays a positive role in CNT synthesis, which leads to maximum carbon-to-CNT conversion efficiency. This is a good example of atom economy. Further, by virtue of a low-temperature and atmospheric pressure CVD process, the energy requirement of this technique is very low (as compared to high-temperature low-pressure CVD-CNT processes). Certainly, it is an energy-efficient method. And last but not the least, the main raw material–camphor being an agricultural product, is absolutely a regenerative feedstock; so there is no danger of depleting a natural resource. Thus to a great extent (as far as practicable in an academic research laboratory), the camphor-based CNT synthesis technique complies with the principles of green chemistry, and therefore, it is environment-friendly.

5. CONCLUSIONS

Camphor is shown to have an amazing CNT production efficiency of 50 Wt per cent of the feed-stock used. There is a gigantic growth in the zeolite bed by 1000 Wt per cent and 10,000 vol per cent. As-grown CNTs have a purity of ~88 per cent and average dia of ~10 nm. With respect to the carbon present in camphor, net carbon-to-CNT conversion efficiency is 61 Wt per cent. These figures are incomparably higher than those obtained from the conventional CNT precursors. The method is simple, energy-saving, and scalable for industrial production of CNTs. In conclusion, camphor seems to be an excellent CNT precursor, not only in terms of ease of fabrication, high yield and high purity, but also in terms of growth control and application prospects. Last but not the least, this environment-friendly precursor of CNTs, opens an avenue of green nanotechnology. 'So many good things in one package?' Don't suspect, try it; verify it. Grow CNTs from camphor and save time, money, energy, and the environment.

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Dr Yoshinori Ando obtained his PhD (Applied Physics) from Nagoya University, Japan. Since 1974 till date, he has been serving as a faculty staff of Meijo University. During 1987-1988, he was a visiting research fellow at Bristol University, UK. His research areas include X-ray diffraction topography of distorted crystals, electron microscopy of thin films and ultrafine particles, arc-discharge synthesis of fullerenes and carbon nanotubes. It is noteworthy that the first carbon nanotubes reported by Iijima [*Nature*, 1991, **354**, 56] were found in Prof Ando's specimen. He has published over 200 research papers in reputed journals, presented over 100 papers at various conferences worldwide and owns a dozen of patents.