MAKING NANOTUBES FROM MICROPOROUS CARBONS

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Introduction

At present, the arc-evaporation technique remains probably the best method for the synthesis of high quality multiwalled carbon nanotubes. However, arc-evaporation suffers from a number of serious disadvantages: it is labour intensive, the yield is rather low, and the nanotubes are "contaminated" with nanoparticles and other graphitic debris. While it is true that nanotubes can be produced in high yield by catalytic chemical vapour deposition, the quality of tubes formed in this way is relatively poor. This paper describes a new approach to the synthesis of fullerene-related multiwalled carbon nanotubes, which involves the rapid high temperature heat treatment of fullerene soot. This new method has the potential to produce good quality nanotubes in high yield, and may also enable new insights to be obtained into the mechanism of nanotube growth.

The first indication that it might be possible to prepare nanotubes by high temperature heat treatment of disordered carbon came in a 1994 study by the present author and colleagues [1]. In this work, fullerene soot was rapidly heated to high temperature (ca. 3000^{o}C) in a positive-hearth electron gun. High resolution transmission electron microscopy showed that this heat-treatment produced a structure apparently made up of large pores which were often extended in shape, resembling large-diameter single layer nanotubes, as can be seen in Fig. 1. Like nanotubes, the extended pores were almost invariably closed, and exhibited a variety of capping morphologies. These observations led the authors to propose a model for nanotube formation in which the tubes were envisaged to form as a result of high temperature annealing of fullerene soot deposited onto the cathode, rather than directly from the vapour phase. They also suggested that high

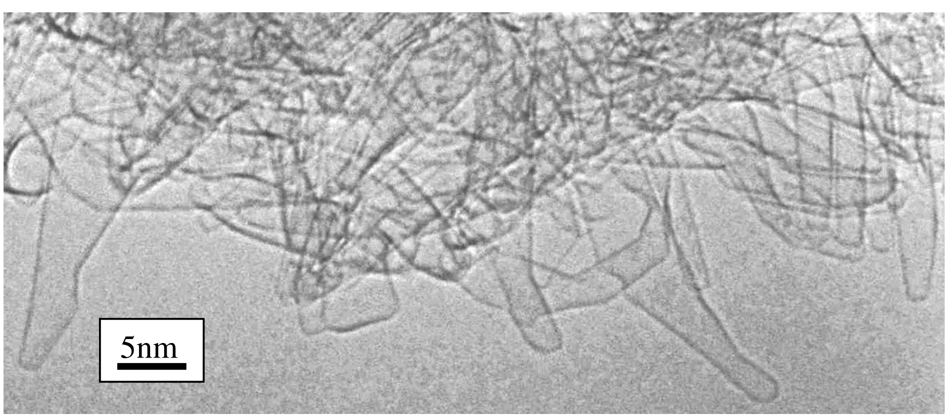

Figure 1. Tube-like structures observed in fullerene soot following high temperature heat treatment in an electron gun.

temperature heat treatments of microporous carbon materials might be a valuable method of nanotube synthesis. In the present work, further high temperature heat treatments of fullerene soot are described, this time using a small scale graphite furnace. This allows rather more control over the temperature, ramp rate and heating time than is possible in the electron gun apparatus. The aim is both to gain an understanding of the nanotube growth mechanism and to explore the feasibility of using this technique for bulk nanotube synthesis.

Experimental

Fullerene soot samples prepared using the standard arc-evaporation method were used as the raw materials in this work. The heat treatments were carried out using a graphite furnace designed for the atomisation of samples for atomic absorption spectroscopy (AAS). Such furnaces are capable of heating small amounts of material to temperatures up to 3000°C in a few short time (typically less than 30s). Following heat treatment the carbon was examined in a JEOL 2010 TEM, with a point-to point resolution of 0.19 nm, operated at 200kV.

Results and Discussion

A typical micrograph of fullerene soot heated to 3000°C in 10 seconds, held at this temperature for 10 seconds and then cooled, is shown in Fig. 2. This carbon contained a mixture of structures, including sheets of graphite, faceted nanoparticles with large interior cavities and extended, tubular structures. As can be seen, the tubular particles in the heated samples were shorter and less perfect in structure than multiwalled carbon nanotubes produced by arc-evaporation. This may be because carbon in the arc experiences even higher temperatures than 3000°C, and experiences these temperatures for a longer period than was the case in the current work. Experiments with microporous non-graphitizing carbons, which are believed to have a similar structure to fullerene soot [2], also resulted in the formation of nanotubular structures.

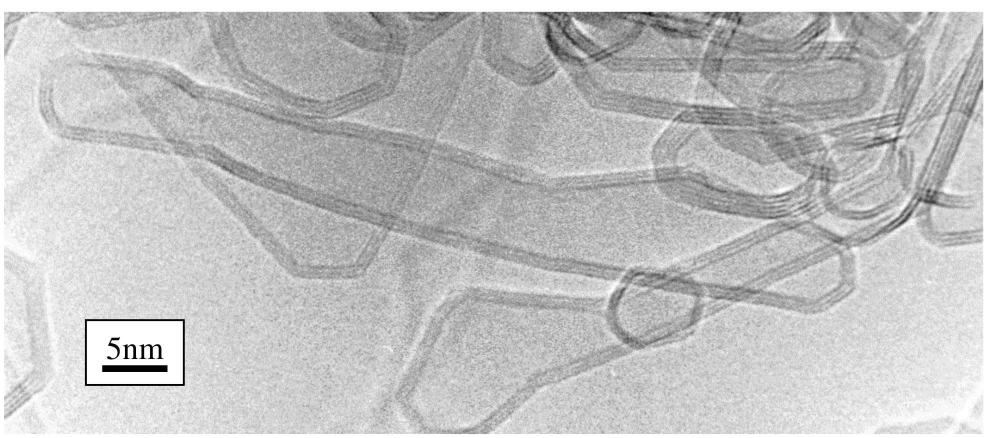

Figure 2. Structure of fullerene soot following high temperature heat treatment in a graphite furnace.

Conclusions

The mechanism of carbon nanotube formation during arc-evaporation remains poorly understood. Many models have been put forward, most of which assume that the tubes nucleate and grow in the arc plasma. Studies of the effect of high temperature heat treatment on disordered carbon led the present author and colleagues to put forward a quite different theory of nanotube growth [1, 3]. In this model, the nanotubes and nanoparticles do not grow in the arc plasma, but rather form on the cathode as a result of a solid-state transformation. Thus, nanotube growth is not a consequence of the electric field, but simply a result of the very rapid heating to high temperatures experienced by material deposited on the cathode during arcing. The present study has confirmed that nanotubes can be formed by simple heating of fullerene soot to high temperatures, showing that it is a solid phase transformation rather than a gas phase process. It is important to note that samples heated to 3000^{o}C over an extended time (several minutes) contained no tubular structures, suggesting that rapid heating is the key to nanotube growth.

Other groups have also demonstrated the formation of carbon nanotubes by heat treatment of disordered carbon. For example, Chang and colleagues have shown that nanotube-like structures can be formed by heat treatment of microporous carbon derived from sucrose [4]. The same group have also prepared nanotubes by heating carbon black [5]. More work is needed to establish whether macroscopic amounts of nanotubes can be produced in this way.

References

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