Large aligned-nanotube bundles from ferrocene pyrolysis

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Aligned-nanotube bundles have been obtained in copious quantities by the pyrolysis of ferrocene or ferrocene–acetylene mixtures.

Aligned carbon nanotubes have aroused much interest because of their mechanical properties[1,2] as well as their interesting anisotropic optical and other properties.[2] Aligned carbon nanotube films have also been considered to be good candidates as electron field emitters.[3] One of the procedures employed to prepare nanotube films is to pass a dispersion of arc-produced carbon nanotubes in ethanol through an alumina micropore filter and then press the nanotube-covered filter onto a polymer sheet.[4] Under pressure, the nanotubes are printed onto the sheet in an aligned manner. Aligned nanotubes have also been obtained by the chemical vapor deposition of acetylene catalyzed by iron nanoparticles embedded in mesoporous silica,[5] the pores of the silica controlling the growth direction of the nanotubes. Recently, aligned-nanotube bundles have been prepared by the pyrolysis of 2-amino-4,6-dichloro-*s*-triazine over thin films of a cobalt catalyst, patterned on a silica substrate by laser etching.[6] We have been interested in finding a simple means of producing aligned nanotubes in large quantities and were encouraged in this direction by the discovery that the pyrolysis of hydrocarbons in the presence of organometallic precursor molecules gives good yields of carbon nanotubes.[7] Realizing that a precursor such as ferrocene not only gives rise to small catalytic metal particles but also acts as a carbon source, we carried out systematic experiments on the pyrolysis of ferrocene. Initial experiments showed that aligned nanotubes are produced under certain conditions. We have varied the conditions of the pyrolysis of ferrocene and also carried out the pyrolysis in the presence of acetylene which acts as an additional carbon source, and have found these methods to yield large quantities of aligned-nanotube bundles. In this communication, we report this rather impressive result obtained by a very simple technique.

The procedure employed for the pyrolysis of ferrocene was as follows. A known quantity (100 mg) of ferrocene (presublimed, *ca*. 99.99% purity) was placed in a quartz boat located at one end of a narrow quartz tube (10 mm i.d.), which in turn was placed in a dual furnace system. The part of the quartz tube containing the ferrocene was in the first furnace and the ferrocene was sublimed by raising the temperature of this furnace to 620 K at a controlled heating rate. Argon gas was passed through the quartz tube at a desired rate. The ferrocene vapour was carried by the Ar gas into the second furnace, maintained at 1370 K, where pyrolysis occurred. The main variables in the experiments were the heating rate of ferrocene, the flow rate of the argon gas and the pyrolysis temperature. Large quantities of deposits accumulated at the inlet of the second furnace. These carbon deposits, mainly containing carbon nanotubes, were examined by a LEICA S440i scanning electron microscope (SEM) and a JEOL 3010 transmission electron microscope (TEM).

In Fig. 1(*a*) and (*b*), we show the SEM images of the nanotubes obtained by carrying out the pyrolysis of ferrocene at 1370 K with a fast heating rate of ferrocene (100 °C min^{-1}) and a high flow rate of Ar (1000 sccm; sccm = standard cubic cm per min). The images in Fig. 1(*a*) and (*b*), which are recorded in two different directions with respect to the axis of the nanotubes, clearly reveal the extraordinary alignment. TEM images of these nanotubes revealed that they were multi-walled, some of them partially filled with metallic iron. Pyrolysis of ferrocene at 1170 K under vacuum (10^{-5} Torr) also yielded good quantities of aligned-nanotube bundles. In Fig. 1(*c*) we

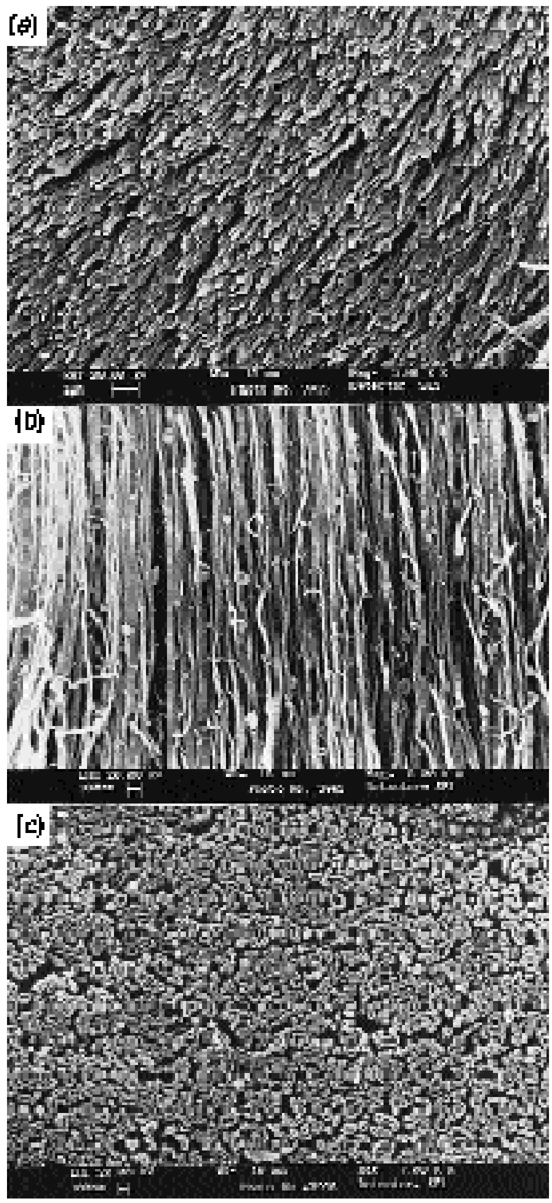

Fig. 1 SEM images of aligned carbon nanotubes obtained by the pyrolysis of ferrocene: (*a*) and (*b*) show views of the aligned nanotubes along and perpendicular to the axis of the nanotubes, (*c*) shows a top view of aligned nanotubes obtained by the pyrolysis of ferrocene under vacuum (10^{-5} Torr) at a slow heating rate (1 °C min^{-1})

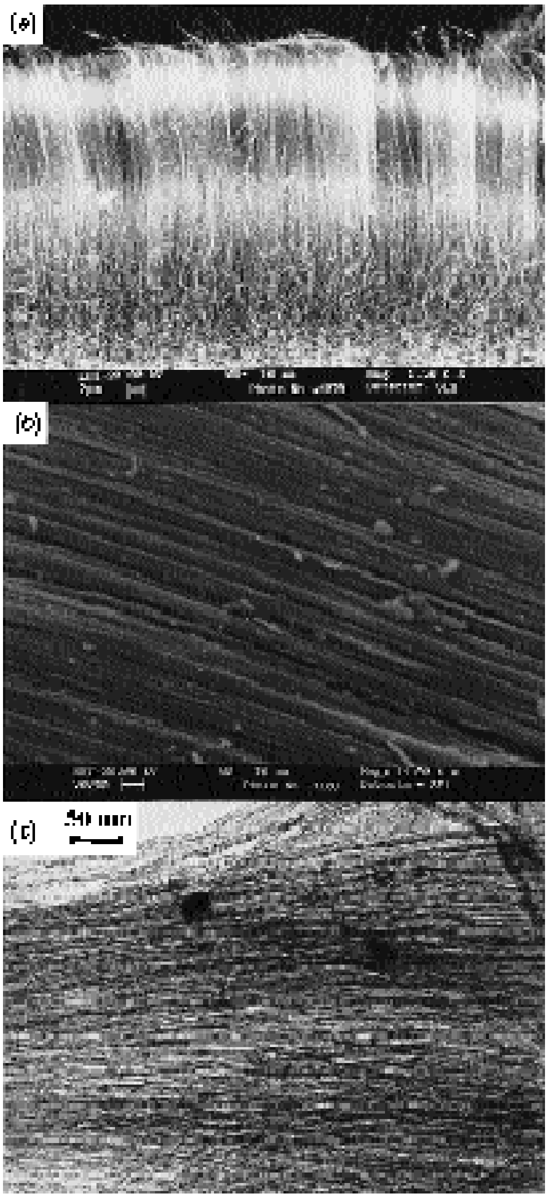

Fig. 2 (*a*) An SEM image of aligned nanotubes obtained by the pyrolysis of ferrocene at 1370 K under a flow of C_2H_2 (5 sccm) and Ar (1000 sccm). In (*b*) and (*c*), we show SEM and TEM images of densely packed aligned nanotubes obtained by the pyrolysis of ferrocene at 1370 K in the presence of a higher proportion of C_2H_2 [flow of C_2H_2 (85 sccm) and Ar (1000 sccm)].

show a top view of such nanotubes. When the rate of heating of ferrocene (1 °C min^{-1}) and the flow rate of argon (10 sccm) were low, fewer aligned nanotubes were obtained at a pyrolysis temperature of 1370 K.

We carried out the pyrolysis of ferrocene with acetylene, by passing a mixture of argon and acetylene through the quartz tube. In Fig. 2(*a*), we show an SEM image of the aligned nanotubes obtained by the pyrolysis of a mixture of ferrocene and acetylene (5 sccm) at 1370 K in flowing Ar (1000 sccm). The alignment could be further improved by increasing the flow rate of C_2H_2. The SEM image in Fig. 2(*b*) obtained in this manner shows densely packed aligned nanotubes. The TEM image in Fig. 2(*c*) reveals how well aligned these nanotubes are. The nanotubes in the bundles were generally closed and were 5–10 μm in length.

Pyrolysis of ferrocene was carried out at a heating rate of 50 °C min^{-1} under a vacuum (10^{-5} Torr). Here, the ferrocene sublimed under vacuum and the vapour was drawn into the pyrolysis zone. In these experiments we mainly obtained

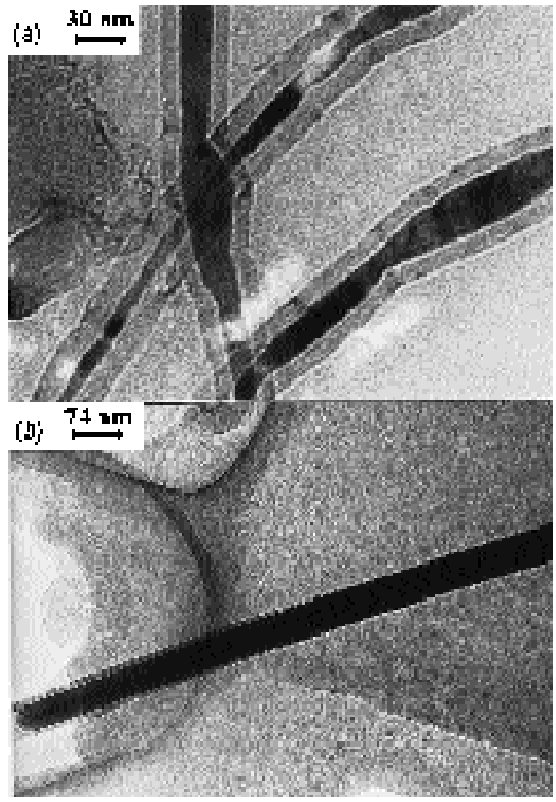

Fig. 3 TEM images of carbon-coated iron nanorods obtained by the pyrolysis of ferrocene (*a*) at 1170 K under vacuum (10^{-5} Torr) and (*b*) at 1370 K under a flow of Ar (10 sccm)

carbon-coated iron nanorods (yield ≥ 60%). In Fig. 3(*a*), we show a TEM image of metal nanorods with a thick carbon coating, obtained by the pyrolysis of ferrocene at 1170 K under vacuum. We also obtained a fair proportion of nanorods when the flow rate of Ar was low (10 sccm). In Fig. 3(*b*) we show a TEM image of a nanorod obtained by the pyrolysis of ferrocene at 1370 K under an Ar flow of 10 sccm. Note that such nanorods have been reported in the literature, produced by the reaction of carbon nanotubes with volatile oxide or halide species.[8] The present method of producing nanorods is much simpler. The formation of metallic iron in the form of particles or rods in the pyrolysis of ferrocene suggests that the mechanism of alignment of the nanotubes may be related to the magnetic nature of the nanorods or particles of iron.

Notes and References

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Received in Cambridge, UK, 23rd March 1998; 8/02258E