Continuous production of aligned carbon nanotubes: a step closer to commercial realization

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Abstract

High-purity aligned multi-walled carbon nanotubes (MWNTs) were synthesized through the catalytic decomposition of a ferrocene–xylene mixture at $\sim 675°C$ in a quartz tube reactor and over quartz substrates, with a conversion of $\sim 25\%$ of the total hydrocarbon feedstock. Under the experimental conditions used, scanning electron microscope images reveal that the MWNT array grows perpendicular to the quartz substrates at an average growth rate of ~ 25 µm/h. A process of this nature which does not require preformed substrates, and which operates at atmospheric pressure and moderate temperatures, could be scaled up for continuous or semi-continuous production of MWNTs. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The synthesis of aligned multi-walled carbon nanotubes (MWNTs) via the catalytic pyrolysis of hydrocarbons has been realized by several research groups around the world [1–12]. Most of these researchers report the use of preformed substrates. For example, high-purity aligned MWNTs were produced by the catalytic decomposition of 2-amino-4,6-dicholoro-s-triazine at 1000°C between tracks generated by laser etching cobalt films supported on silica [2]. Large arrays of aligned MWNTs were grown normal to nickel-coated glass substrates below 666°C by the plasma-enhanced hot-filament chemical-vapor deposition of a mixture of acetylene and ammonia [5]. In this Letter, we describe a method for producing bulk quantities of high-purity aligned MWNTs through the catalytic decomposition of a ferrocene–xylene mixture at temperatures as low as $\sim 650°C$. Our synthesis method does not require preformed substrates. In principle, it is simple and inexpensive. It can be operated at atmospheric pressure and moderate temperatures and gives very high

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selectivity to multi-walled nanotubes. A process of this nature could be easily scaled up and used for continuous or semi-continuous production.

A desirable goal is to be able to produce single-wall nanotubes (SWNTs) by a similar continuous process. Cheng et al. [8] have demonstrated that thiophene serves as a growth promoter for producing long SWNT bundles from the ferrocene-catalyzed decomposition of benzene at 1000°C in a stream of hydrogen. Recently, the Rice group mentioned that they had not been able to reproduce the experimental findings reported by Cheng et al. suggesting that the growth parameters for long SWNT bundles are still not well defined [13]. Nevertheless, it seems most probable that it is only a matter of time before SWNT bundles will also be produced by a continuous economical process, similar to the one reported in this Letter.

2. Experimental

Approximately 6.5 mol% of ferrocene was dissolved in xylene (to obtain a feed solution with ~ 0.75 at % Fe/C ratio) and was fed continuously into a two-stage tubular quartz reactor (diameter, ~ 34 mm) using a syringe pump (Fig. 1). Ferrocene (sublimation temperature, ~ 140°C) has been shown to be a good precursor for producing Fe catalyst particles which can seed nanotube growth, and xy-

lene was selected as the hydrocarbon source since it boils (boiling point, ~ 140°C) below the decomposition temperature of ferrocene (~ 190°C) [14]. The liquid feed is passed through a capillary tube and preheated to ~ 175°C prior to its entry into the furnace. At this temperature, the liquid exiting the capillary, is immediately volatilized and swept into the reaction zone of the furnace by a flow of argon with 10% hydrogen. Various parameters, such as the furnace temperature (650–1050°C), ferrocene/xylene ratio and feed rate, total reaction time, and sweep gas flow rate were adjusted to determine the growth conditions for high purity aligned MWNTs (Table 1). After the reaction, the preheater and the furnace were allowed to cool to room temperature in flowing argon. Carbon deposits were formed on the walls of the quartz furnace tube and on plain quartz substrates (microscope slides) that were placed within the furnace to act as additional sites for nanotube growth. The substrates were weighed before and after each run to determine the quantities of nanotubes produced at different sites within the reactor. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the nanotubes deposited on the substrates allowed us to monitor the quality of MWNTs grown under different operating conditions. The walls of the reactor tube were also scraped clean of nanotube material and weighed. At all times, the reactor was operated
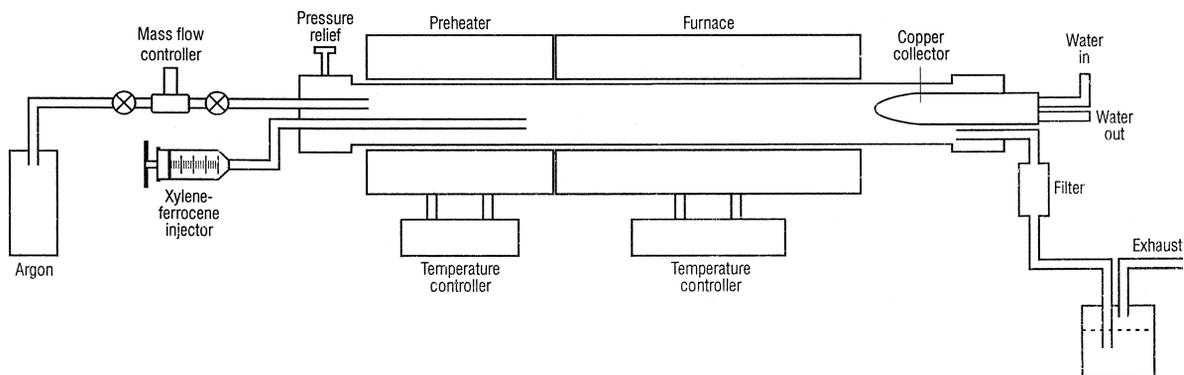

Fig. 1. Schematic of the reactor used for the nanotube synthesis. The ferrocene–xylene liquid feed is injected into the preheater stage using a syringe pump. Using a mass flow controller, Ar/H_2 gas is introduced at the entrance of the preheater to sweep the reactant vapors into the hot zone of the furnace.

Table 1

Operating conditions for three reactor runs with the furnace temperature held at $\sim 675°C$, 0.75 at % Fe/C ratio and run duration ~ 2 h

Run	Ar/H_2 flow rate (sccm)	Ferrocene–xylene feed rate (ml/h)	Ferrocene–xylene partial pressure (mbar)	Nanotube production rate (mg/cm^2/h)
A	675/75	5	20	0.3
B	675/75	1	4	0.08
C	1688/188	2.5	4	0.15

at $1''$ of H_2O pressure above atmospheric pressure to prevent any influx of oxygen.

3. Results and discussion

At $\sim 1050°C$, a small amount of MWNT material was formed at the entrance of the furnace and most of the ferrocene–xylene feed was converted to amorphous carbon which deposited on the available surfaces: tube walls, substrates, and the water-cooled condenser (see Fig. 1). However, when the reactor temperature was lowered to $\sim 675°C$, copious amounts of aligned MWNTs were produced with high selectivity on all surfaces inside the quartz tube: it was estimated that the conversion of the carbon in the feed to MWNTs was $\sim 25\%$. Under these conditions no carbon was deposited on the condenser and only unconverted ferrocene and xylene were collected.

Typical SEM images obtained from MWNTs deposited on the quartz substrates and on the reactor walls are shown in Fig. 2. Fig. 2a shows a SEM image of aligned MWNTs growing normal to the substrate surface. Elemental analyses of the aligned MWNT array near the tip and root regions indicate that Fe catalyst particles are present at either ends of the MWNTs. If this is the case, it is possible that nanotubes can grow upwards from particles that remain on the substrate and also behind particles that move away from the substrate at the growing tip of the nanotubes. In the present study, we find that nanotube growth begins only after Fe has been deposited on the substrate. The role of the ferrocene is to provide a source of Fe in the vapor phase which then deposits in the form of fine particles or clusters on the various surfaces that are present in the furnace. Nanotubes can then nucleate and grow from the metal sites, this mechanism does not preclude the possibility of nucleation and growth on catalyst sites

in the vapor phase, and indeed it seems possible that such a mechanism may be operative in the laser and electric arc systems. However, in this research the presence of the substrate (or walls of the quartz tube) appears to be essential to nanotube formation, and the yield in any given experiment is determined by the surface area that is available in the hot zone of the reactor. The growth of the nanotubes is probably initiated normal to the substrate surface due to the direction of the carbon concentration gradient, when carbon will be first deposited on the exposed upper surface of the metal particle and diffuse through and over the metal to precipitate at the opposite face in the form of nanotubes. Once initial nanotube growth is established, growth will tend to continue in this same direction and may well be reinforced by the presence of surrounding nanotubes, where 'crowding' will limit the possibilities for nanotube propagation in other directions.

Surprisingly, the MWNT arrays can be easily peeled off the quartz substrates while retaining their parallel orientation (Fig. 2b). To the naked eye, the tip and root surfaces look black and shiny grey in color, respectively. Expanded views of the tips and the roots of peeled MWNTs are shown in Fig. 2c and 2e, respectively. From Fig. 2d, it is clear that there is a high degree of alignment between adjacent MWNTs. Under higher magnification (Fig. 2f), the roots of the peeled MWNTs exhibit open ends suggesting that in the predominant growth mode, the Fe nanoparticles detach from the substrate and travel at the head of the growing nanotube. Examination by high resolution TEM confirms that Fe nanoparticles are present at the tips of the MWNTs.

It should be noted that under all operating conditions listed in Table 1, with a xylene partial pressure of ~ 4 mbar, the quartz substrates were coated on both sides with *only* MWNTs. However, when a higher partial pressure (20 mbar) of xylene was used

amorphous carbon deposits were found in the material that was scraped off the reactor walls in the hot zone. At low partial pressure, the nanotube production rates as determined from the *substrate deposits* only are listed in Table 1. They represent the lower boundaries for the rates of nanotube production.

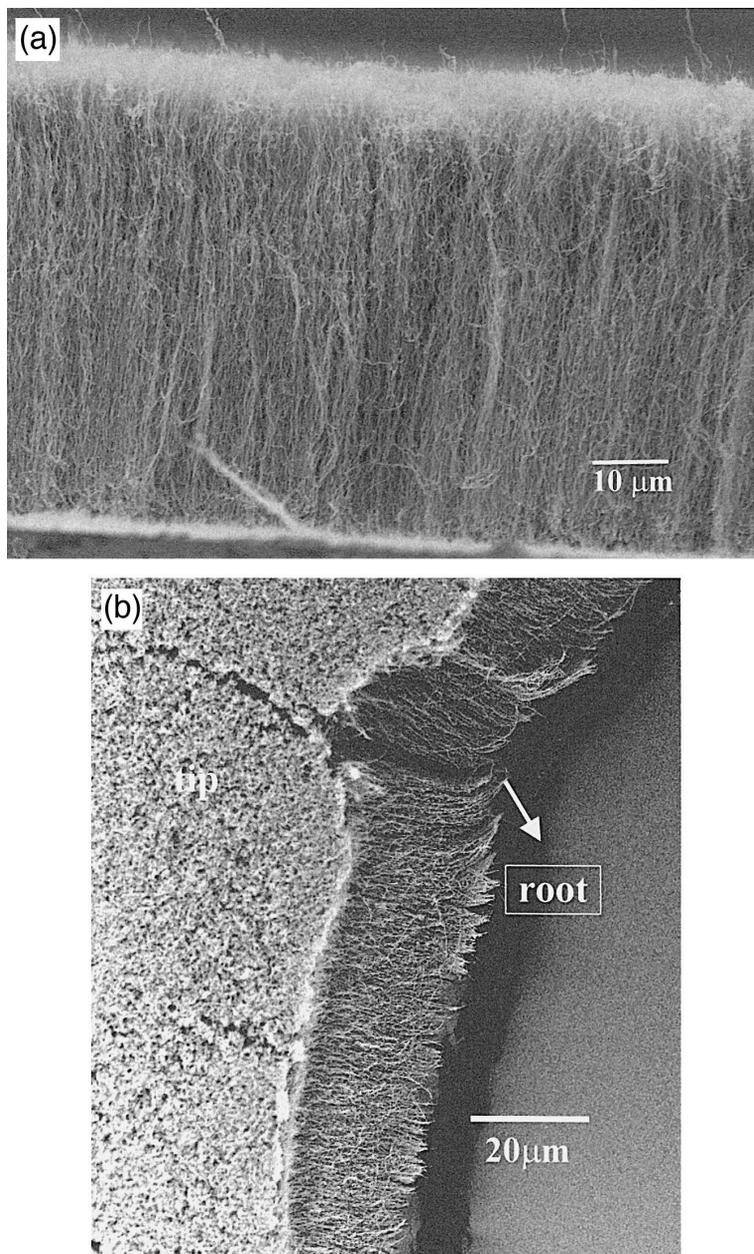Fig. 3 depicts a typical high resolution TEM image of a MWNT obtained using the synthesis

Fig. 2. SEM images (Hitachi 3200N, 5 kV) of as-grown MWNTs on a quartz substrate (a) and a peeled film of as-grown MWNTs (b). Expanded views of the tip (c), the middle section (d), and the root (e) of the peeled MWNTs film. Higher magnification (Hitachi 5900) of the root region reveals the open ends of the MWNTs (f).
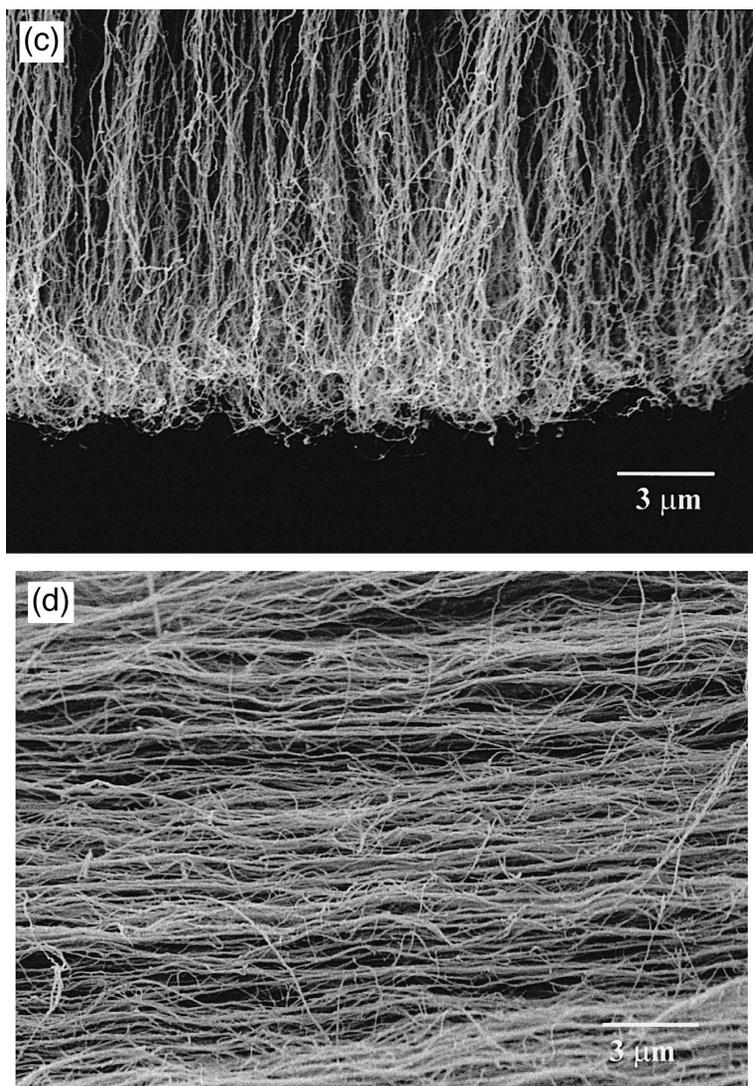
Fig. 2 (continued).

conditions listed in Table 1 for runs B and C. These images confirm the presence of MWNTs in the sample with the dominant tube diameter in the range 20–25 nm. It is interesting to note that the MWNTs produced with a Fe/C ratio of 0.75 at % showed the presence of the Fe catalyst inside the core of the MWNTs. Lowering the Fe/C ratio by a factor of 10 produced longer and thinner nanotubes and the Fe catalyst was absent inside the core of the nanotubes. Microdiffraction patterns obtained on individual MWNTs show the presence of 002 reflections con-firming a high degree of structural order (inset in Fig. 3).

The results of this and other investigations have helped to elucidate the growth mechanism of carbon nanotubes. It seems inescapable that nanotube forma-tion is a specific case or extension of what is already known, and that nanotubes are routinely formed in many systems (even under non-optimal conditions) and have simply been overlooked. A recent example is the occurrence of nanotubes at the core of vapor grown carbon fibers [15,16].
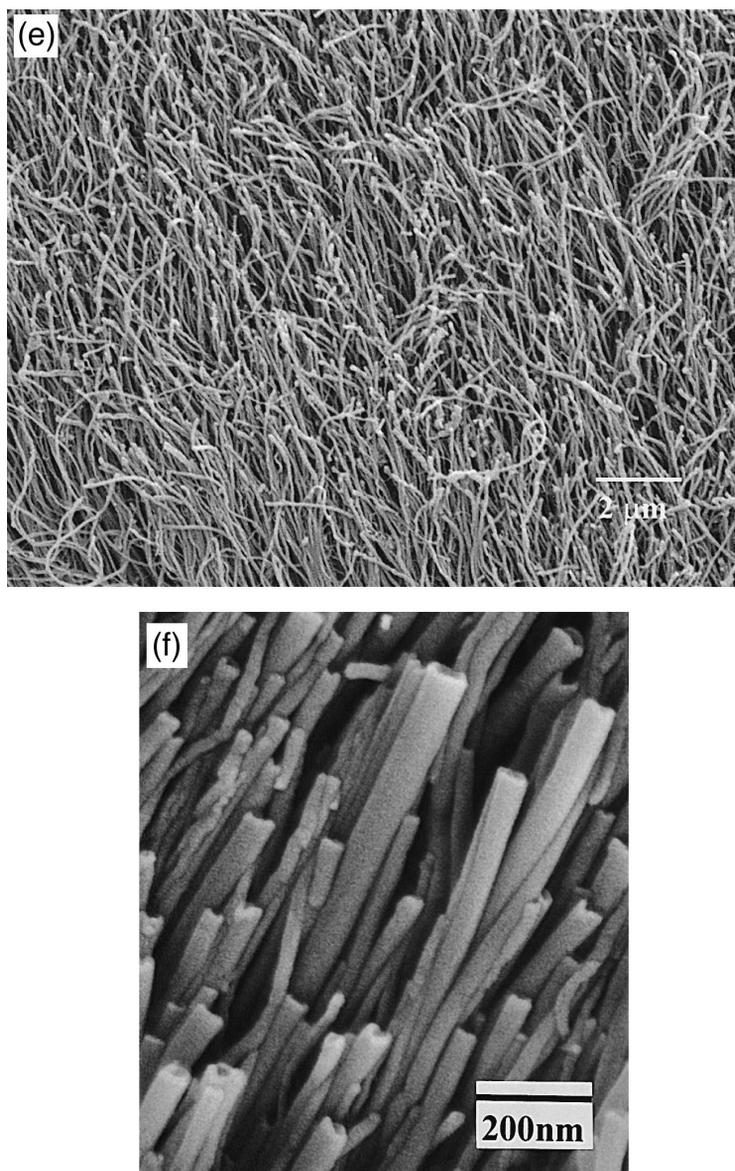
Fig. 2 (continued).

It is well known that different carbon structures can be formed by the reaction of gaseous carbon-containing precursors over metal surfaces, particularly Fe, Co, and Ni. In these reactions, which generally are operated at temperatures up to about 1100°C, a distinction should be made between the carbon that is formed by interaction with the metal and that which is co-produced. For high selectivity, it is important to confine the reaction to the immediate vicinity of the metal surface. Carbon atoms or fragments produced by the catalytic decomposition of the precursor can be extremely mobile on metal surfaces, and vice versa. Hence, carbon atoms can diffuse rapidly over and through the metal, driven by a temperature or concentration gradient, to a location where they assemble into an ordered structure. To
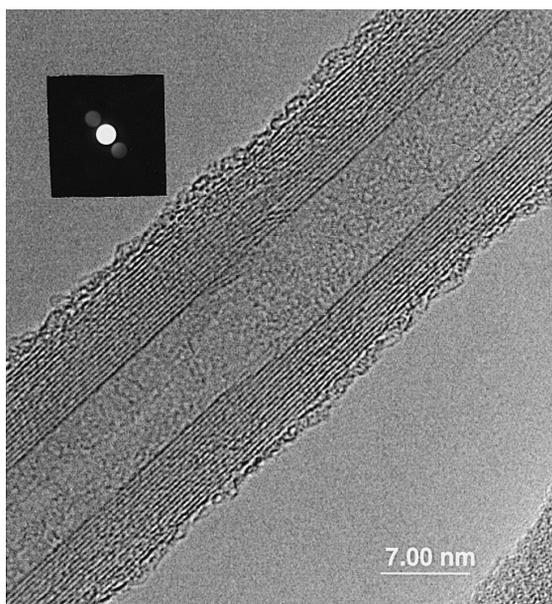
Fig. 3. HRTEM image (Phillips CM 200, 200 kV) showing the multilayered structure of a single MWNT. Inset: Typical (002) electron diffraction spots observed in a microdiffraction pattern.

minimize the incidence of reactions away from the metal, the rate of carbon production must be limited. This can be achieved through an appropriate selection of the precursor compound (relating to its thermal stability and partial pressure), the catalyst metal, and the reaction temperature. As demonstrated in our experiments, under a given set of conditions, a reduction in xylene partial pressure has this very effect, reducing the production of 'amorphous' carbon and increasing the selectivity to nanotubes.

Over metal foils (millimeter dimensions), highly crystalline graphite films, oriented parallel to the surface, can be formed by solid solution and subsequent precipitation [17,18]. With supported metal particles (tens of nanometers in diameter), carbon filaments can be formed with diameters of the order of tenths of a micrometer [19]. In the proposed mechanism, carbon is deposited on the particle surface in contact with the gas phase and diffuses through or over the metal to precipitate at the opposite surface. The metal particle is carried at the head of the growing filament. In going from a foil to a small particle the essential change in the carbon structure is that the precipitated graphitic or graphite-like basal planes grow parallel to the metal surface in the former case, and tangentially to it in the latter case, forming the axis of the fiber. Around the fiber circumference, it appears that the graphitic basal planes approximate to the curved surface as a series of small planar crystallites. It is suggested that the change in form between foil and particle is due entirely to the dimensions and shape of the metal, where the small size and curvature of the metal particles necessitate growth away from the surface. The question then remains as to why the structure changes from a series of planar crystallites to closed tubes as the metal particle size decreases. An article by Endo et al. [16] may provide an important clue. They show that the interlayer spacing increases as the 'tube' diameter is reduced, passing down through the series of carbon filaments to nanofibers to nanotubes. The increase in the interlayer spacing in nanotubes with smaller diameter is indicative of strain imposed by the increasing curvature. Looking at the result another way, it could be that as the metal particle size is progressively reduced below that employed to form fibers or filaments, a point is reached where the radius is so small that the imposed strain will necessitate a transition from approximating to a curved surface to adopting a tubular form: that is, as multi-walled or, ultimately, single-walled nanotubes.

4. Conclusions

In conclusion, it should be noted that a process of this nature could be easily scaled up and used for the continuous or semi-continuous production of multi-walled nanotubes. Based upon our results, it seems most probable that it is only a matter of time before nanotubes are produced cheaply and in quantity for around the same cost as carbon fibers, and probably less. Only a few months ago, Prof. Rick Smalley predicted that in the next 10 years, an economical process to produce single-wall nanotubes in ton quantities from the gas phase will be discovered [20]. While we have not yet produced single-wall nanotubes by our method, the potential certainly exists, and the availability of multi-walled nanotubes may be more than adequate for many practical applica-

tions. There is every reason to believe that we have truly stepped on the road to commercialization.

Acknowledgements

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