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Carbon Nanotubes from Camphor: An Environment-Friendly Nanotechnology

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Abstract. High-purity carbon nanotubes (CNTs) are produced by chemical vapour deposition of camphor, an environment-friendly hydrocarbon. In a small CVD reactor (1-m long and 26-mm wide), CVD of 3 g camphor at 650°C for 1 hour yields ~1.62 g MWNTs of diameter ~10 nm with an as-grown purity over 88%; that is, camphor-to-CNT production efficiency is 50%. This is the highest efficiency ever achieved from any material by any method. Moreover, camphor-based CNT synthesis technique stands fairly good against the 12-principle protocol of green chemistry.

1. Introduction

Nanotechnology is a hot topic today attracting scientists, industrialists, journalists, governments, and even a common people alike. And carbon nanotubes (CNTs) are supposed to be a key component of this nanotechnology. It is our pride privilege that the first CNT specimen reported by Iijima [1] was made by one of us (Y. Ando). Although CNTs are just 15 years old; crazy success stories are floating in media about this teen-aged heroine of the scientific Hollywood. Having realized its tremendous application potential in nanotechnology, a huge amount of efforts and energy is invested in CNT projects worldwide. Till date, the art of CNT synthesis lies in the optimization of the preparative parameters for a selected group of materials (carbon source, catalyst and support) on a particular experimental set-up. And the CNT produced is not more than 10-20% of the raw material used. In other words, 80-90% of the feed stock goes waste and contributes to the environmental load. As viewed from the perspective of green chemistry, sustaining the environment implies sustaining the human civilization. Apart from immediate concern towards the environment and human health, the long-term key of a sustainable society lies in 'stable economy' that uses energy and resources efficiently. Therefore, it is high time to evaluate the existing CNT techniques on these parameters.

Let us examine three popular methods of CNT synthesis. Arc-discharge method, in which the first CNT was discovered [1], employs evaporation of graphite electrodes in electric arcs that involve very high temperatures (~4000°C). Although arc-grown CNTs are well crystallized, they are highly impure. Laser-vaporization technique employs evaporation of high-purity graphite target by high-power lasers in conjunction with high-temperature furnaces [2]. Although laser-grown CNTs are of high purity, their production yield is very low. Thus it is obvious that these two methods score too low on account of efficient use of energy and resources. Chemical vapor deposition (CVD), incorporating catalyst-assisted thermal decomposition of hydrocarbons, is the most popular method of producing CNTs, and it is truly a low-cost and scalable technique for mass production of CNTs. Unfortunately, however, till date only purified petroleum products such as methane, ethylene, acetylene, benzene, xylene are in practice for synthesizing CNTs. In view of the foreseen crisis of fossil fuels in near future, it is the time's prime demand to explore regenerative materials for CNT synthesis. We have succeeded in growing **gram** quantities of CNTs per hour (in our academic laboratory) from camphor ($C_{10}H_{16}O$), a botanical hydrocarbon. Camphor is simply extracted from the latex of cinnamomum camphora tree of lauracea family. It is a white crystalline solid that sublimates at room temperature. It has long been valued for its great medicinal uses in Asia but remained less known in Europe and America. It is used as a room freshener and food disinfectant. Indian people use to burn camphor in temples while offering prayer. Unlike common fumes, the camphor fume is non-irritant to eyes. Camphor-soot paste is, therefore, also used in eye make-up. Its modern applications include use as a plasticizer. Being a green-plant product, camphor is quite an eco-friendly source and can be easily cultivated in as much quantity as required. Unlike any fossil/petroleum product, there is no fear of its ultimate shortage 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.

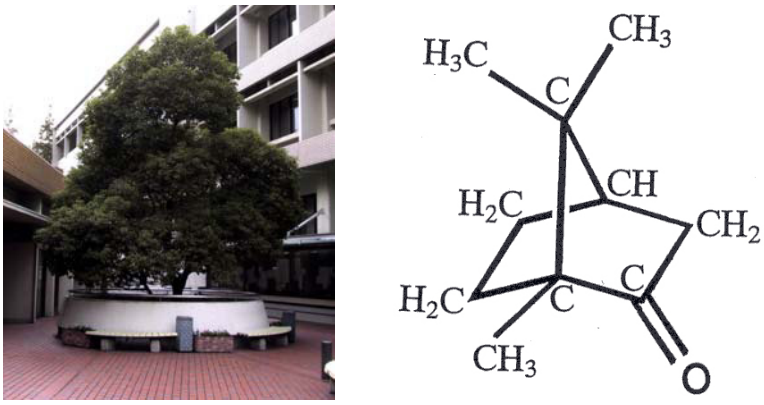

Fig. 1 Picture of a camphor tree and structure of a camphor molecule.

This well-valued material of biotechnology research was successfully brought to nanotechnology research with the first report of "CNTs from camphor" [3] in 2001. Since then, we remained involved with this environment-friendly source of CNTs and established the conditions for growing multiwall nanotubes (MWNTs) [4,5] single-wall nanotubes (SWNTs) [6] and vertically aligned MWNTs [7] on quartz and silicon plates by a simple and inexpensive CVD technique. As-grown CNTs have shown appreciable field emission properties [8]. Recently, using a zeolite powder as the catalyst support, we have been able to grow MWNTs at a temperature as low as 550°C, whereas SWNTs could be grown at relatively high (850°C) temperature [9]. Using the same materials and method, we have now optimized the relative concentrations of camphor, catalyst and support material in the reactor to achieve very high growth rate of MWNTs at 650°C at atmospheric pressure.

2. Experimental result

In a small CVD reactor (1-m long and 26-mm wide), 3 g camphor is vaporized at 200°C under a mild argon flow of 50 sccm, and is pyrolyzed over 0.3 g Fe-Co-impregnated zeolite support at 650°C. Such a simple process for 1 hour apparently inflates the zeolite bed over 50 times by volume and yields 1.62 g MWNTs of diameter ~10 nm with an as-grown purity over 88% as shown in figures 2 and 3 below. Camphor-to-CNT production efficiency is ~50%, which is incomparably higher than that of any CNT precursor by any method. Most efficient ways of MWNT production by CVD have a carbon source-to-CNT conversion efficiency around 20-30% [10].

Fig. 2 Optical photograph of camphor and zeolite bed before and after CVD.

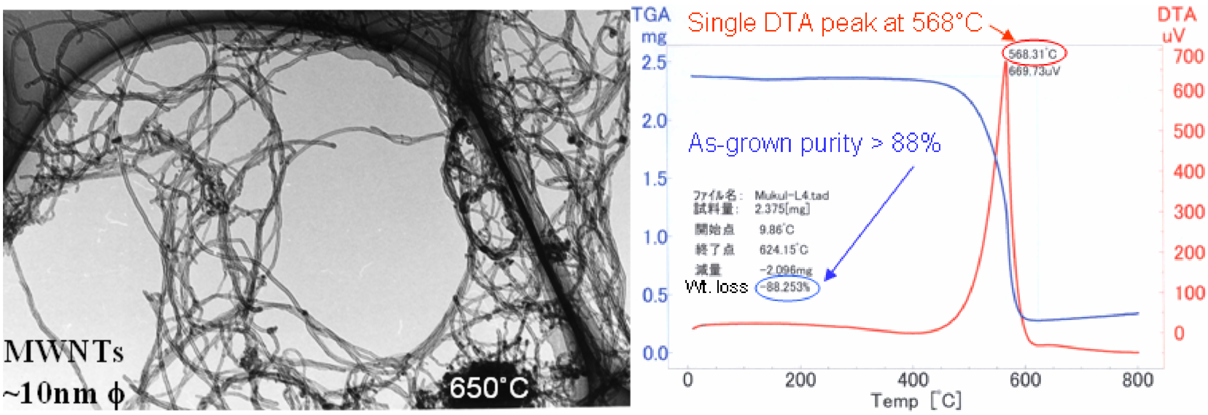

Fig. 3 TEM image and TGA curve of as-grown CNTs

It may be debatable whether the key of this enormous growth lies in the source material: camphor, or in the optimization of the control parameters, or in both (as we believe); however, there is no doubt that this is a breakthrough in the utmost utilization of a carbon source for CNT growth.

3. How environment-friendly

United States Environmental Protection Agency has developed 12 principles of green chemistry [11] that explain what the green chemistry means in practice. Using those definitions as a protocol, we can evaluate our camphor-based CNT synthesis method as follows.

1. Prevention: With the highest CNT-production efficiency, camphor complies with waste-prevention rule significantly.
2. Atom Economy: Camphor gets maximum incorporation of its constituent atoms into the final product, CNTs.
3. Less Hazardous Chemical Syntheses: All the substances involved in our technique (carbon source, catalyst and support material) possess little or no toxicity to human health and the environment.
4. Designing Safer Chemicals: Our final product is ‘common-grade CNTs’ that are apparently safe, though it is still a subject of ongoing research; too early to comment on.
5. Safer Solvents and Auxiliaries: The only auxiliary used in our method is the metal catalyst that are apparently safe.
6. Design for Energy Efficiency: By virtue of a low-temperature atmospheric-pressure CVD process, the energy requirements of our technique are significantly low.
7. Use of Renewable Feedstocks: The main raw material, camphor, is purely a regenerative material; so there is no danger of depleting a natural resource.

8. Reduce Derivatives: No derivatization is involved in our technique; solely catalyst-assisted in-situ decomposition of camphor leads to CNTs.

9. Catalysis: It is a purely catalytic process, no stoichiometric reagents are involved.

10. Design for Degradation: CNTs as such are non-biodegradable; however, their intentional degradation can be achieved with certain functionalization. It is still a subject of ongoing research; too early to comment on.

11. Real-time analysis for Pollution Prevention: This could not be done at our academic research laboratory due to the financial constraints; however, our technique as such is fully compatible with real-time analysis for pollution prevention, if executed at an industrial laboratory.

12. Inherently Safer Chemistry for Accident Prevention: Substances and their form used in our process are chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

4. Conclusion

Thus we see that, to a great extent (as far as practicable), our camphor-based CNT synthesis technique complies with the 12-principle protocol of green chemistry. 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. "*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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