GIGAS GROWTH OF CARBON NANOTUBES FROM CAMPHOR: A STEP TOWARDS GREEN NANOTECHNOLOGY

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Abstract

Camphor ($C_{10}H_{16}O$) is shown to have an amazing efficiency of producing carbon nanotubes (CNTs) by a technique greatly complying with the principles of Green Chemistry. Right from the first report of CNTs from camphor, we remained involved with this environment-friendly CNT precursor and established the conditions of growing single-wall & multiwall CNTs, and vertically aligned CNTs by thermal CVD. Recently, using a zeolite powder as the catalyst support, we reported MWCNT growth at a temperature as low as 550°C. Using the same process, we have now optimized the concentrations of camphor, catalyst and support material in the reactor to achieve an exceptionally high growth of CNTs. A simple 30-min CVD of 12g camphor over Fe-Co-impregnated zeolite at 650°C yields 6g MWCNTs of diameter ~10 nm with as-grown purity of ~88%. Owing to the enormous CNT growth, the zeolite bed inflates by 1000wt% and 10,000vol%. Camphor-to-CNT production efficiency is 50% (net carbon-to-CNT conversion efficiency is 61%), which is incomparably higher than that of any CNT precursor by any method. Hence we call it ***gigas growth***.

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 was discovered in the experimental specimen of one of us (Y. Ando).[1] 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, by any method, 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. However, there are two weak points of the existing CVD-CNT technique. No.1: it is a natural resource-dependent technique. Till date only purified petroleum products such as methane, ethylene, acetylene, benzene, xylene are in practice for synthesizing CNTs. It is important to note that we cannot generate gasoline (petrol); we just extract them from the earth. No.2: the CNT yield from these conventional precursors is not more than 10–20% of the raw material used. That is, the feedstock-to-CNT conversion efficiency is poor. According to the principle of *green chemistry*, the feed stock 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 feed stock) into the final product. Hence it is the time's prime demand to explore regenerative materials for CNT synthesis with high efficiency. We have succeeded in growing *gram* quantities of CNTs (on our academic laboratory set-up) from camphor ($C_{10}H_{16}O$), a botanical product. Camphor is simply extracted from the latex of cinnamomum camphora tree of lauracea family (**Figure 1**). It is a white crystalline solid that sublimes 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 fuel or 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 (US$30/kg) and also user-friendly for CVD due to its volatile and non-toxic nature.

This well-valued material of biotechnology research was successfully brought to nanotechnology research with the first report of "CNTs from camphor" in 2001.[3] 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 on quartz and silicon plates[7] by a simple and inexpensive CVD technique. As-grown CNTs have shown appreciable field emission properties.[8,9] Recently, using a zeolite powder as the catalyst support, we grew MWNTs at a temperature as low as 550°C, whereas SWNTs could be grown at relatively high (950°C) temperature.[10] 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 of MWNTs at 650°C at atmospheric pressure.

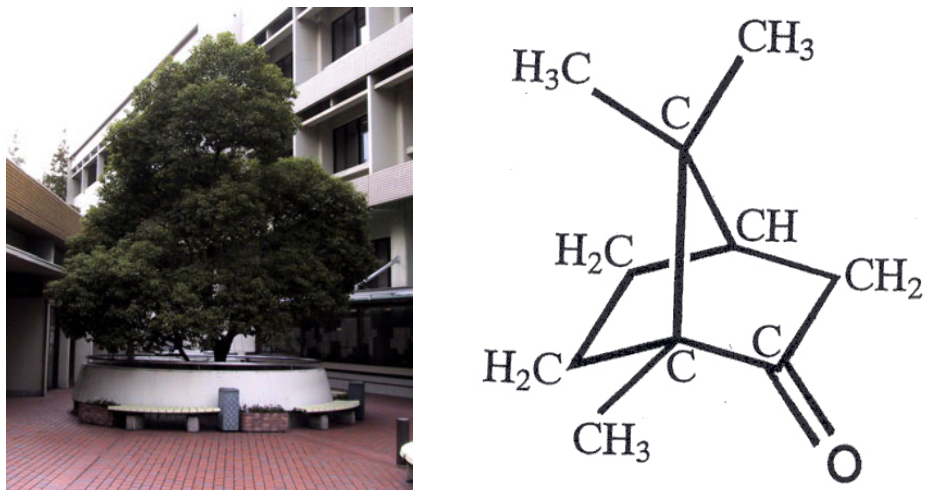

Figure 1. Picture of a camphor tree and the structure of a camphor molecule.

Experimental

In an ordinary CVD reactor (a horizontal quartz tube in a split furnace), a desired quantity of camphor is vaporized at 100–200°C and is pyrolyzed over a calculated quantity of Fe-Co-impregnated zeolite support at 650°C for 30 min at atmospheric pressure. The experimental set up and the catalyst preparation method is the same as reported earlier.[9] However, the metal concentration in zeolite, CVD time and camphor vaporization rate were changed in a wide range and optimized for the highest CNT yield. Structural characterizations were done by transmission electron microscope (TEM, Hitachi: H7000) and CNT purity was determined on the basis of thermo-gravimetry analysis (TGA, Shimadzu TA-60 WS).

Results

The simple process described above is extremely effective towards CNT production. In the best optimized condition, 30-min CVD of 12 g camphor over 1.2 g Fe-Co-impregnated zeolite yields about 6 g MWNTs. That is, Camphor-to-CNT production efficiency is ~50%. Owing to the mosterous CNT growth, the zeolite bed inflates by 1000wt% and 10,000vol%, which is incomparably higher than that of any CNT precursor by any method. Hence we call it ***gigas growth***. Here it is important to note that camphor is not 100% carbon. Calculated from its molecular weight, the carbon content of camphor is nearly 80%. Hence, with respect to C atoms present in the feed, the net carbon-to-CNT conversion efficiency is 61%.

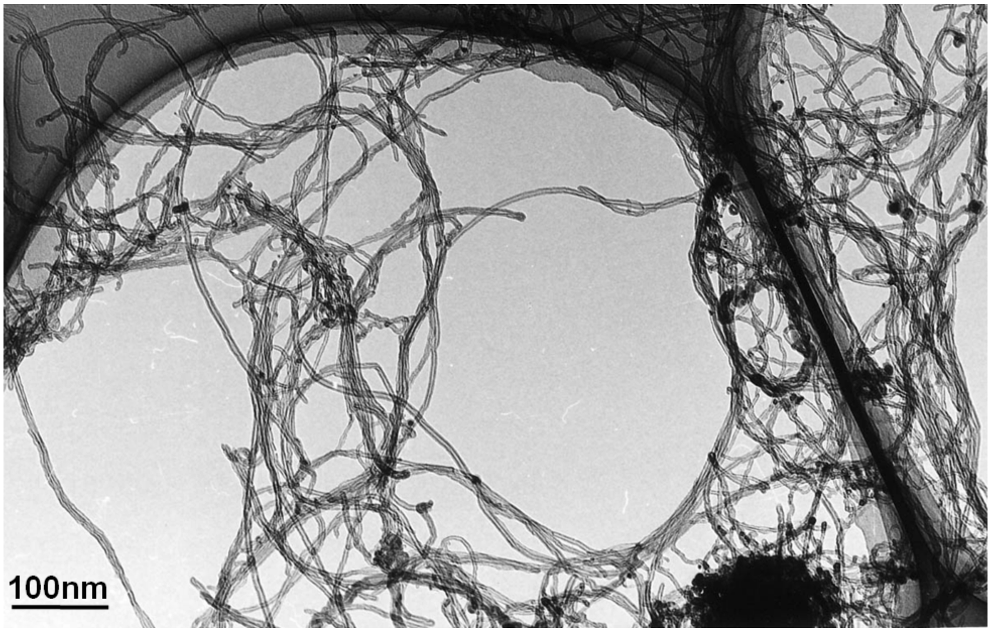

Figure 2. TEM image of as-grown CNTs.

Figure 2 shows a typical TEM image of camphor-grown CNTs. It clearly illustrates that as-grown samples are multiwall nanotubes of fairly uniform diameter. The CNT growth is so huge that it is hard to locate a zeolite particle. Careful diameter measurement from several TEM images shows a diameter distribution from 5nm to 20 nm with a peak at ~10 nm. Presence of amorphous carbon or graphite particles was negligible.

The CNT purity was determined based on thermogravimetric analysis. **Figure 3** shows typical DTA and TGA plots of as-grown samples 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 between 350°C and 450°C) or graphite particles (usually appearing between 650°C and 750°C). The TGA weight loss, on the other hand, suggests the as-grown CNT purity of >88%.

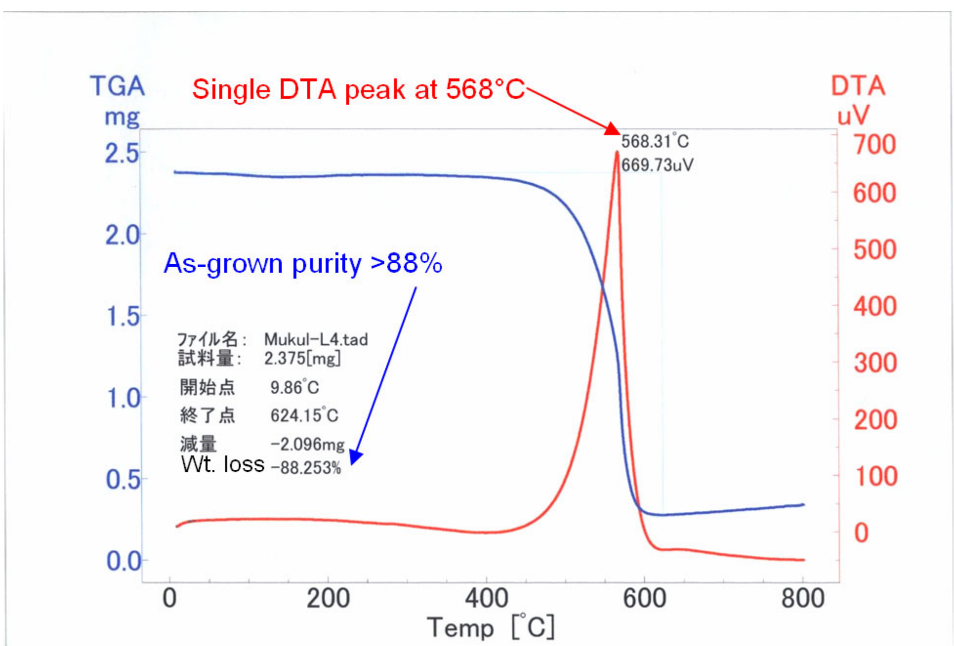

Figure 3. TGA and DTA curves of as-grown CNTs.

Discussion

In order to find a reason why camphor is so efficient towards CNT formation, let us look into the structure of the camphor molecule. 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. We believe that camphoric carbon rings (already being in pentagonal and hexagonal form) constitute CNT with high efficiency. The abundance of hydrogen in camphor helps reducing the metal oxide into pure metal to act as a catalyst. And oxygen atom helps oxidizing amorphous carbon in-situ. Thus every atom of camphor has a positive role towards CNT synthesis. We have described a probable growth mechanism of CNTs from camphor in an earlier report.[6] Recently, a Chinese group carried out in-situ mass spectroscopy of benzene CVD and supported our ring-based CNT growth hypothesis.[11]

It may be debatable whether the key of this ***gigas 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.

The United States Environmental Protection Agency has formulated *12 Principles of Green Chemistry* that explain what *green chemistry* means in actual practice.[12] Using those principles as a standard protocol, we can see that, to a great extent (as far as practicable in an academic research laboratory), our camphor-based CNT synthesis technique complies with the principles of *green chemistry*.

Conclusions

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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