CVD synthesis of carbon nanotubes

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Reports of the synthesis and identification of carbon nanotubes, both multi-walled [1] and single-walled [2, 3], in arc-discharge soot products have excited great interest in the field of study of this newly discovered allotropic nanostructure of carbon. Extraordinary properties, such as electronic [4–6] and mechanical [7, 8] properties, have been demonstrated both theoretically and experimentally. Although it has been the primary method of producing carbon nanotubes, the arc-discharge technique suffers from a few drawbacks that might prevent it from becoming the best candidate for precisely controlled syntheses of carbon nanotubes of high quality. It is therefore important to search for new processing techniques, especially in the low temperature regime, which can produce high-quality carbon nanotubes in large quantities, while allowing control of the fabrication process with ease and precision. With these considerations in mind, a low-temperature chemical vapour deposition (CVD) apparatus has been set up in an effort to seek new processing routes for large-scale production of carbon nanotubes.

Based on the early success of growing carbon fibers [9] using the pyrolytic decomposition of hydrocarbon gases, such as acetylene (C_2H_2), benzene (C_6H_6), carbon monoxide (CO), methane (CH_4) etc., the CVD technique has become one of the preferred methods for fabricating carbon nanotubes in much lower temperature regimes than is possible with the arc-discharge technique. CVD methods utilize the pyrolytic decomposition of hydrocarbon gases at elevated temperatures in the range 600–1200 °C. Several researchers have reported successful syntheses of carbon nanotubes using CVD techniques recently. For example, Endo *et al.* [10] reported the observation of nanotubes in the pyrolytic product of benzene (C_6H_6) decomposition at about 1100 °C, Jose-Yacaman *et al.* [11] and Ivanov *et al.* [12] observed nanotubes and related nanostructures in the catalytic decomposition product of acetylene (C_2H_2) in the temperature range 1050–1350 °C, and Jaeger and Behrsing [13] found similar structures in a mixture of natural gas, methane and benzene decomposition products.

In this letter we report the synthesis of carbon nanotubes at about 750 °C using a CVD technique. The reactant gases employed were high-purity methane (CH_4) and hydrogen (H_2) gases, and ferrocene ($C_{10}H_{10}Fe$) was used as catalyst.

The reaction was carried out in an electrical tube furnance. A quartz tube, used as the substrate for CVD, was placed inside the ceramic furnace tube of inner diameter about 3 cm and length about 80 cm. The temperature of the furnace was controlled by a Eurotherm unit. The furnace was first pumped to vacuum in order to remove the air inside the chamber, and then flushed with argon gas. When the temperature at the centre of the furnace tube reached about 900 °C, the argon gas was pumped out of the chamber before methane and hydrogen gases were allowed to flow into the chamber. The flow rates of methane and hydrogen gases were kept at about 150 ml min^{-1} and about 350 ml min^{-1}, respectively, while the total pressure in the reaction chamber was kept at approximately 79.99 kPa. The furnace was heated to 1150 °C in about 15 min and was kept at this temperature for about 5 min to allow the following reaction to occur with the addition of ferrocene vapours:

$$CH_4(g) + H_2(g) \overset{600-1200\,°C}{\underset{Ferrocene}{\longrightarrow}} C(s) + 3H_2(g)$$
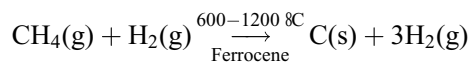
in which s and g designate solid and gaseous phases, respectively.

After the reaction was completed, the supply of methane and hydrogen gases was discontinued, and the chamber was evacuated quickly in order to terminate the pyrolytic decomposition of the residual gases. Argon gas was subsequently introduced to flush the reaction chamber. The furnace was cooled naturally to about 300 °C in argon by shutting off the power supply before the chamber was opened to let air in.

A large quantity of powder-like soot deposits was found on the inner walls of the quartz tube where the reaction temperature was around 750 °C. These powders were dispersed in ethanol, and then collected on to copper grids coated with perforated carbon films for electron microscopy examinations.

High-resolution electron microscopy was carried out using a Topcon 002B analytical transmission electron microscope operated at 200 kV. No objective aperture was used while the electron micrographs were taken.

Fig. 1 shows an electron micrograph of a typical carbon nanotube found in the CVD soot. This nanotube has an inner diameter of about 10 nm and an outer diameter of about 30 nm, while the wall thickness is about 10 nm. The tubule is composed of about 30 graphene shells. Although the graphitic lattice is distorted along the length of the tubule, the diameter of the hollow core maintained an approximately constant diameter. We note that the innermost layer is not continuous. It has been terminated at
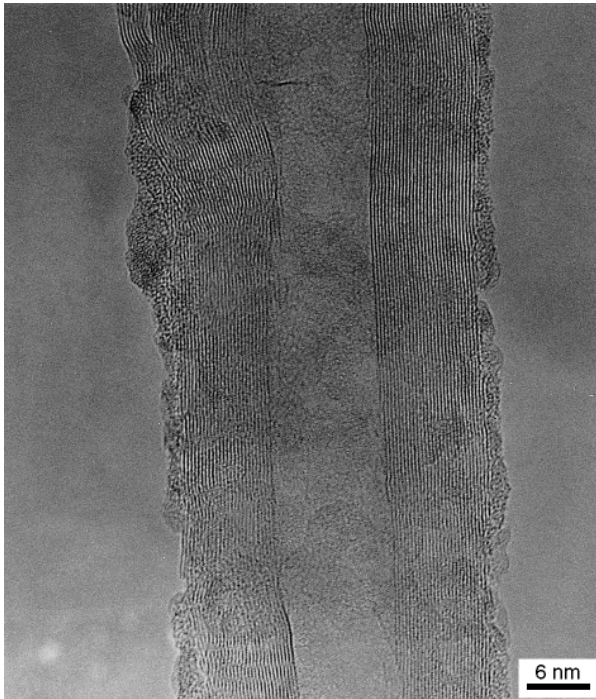
Figure 1 Electron micrograph of a typical carbon nanotube found in CVD soot. It is multi-walled with an inner diameter of about 10 nm and an outer diameter of about 30 nm. The wall thickness is about 10 nm.

several locations, which indicates uncompleted growth of the innermost shell.

Fig. 2 is an electron micrograph of a carbon nanotube synthesized by the arc-discharge evaporation technique, which has a similar morphology to that in Fig. 1. However, the CVD-grown tubule has more amorphous carbon material attached to the outer surface of the tubule, because of the sustained supply of the decomposed carbon species in the CVD chamber and the much lower temperature
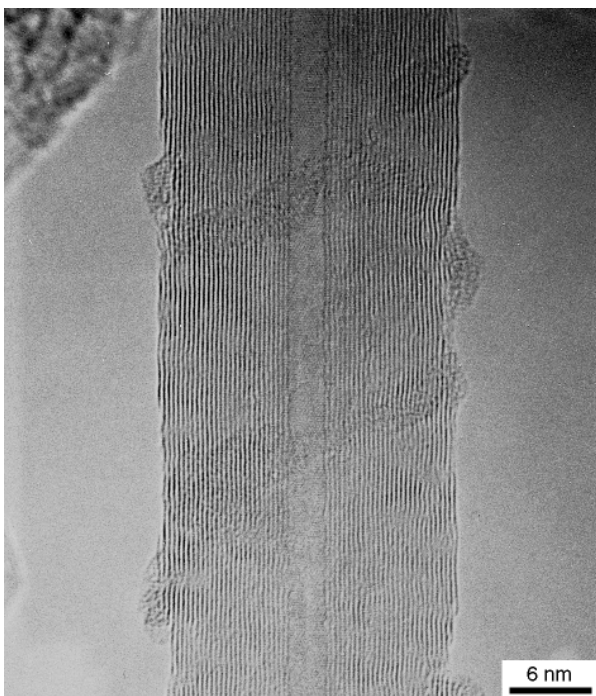
gradient compared with that available in an arc-discharge chamber.

An electron micrograph of a thicker carbon nanotube is shown in Fig. 3. This tubule has a set of much less distorted graphitic lattice fringes. Although the wall thickness (about 15 nm) is almost constant along the length of the tubule, the inner diameter varies along the tubule axis, ranging from about 7.5 nm to about 2.5 nm. The uncompleted graphitic shell at the innermost wall is also visible. The outermost surface contains much less carbon debris compared with that shown in Fig. 1.

It was also often found that the hollow cores of CVD-grown carbon nanotubes were filled with heavy compounds, as evidenced by the darker contrast caused by the filling. Fig. 4 shows an electron micrograph of a typical carbon nanotube where some iron carbides have been encapsulated. Detailed examination of the micrograph revealed that the filling was actually contained in a closed carbon cage. The tip of the iron carbide filling was covered by a single shell of graphitic carbon, as can be seen by the change of the number of lattice fringes across the tip. Beyond the tip, there were 11 layers of graphene, marked A in the figure, while below the tip where the filling was encapsulated there were 12 layers of graphene, marked B for clarity. The fillings have been identified by high-resolution electron microscopy as austenite [14].

The iron-containing catalytic vapours were found necessary in this reaction in order to produce carbon nanotubes. At elevated temperatures, the iron-containing ferrocene vapour will react with carbon atoms that were made available in the chamber by
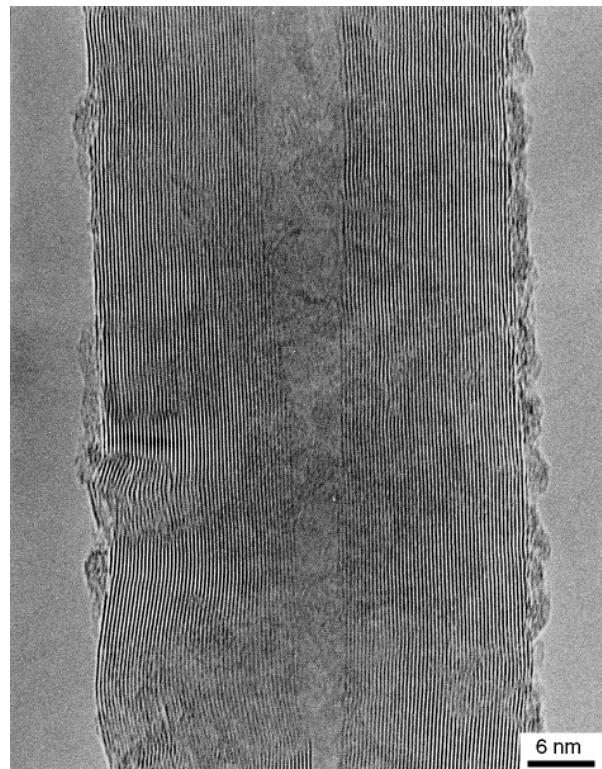

Figure 2 A typical carbon nanotube observed in arc-discharge soot, with a similar morphology to that of Fig. 1.

Figure 3 A carbon nanotube with a thicker wall. The inner hollow diameter changes from about 7.5 nm to about 2.5 nm.

Figure 4 A CVD-grown carbon nanotube encapsulating a filling. The filling was covered completely by a single graphitic shell. There are 11 graphene shells at A and 12 at B.

the decomposition of hydrocarbon gases. Noting that there is a eutectic point at 727 °C in the Fe−C phase diagram, where austenite can transform into ferrite and cementite, the excess amount of carbon that was contained in the higher temperature phase of austenite would be precipitated onto the surface of the iron carbide particles. This also lends a thermodynamics argument to supporting the postulation that the fillings are actually austenite. The free carbon atoms on the surfaces of these particles would therefore be expected to form certain structures of carbon, and the tubular structure is certainly one of the favourable forms, given the low formation energy.

The significance of the current experiment is two-fold: firstly, this experiment has demonstrated a new route to synthesize carbon nanotubes with well-defined morphologies, and, secondly, the confirmed formation of nanotubes is a step towards the next objective: the growth of carbon nanotubes on well-defined substrates in an aligned manner.

In summary, carbon nanotubes have been synthesized by CVD at about 750 °C using methane and hydrogen gases catalysed by ferrocene vapours. The morphology of the vapour-grown nanotubes is similar to that of nanotubes obtained using arc-discharge. The CVD technique offers a new route to fabricate carbon nanotubes at much lower temperatures and may allow better control over the synthesizing parameters. Encapsulation of ferric compounds was also found in this temperature range.

Acknowledgements

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