1. Carlton, J. T. *Oceanogr. Mar. Biol. Annu. Rev.* **23,** 313–374 (1985).
2. Carlton, J. T. & Geller, J. B. *Science* **261,** 78–82 (1993).
3. Ruiz, G. M., Fofonoff, P. W., Carlton, J. T., Wonham, M. J. & Hines, A. H. *Annu. Rev. Ecol. Syst.* (in the press).
4. Galil, B. S. & Hülsmann, N. *Eur. J. Protistol.* **33,** 244–253 (1997).
5. Carlton, J. T., Reid, D. & van Leeuwen, H. *The Role of Shipping in the Introduction of Nonindigenous Aquatic Organisms to the Coastal Waters of the United States (other than the Great Lakes) and an Analysis of Control Options* (Tech. Rep. No. CG-D11-95, US Coast Guard, Washington DC, 1995).
6. Grimes, D. J. *Estuaries* **14,** 345–360 (1991).
7. Hallegraeff, G. M. *Mar. Ecol. Prog. Ser.* **168,** 297–309 (1998).
8. McCarthy, S. A. & Khambaty, F. M. *Appl. Environ. Microbiol.* **60,** 2597–2601 (1994).
9. Colwell, R. R. *Science* **274,** 2025–2031 (1996).
10. Colwell, R. R. & Huq, A. in *Vibrio cholerae and Cholera: Molecular to Global Perspectives* (eds Wachsmuth, I., Blake, P. & Olsvik, Ø.) 117–134 (Am. Soc. Microbiology, Washington DC, 1994).
11. Williamson, M. *Biological Invasions* (Chapman & Hall, London, 1996).
12. Brock, T. D., Madigan, M. T., Martinko, J. M. & Parker, J. *Biology of Microorganisms* 7th edn (Prentice Hall, Englewood Cliffs, NJ, 1993).
13. Harvell, C. D. *et al. Science* **285,** 1505–1510 (1999).
14. Daszak, P., Cunningham, A. A. & Hyatt, A. D. *Science* **287,** 443–449 (2000).

Materials science

The smallest carbon nanotube

We report here the discovery of the smallest possible carbon nanotube. This has a diameter of 4 Å, which is the narrowest attainable that can still remain energetically stable, as predicted by theory. These nanotubes are confined inside multiwalled carbon nanotubes and their diameter corresponds to that of a C_{20} dodecahedron with a single carbon atom at each of its twenty apices. Unlike larger carbon nanotubes, which, depending on their diameter and helicity, can be either metallic or semiconducting, these smallest nanotubes are always metallic.

Many of the extraordinary properties of carbon nanotubes[1] depend on their diameter. The smallest carbon nanotubes have been associated with the smallest fullerenes[2], with nanotube diameters of 7 or 5 Å corresponding to those of C_{60} and C_{36} structures, respectively. Carbon nanotubes with such small diameters have been observed experimentally[3–5].

The carbon nanotubes reported here were seen in cathodic deposits produced by arc-discharge of graphite rods in a hydrogen atmosphere without a metallic catalyst[6]. Under these conditions, more carbon nanotubes (all multiwalled) are kept open as hydrogen etches away the capping atoms, a unique feature that helps maintain a favourable environment for smaller carbon nanotubes to form inside already-grown multiwalled carbon nanotubes.

Figure 1 shows a high-resolution transmission electron micrograph of an 18-shell carbon nanotube produced in this way: each dark line represents the side wall of a cylindrical graphene shell in projection and the innermost shell has a diameter of 4 Å. The cylindrical structure of the nanotube is shown by the reduced contrast towards the centre of the nanotube, where there are fewer atoms in the smaller tubes. Multiwalled carbon nanotubes with innermost shells of diameter 5 or 7 Å were also detected in the same material.

Some of the smallest nanotubes seen were capped, and electron micrographs of the cap of a 4 Å nanotube indicate that the smallest nanotubes have an antichiral [3, 3] 'armchair' structure[7] (Fig. 1, inset). We propose that these 4 Å nanotubes grow out of half of a C_{20} dodecahedron, in which the C–C bonding angle is 108° — very close to the bonding angle (109.5°) in the sp^3 configuration of diamond. Growth into a full nanotube is realized through a step-by-step mechanism on both the outer and inner surfaces[8] (Fig. 1, inset). The hydrogen atmosphere facilitates the formation of the

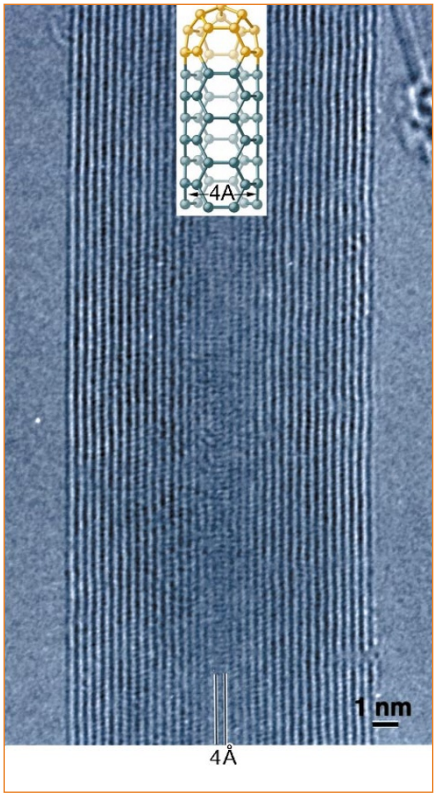

Figure 1 High-resolution electron microscope image of a 4 Å tubule (side walls are marked by lines) confined inside an 18-shell carbon nanotube. Dark lines correspond to the side walls of the single-wall shells. The blurring towards the centre is due to the smaller number of atoms in the smaller tubules. Inset, model for the formation and growth of a [3,3] armchair tubule of 4 Å diameter. Half of the C_{20} dodecahedron (yellow) serves as a nucleus and further growth into the tubule is realized by adding carbon atoms (blue).

halves of the C_{20} dodecahedron, stabilizing the structure by terminating certain dangling bonds with hydrogen, and keeps the inside of the nanotubes open so that, after the confining outer shells have been formed, carbon species can enter the core to form the innermost shell.

Although these tiny 4 Å carbon nanotubes should be energetically stable[9], the severe steric distortion resulting from the planar graphene changes the electronic structure significantly[10]. Electronic band-structure calculations indicate that all such tubules tend to be metallic, regardless of their helicity.

C_{20} fullerenes have recently been made using a gas-phase reaction method[11]. Our finding indicates that C_{20} fullerenes could also be produced by the arc-discharge method. It remains a challenge to produce single-walled carbon nanotubes of 4 Å diameter experimentally.

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1. Iijima, S. *Nature* **354,** 56–58 (1991).
2. Heath, J. R. *Nature* **393,** 730–731 (1998).
3. Ajayan, P. M. & Iijima, S. *Nature* **358,** 23 (1992).
4. Kataura, H., Achiba, Y., Zhao, X. & Ando, Y. *Mat. Res. Soc. Symp. Proc.* **593,** 113–118 (2000).
5. Sun, L. F. *et al. Nature* **403,** 384 (2000).
6. Zhao, X. *et al. Carbon* **35,** 775–781 (1997).
7. Qin, L.-C. *et al. Chem. Phys. Lett.* **268,** 101–106 (1997).
8. Iijima, S., Ajayan, P. M. & Ichihashi, T. *Phys. Rev. Lett.* **69,** 3100–3103 (1992).
9. Sawada, S. & Hamada, N. *Solid State Commun.* **83,** 917–919 (1992).
10. Blase, X., Benedict, L. X., Shirley, E. L. & Louie, S. G. *Phys. Rev. Lett.* **72,** 1878–1881 (1994).
11. Prinzbach, H. *et al. Nature* **407,** 60–63 (2000).

Materials science

Single-walled 4 Å carbon nanotube arrays

Here we describe the smallest carbon nanotubes possible[1], prepared by the pyrolysis of tripropylamine molecules in the channels of porous zeolite $AlPO_4$-5 (AFI) single crystals[2]. These uniformly sized carbon nanotubes have a diameter of 0.4 nm and are the best example of one-dimensional quantum wires.

AFI is a type of transparent microporous crystal (Fig. 1) containing one-dimensional channels packed in hexagonal arrays, with an inner diameter of 0.73 ± 0.01 nm (ref. 3). The starting material we used for synthesizing single-walled carbon nanotubes (SWNTs) was tripropyl-

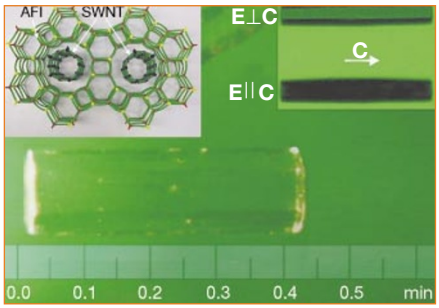

Figure 1 An as-grown zeolite $AlPO_4$-5 (AFI) single crystal. Left inset, model of the AFI crystal structure showing single-walled nanotubes (SWNTs) inside the channels. Right inset, polarization characteristics of the SWNT–AFI sample: no absorption (top) and high absorption (bottom) for light polarized perpendicular ($\mathbf{E}_{\perp C}$) and parallel ($\mathbf{E}_{\parallel C}$) to the tube direction, respectively. **E**, electric field of polarized light; **C**, zeolite channel direction.

amine, introduced into the channels during growth of AFI. SWNTs form inside the AFI channels when the pyrolysed carbon is thermally treated[2] (Fig. 1). The resulting brown AFI crystallites have good polarization characteristics (Fig. 1, inset). Polarized Raman spectra of these AFI crystals match well with theoretically predicted Raman-active modes, including the breathing modes[4,5].

To view the SWNTs in a transmission electron microscope (TEM), we first dissolved the AFI framework in 30% hydrochloric acid; the SWNT-containing solution was then enriched and dispersed on a lacey carbon film for high-resolution TEM (JEOL2010 microscope operating at 200 kV). Figure 2 shows a typical image in which the specimen is represented mainly by two types of morphology: small pieces of highly curved, raft-like graphite stripes ('G' in Fig. 2) and ultrathin SWNTs ('T' and large arrowheads in Fig. 2). In the 'G' areas, the spacing between neighbouring parallel fringes is measured to be about 0.34 nm, which matches well with the {002} lattice plane spacing of graphite. The SWNTs show a typical contrast effect, with the tube walls appearing as paired dark fringes; this contrast effect is very weak because of the small dimension of the tubes.

By using the {002} spacing of graphite as an internal reference and measuring the separation between the paired dark fringes of the SWNT images, we determined the diameters of the SWNTs to be 0.42 ± 0.02 nm. In the image shown in Fig. 2, there are ten or more SWNTs visible, all having the same morphology. The SWNTs in our samples were unstable under electron beam radiation, fading during observation in 10–15 seconds, whereas the raft-like layers of graphite persisted. We believe that the large number of small graphite pieces, which generally contain several layers, are transformed from SWNTs during extraction from the AFI crystal.

The narrowest diameter reported in the centre of multiwalled nanotubes is 0.5 nm (ref. 6), the same as that of a C_{36} molecule[7]. The smallest free-standing SWNT, of diameter 0.7 nm (the same as that of C_{60}), is stable[8]. The SWNTs observed here, which are consistent with a diameter of about 0.4 nm, are to our knowledge the smallest found so far. By considering the inner diameter of the AFI channels (0.73 ± 0.01 nm), and taking the distance between graphite sheets (0.34 nm) as the separation between the nanotube carbon atoms and the oxygen atoms on the channel wall, the diameter of the SWNTs allowed in the channels is 0.39 ± 0.01 nm (0.73 ± 0.01 nm $- 0.34$ nm).

There are three possible nanotube structures with a diameter of about 0.4 nm: these are the zigzag (5,0) (diameter, $d = 0.393$ nm), the armchair (3,3) ($d = 0.407$ nm) and the chiral (4,2) ($d = 0.414$ nm), where (m,n) is a roll-up vector defining the tube symmetry. Of these, the zigzag (5,0) tube can be exactly capped by half a C_{20} fullerene[9], which makes it more likely that this structure is formed. Because of the strong bending of carbon bonds, plus the size-confinement effect of the channels and the imperfection of such ultrasmall SWNTs (for example, point defects), there could be high-energy regions in these nanotubes. When they are released from their channels, the defects may cause instability which then permeates the whole tube, leading to the formation of the observed graphite stripes.

Because our SWNTs are highly aligned and uniform in size, their electrical transport properties are easy to measure. Local density functional calculations indicate that when the diameter of the SWNT is smaller than 0.5 nm, strong curvature effects induce strong σ–π mixing of the unoccupied orbitals, so metallicity can no longer be predicted by the simple band-folding picture[10]. Such small-radius nanotubes generally have finite density of states at the Fermi level. Preliminary electrical measurements on AFI crystals containing SWNTs[11] indicate that the temperature dependence of the SWNT conductivity is consistent with variable-range hopping in a disordered one-dimensional metallic system.

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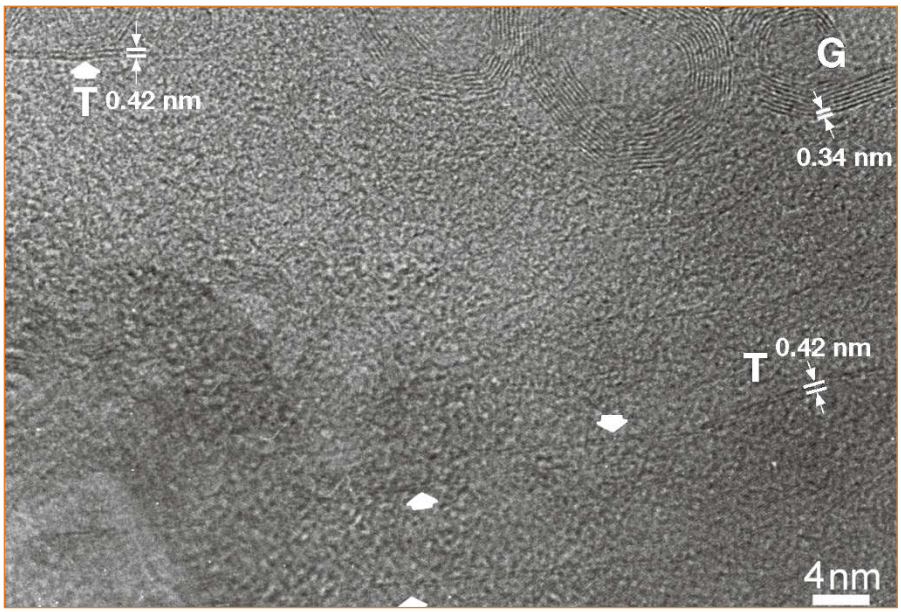

Figure 2 High-resolution transmission electron microscope image showing single-walled carbon nanotubes (indicated by T and large arrowheads) coexisting with graphite in raft-like stripes (G). More than ten single-walled carbon nanotubes are visible.

1. Iijima, S. *Nature* **354,** 56–58 (1991).
2. Tang, Z. K., Sun, H. D., Wang, J. N., Chen, J. S. & Li, G. D. *Appl. Phys. Lett.* **73,** 2287–2289 (1998).
3. Meier, W. M. & Olson, D. H. (eds) *Atlas of Zeolite Structure Types* (Butterworth-Heinemann, London, 1992).
4. Sun, H. D., Tang, Z. K., Chen, J. S. & Li, G. D. *Appl. Phys. A* **69,** 381–384 (1999).
5. Rao, A. M. *et al. Phys. Rev. Lett.* **84,** 1820–1823 (2000).
6. Sun, L. F. *et al. Nature* **403,** 384–384 (2000).
7. Piskoti, C., Yarger, J. & Zettle, A. *Nature* **393,** 771–774 (1998).
8. Ajayan, P. M. & Iijima, S. *Nature* **358,** 23 (1992).
9. Prinzbach, H. *et al. Nature* **407,** 60–63 (2000).
10. Blau, X., Benedict, I. X., Shirley, E. I. & Louie, S. G. *Phys. Rev. Lett.* **72,** 1878–1881 (1994).
11. Tang, Z. K., Sun, H. D. & Wang, J. *Physica B* **279,** 200–203 (2000).

Neurobiology

Hydrodynamic stimuli and the fish lateral line

Sensory systems need to distinguish biologically relevant stimuli from background noise. Here we investigate how the lateral-line mechanosensory system of the fish senses minute water motions[1] in the vicinity while exposed to running water. We find that one class of receptor in