Nanotechnology

'Buckypaper' from coaxial nanotubes

Double-walled carbon nanotubes are needed in a pure, highly crystalline form before features such as their electronic properties, thermal transport and mechanical behaviour can be investigated. Here we fabricate a paper-like material that consists of hexagonally packed bundles of clean, coaxial carbon nanotubes whose double walls vary little in diameter; it is prepared in high yields using chemical-vapour deposition with a conditioning catalyst and two-step purification. Our results will enable investigation of the physical properties of double-walled carbon nanotubes, which are predicted to be superior to those of both their single- and multi-walled relatives.

Double-walled carbon nanotubes, or DWNTs, consist of two concentric graphene cylinders, a structure that is intermediate between single-walled and multiwalled carbon nanotubes (SWNTs and MWNTs, respectively). Because they may have striking new electronic and mechanical properties, several attempts have been made to produce very pure DWNTs[1–7]; however, these have typically generated a mixture of DWNTs and SWNTs that is contaminated with metal particles, amorphous carbon and multilayer carbon nanotubes. Catalytic chemical-vapour deposition is generally considered to be the most efficient method for the large-scale production of nanotubes[8,9]; arc-discharge methods and thermal treatments of peapods of C_{60} (buckminsterfullerene, or 'buckyballs') result in unwanted carbon nanomaterials as well as DWNTs[1,4]. But measuring the cross-section of such DWNTs by high-resolution transmission electron microscopy shows that their uniformity and purity fail to approach those of SWNTs[1–7].

We synthesized DWNTs using a conditioning catalyst of molybdenum at one end of the furnace and a nanotube catalyst of iron in the central part of the furnace (for details of methods, see supplementary information). A methane–argon gas mixture (1:1) was then fed into the reactor for 10 min at 875 °C. Use of the conditioning catalyst[10] caused more DWNTs than SWNTs to grow, possibly because of an increase in the amount of active carbon species.

To obtain sheets of pure DWNT paper, we applied a two-step purification process to the synthesized products. Hydrochloric acid (18% by weight HCl at 100 °C for 10 h) was used to remove the iron catalyst and supporting material, followed by oxidation in air at 500 °C for 30 min, which removed amorphous carbon and chemically active SWNTs. After filtration, we obtained a dark, paper-like sheet, which was very flexible and mechanically stable (Fig. 1a).

Transmission electron microscopy revealed that the yield of DWNTs was extremely high (more than 95%) and that they were arranged in bundles (Fig. 1b–d). The DWNT paper consists of nanotubes with two remarkably consistent diameters that are hexagonally packed (Fig. 1d). Raman spectra verified the tube-diameter distributions from the radial breathing-mode (RBM) frequencies (see supplementary information), which are inversely related to tube diameter. Raman peaks appear above 250 cm^{-1} (corresponding to the inner shells of DWNTs) and below 250 cm^{-1} (usually associated with the outer shells of DWNTs). Using the equation $\omega_{RBM} = 234/d_t + 10$, where d_t is the tube diameter (in nanometres) and ω_{RBM} is the RBM frequency (in cm^{-1})[11], we were able to define two sets of DWNT pairs having inner-to-outer diameter ratios of 0.77:1.43 and 0.90:1.60, respectively.

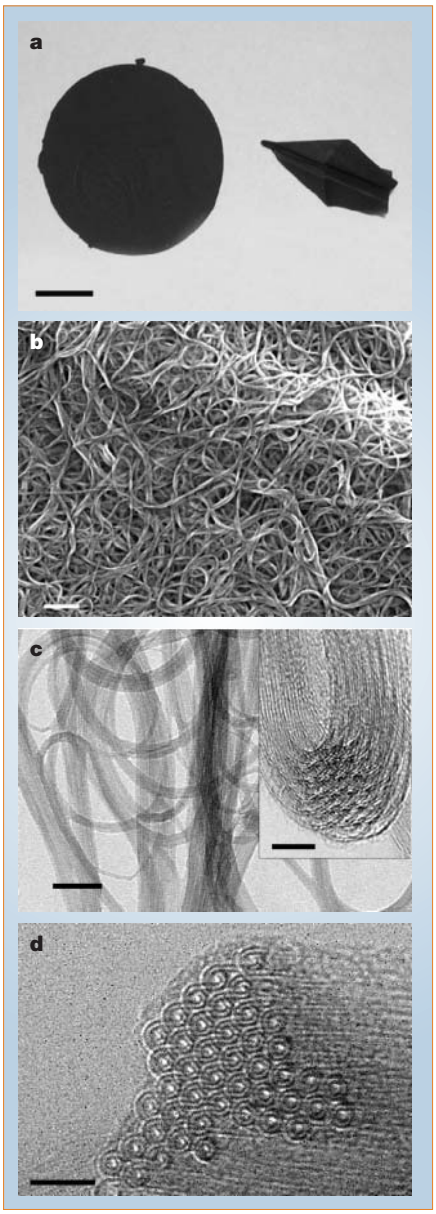

Figure 1 Production of pure and clean double-walled carbon nanotubes (DWNTs) in high yield. **a,** Photograph of double-walled carbon nanotube 'buckypaper'; the paper (left) is tough and flexible enough to fold into an origami plane (right). **b,** Scanning electron micrograph and **c,** low-magnification transmission electron micrograph (TEM; JEOL JEM-2010FEF) of DWNT paper, showing bundles of carbon nanotubes (insert, a single bundle; note the material's resistance to bending). Impurities are notably absent in these images. **d,** Typical high-resolution TEM image of a different bundle, showing the perfect hexagonal packing structure in both cross-section and side view. Scale bars: **a,** 1 cm; **b,** 300 nm; **c** 50 nm; inset, 5 nm; **d,** 5 nm.

Now that this pure material is available, it will be possible to investigate whether DWNTs behave as quantum wires and whether there is a chirality relationship between concentric tubes during growth, as well as the effect of tube concentricity on electronic conductance and the adsorption properties of coaxial nanotube ropes. This material should be useful in the fabrication of, for example, nanocomposites, field emission sources, nanotube bi-cables and electronic devices[12,13]. It is possible that DWNTs will eventually replace SWNTs or MWNTs in various applications because their mechanical properties, thermal conductivity and structural stability are likely to be superior owing to their coaxial structure.

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