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Nanotube ‘crop circles’

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‘Crop circles’ consisting of carbon nanotubes aligned in a direction normal to the substrate surface have been produced by pyrolysis of iron(II) phthalocyanine, which could lead to novel applications.

The alignment and pattern formation of carbon nanotubes are important for testing the properties of individual nanotubes with existing techniques and to effectively incorporate them into devices.[1] A few approaches to aligned and/or patterned carbon nanotubes have been recently reported.[2] The use of certain organic–metal complexes (*e.g.* ferrocene[2i] or nickel phthalocyanine[2j]), which contain both the metal catalyst and carbon source required for nanotube growth, for producing aligned nanotubes is of particular interest. In this regard, we have developed a technique for large-scale synthesis of carbon nanotubes (up to several square centimetres) aligned in a direction normal to the substrate surface (typically, quartz glass plates) by pyrolysis of iron(II) phthalocyanine (FePc) [Fig. 1(a)].[3] As can be seen in Fig. 1(a), the constituent carbon nanotubes have a fairly uniform tubular length and diameter. A high resolution transmission electron microscopic (HR-TEM) study shows that most of the nanotubes are well graphitised with *ca.* 40 layers of graphite sheets and an outer diameter of *ca.* 50 nm [Fig. 1(b)]. In addition to the nanotube ‘carpets’ as shown in Fig. 1(a), nanotube ‘crop circles’ have also been observed in deposits formed by the pyrolysis of FePc (Fig. 2). These nanotube ‘crop circles’ differ from those reported by Liu *et al.*[4] in that the former consist of aligned nanotubes normal to the substrate surface [see Fig. 2(b)], whereas the latter contain single-wall carbon nanotube (SWNT) ropes lying *flat* on the substrate.

We have studied the growth mechanism of the aligned carbon nanotubes by taking SEM images at different stages during the pyrolysis. It was demonstrated that Fe particles, surrounded by carbon, formed on the substrate surface upon thermal decomposition of FePc. Segregation of Fe then occurred, followed by a structural transition of the associated carbon into a graphitic tube once the Fe particles reached an optimum size for carbon nanotube nucleation.[5] Further decomposition of FePc released carbon to the contact region between the metal particle and the already formed tubule segment leading to a continuous growth of the carbon nanotube normal to the substrate surface[6] while iron atoms are preferentially left at the first part of the reactor[2e] (where the temperature was deliberately set above the FePc decomposition point during this stage of the pyrolysis). The high surface density of the as-growing nanotubes and strong van der Waals forces between them are considered to be responsible for the aligned growth.[2k] Thus, the formation of a ringlike basement of the Fe particles could lead to a growth of nanotube ‘crop circles’. Ring formation in volatile, thin films containing organically passivated metal nanoparticles on a solid substrate is a known process,[7] caused by the hole nucleation associated with evaporation and/or disjoining pressure.[8] We did, indeed, observe the formation of annular rings by the Fe particles at the initial stage of the pyrolysis. Therefore, the interplay between the segregation of the Fe particles and the growing away of the associated carbon from the substrate surface may be responsible for the ring formation in this study. For ring formation by passivated metal nanoparticles, it has been demonstrated that the nature of the metal, the substrate, and evaporation conditions play important roles in regulating the ring diameter and ringlike configuration.[8] As shown in Fig. 2(a), nanotube ‘crop circles’ of various configurations with ring diameters in the range 10–80 μm are clearly evident due, most probably, to the presence of different (localized)

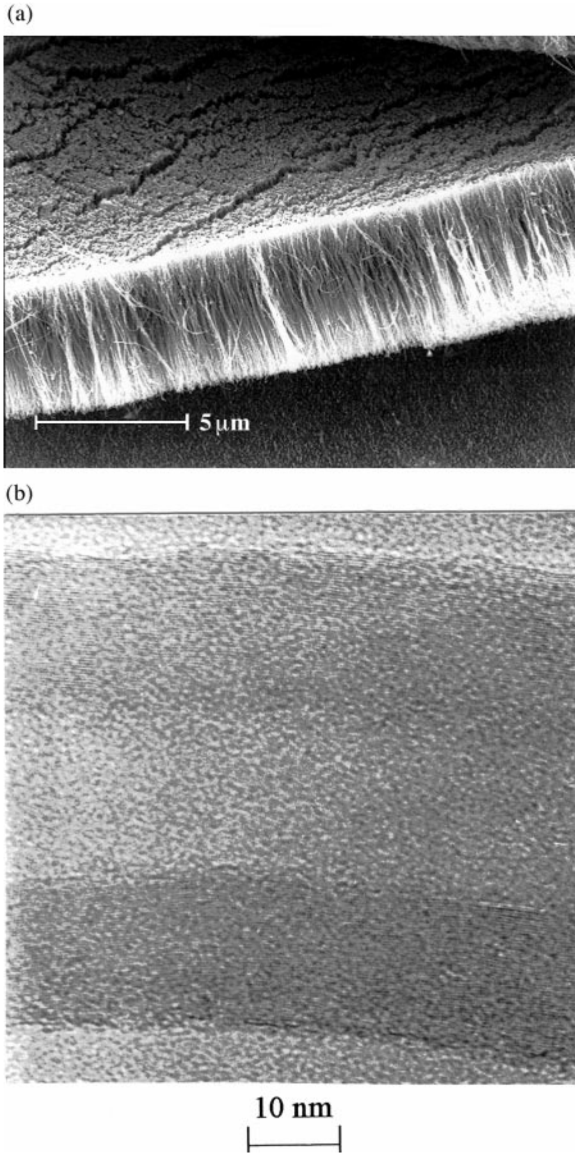

Fig. 1 (a) A scanning electron microscopic (SEM) image of the large-scale aligned nanotube film on a quartz glass plate prepared by the pyrolysis of FePc. (b) A typical HR-TEM image of the constituent nanotubes.

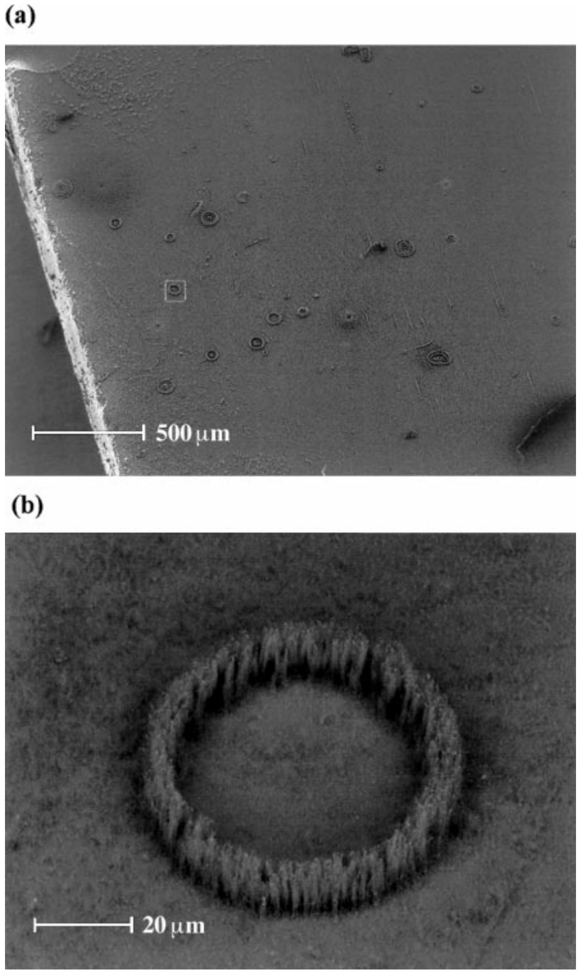

Fig. 2 (a) A low magnification SEM image of the nanotube 'crop circles'. (b) A higher magnification SEM image of the area selected by the square in (a), showing that the 'crop circles' consist of nanotubes aligned normal to the substrate surface.

micro-environments for segregation of the Fe particles into ringlike basements with distinctive characteristics.

Owing to their interesting electronic, magnetic and nonlinear optical properties,[1] carbon nanotubes have been proposed as new molecular materials for a wide range of electronic and photonic applications (*e.g.* as new electron field emitters for panel displays and single-molecular transistors for microelectronics).[9] The construction of aligned and/or patterned nanotubes is a key prerequisite for most of these applications. The nanotube 'crop circles' reported above should have important implications for potential use of carbon nanotubes, for example, in microelectronics, field emission displays, and information storage devices.

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3 We had briefly mentioned our method for synthesising aligned nanotubes in a conference paper (see: L. Dai, B. Winkler, S. Huang and A. W. H. Mau, in *Semiconductive Polymers* ed. B. Hsieh, M. Galvin and Y. Wei, *ACS Symp. Ser.*, 215th ACS Meeting, Dallas, TX, March 29–April 2, 1998). To prepare nanotube 'crop circles', 0.1 g FePc and a clean quartz glass plate (4 × 1 × 0.125 cm, ultrasonicated in acetone) were placed in a flow reactor consisting of a quartz glass tube and a dual furnace fitted with independent temperature controllers.[2e] A flow of Ar–H$_2$ (1 : 1 v/v, 40 cm^3 min^{-1}) was then introduced into the quartz tube during heating. After the second furnace reached 1000 °C, the first furnace was heated to 600 °C for 20 min. Thereafter, both furnaces were kept at the pyrolysis temperature (1000 °C) for an additional 20 min for the deposition of nanotubes to be completed.

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