Carbon shells in flames

SIR — Fullerenes[1,2] can be formed in hydrocarbon flames[3]. We have now found that carbon nanotubes[4,5] and nanoparticles[4,6–8], along with soot particles containing fullerene-like shells, can also be formed in this way. Previously, such structures have been produced only by more energetic processes such as arc vaporization of carbon[4–8].

Flames of acetylene, benzene or ethylene premixed with oxygen and a diluent were stablized on a burner[3] in a low-pressure chamber. Samples of condensable material were collected from within the flames using a water-cooled suction probe and from the water-cooled surface of the chamber under different sets of conditions over the ranges: burner chamber pressure, 20–97 torr; C/O atomic ratio, 1.06 (C_2H_2), 0.86–1.00 (C_6H_6) or 1.07 (C_H4); gas velocity at the burner (298 K), 25–50 cm s^{-1};, diluent concentration, 0–44 mol%; peak temperature 1,930–2,050 K.

The samples were analysed in a high-resolution transmission electron microscope (HRTEM) operated at 200 keV with a point resolution of 0.17 nm, a spherical aberration coefficient of 0.4 mm, and exposure times below the minimum for electron beam damage. Each sample was dispersed in toluene using mild sonication. Drops of the dispersion were placed on holey carbon films on electron microscope grids and dried under vacuum.

Both probe and surface samples from the low-pressure acetylene and benzene flames were found to contain fullerenic carbon structures consisting of nested shells separated by 0.34–0.36 nm, close to the interlayer spacing of graphite, with spheroidal, elongated and other spares (*a* in figure). The nanostructures are mostly in the size range 2–15 nm, considerably smaller than the soot, which consists of particles of about 35–50 nm diameter in 100–3,000-nm agglomerates. The yield of nested nanostructures is typically ~10% of the soot yield and ~1% of the carbon fed in the benzene flames, somewhat less in the acetylene flames, and nil in the ethylene flames.

Some of the elongated structures are coaxial cylinders with spheroidal caps (*b* in figure), similar to multi-shelled nanotubes produced in arc-discharge graphite vaporization systems[4]·5. However, the present results include fullerene tubes with both ends capped, reflecting growth with both ends free. The nanotube in panel *b* of the figure appears to have grown from left to right, with more than one shell froming simultaneously.

Some of the nanoparticles are polyhedral, with smoothly curved continous junctions between nearly flat faces that reveal fullerenic structure. Others, also fullerenic, are strikingly spherical, similar to some nanotube caps[4,5] and nanoparticles[7] produced by vaporization[4,5] and electron-beam irradiation7 of carbon. Prolate spheroids are shown in *c* in the figure, the left one expanding upwards to the left with an angle of about 11°, consistent with the lower cap of each shell having fivce pentagons and the upper cap seven, implying an expansion angle of 20° or more[5] orthogonal to the angle seen here.

Nanostructures observed but not shown here include nested conical tube tips similar to those seen in arc-discharge samples5, and curved layers or incompletely closed shells (fullerene carbon) that comprise the internal structure of the soot particles. The possible existence of shell structures in flame soot was suggested early in fullerene research[9] but was not previously assessed by high-resolution electron microscope analysis of soot from fullerene-forming flames.

Considering the single-shell fullerene[3] and curved plycyclic[10] molecules previously quantified in these flames and the nested nanostructures and shells within soot particles observed here, fullerene shells are far more prevalent than graphic flat sheets in the material of these flames. Thus carbon with curved layer structure can be formed not only under highly energetic all-carbon conditions of arc-discharges[4–6,8] and electron-beam irradiation[7], but also under the thermally milder and oxygen- and hydrogen-containing conditions that are found in flames.

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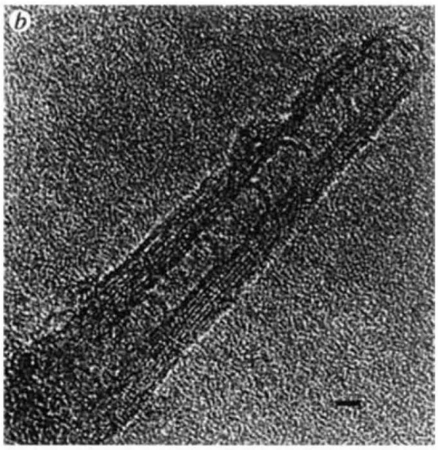

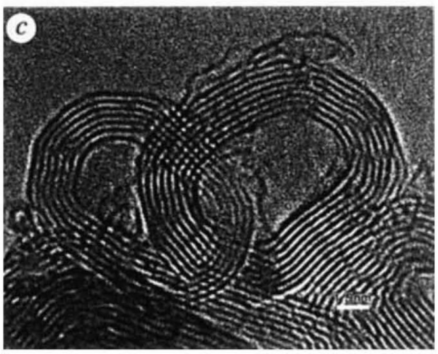

Electron microscope images of carbon nanostructures from benzene-oxygen flames. *a*, Low-magnificent image of an assembly of nanostructures extending from the left over a hole in the carbon film of the electron-microscope grid. Scot agglomerates, an order of magnitude larger in size than the nanostructures, are not in the field of view. *b*, Multi-shelled nanotube showing lengthening at cap and thickening radially. *c*, Multi-shelled nanoparticles consisting of nested prolate spheroids, tapered (left) and of approximately uniform cross-section (right). Experimental conditions: samples from burner chamber surface deposits: *a* and *c*, pressure $P = 97$ torr, C/O = 0.99 atomic ratio, velocity at burner (298 K) = 36 cm s^{-1}, 43.5% diluent (He/Ar = 2.6); *b*, composite sample from ranges of conditions given in the text. Scale bars: *a*, 6 nm; *b*, 1.5 nm; *c*, 1.5 nm.

1. Kroto, H. W., Heath, J. R., O'Brien, S. C., Curt, R. F. & Smalley, R. E. *Nature* **318**, 162–164 (1985).
2. Krätschmer, W. Lamb, L. D., Fostiropoulos, K. & Huffmann, D. R. *Nature* **347**, 354–358 (1990).
3. Howard, J. B., McKinnon, J. T., Mckinnon, J. T. Makarovsky, Y., Lafleur, A. L. & Johnson, M. E. *Nature* **352**, 139–141 (1991).
4. Lijima, S. *Nature* **354**, 56–58 (1991).
5. Lijima, S. Ichihashi, T. & Ando, Y. *Nature* **356**, 776–778 (1992).
6. Lijima, S. *Cryst. Growth* **50**, 675–683 (1980).
7. Ugarte, D. *Nature* **359**, 707–709 (1992).
8. Ruoff, R. S., Lorents, D. C., Chan, B., Malhotra, R. & Subramoney, S. *Science* **259**, 346–348 (1993).
9. Zhang, Q. *et al. J. phys. Chem.* **90**, 525–528 (1986).
10. Lafleur, A. L., Howard, J. B., Marr, J. A. & Yadav, T. *J. phys. Chem.* **97**, 13539–13543 (1993).