Purification of nanotubes

SIR — Carbon nanotubes can now be produced in large quantities, either as multi-shell[1,2] or as single-layer[3,4] tubes. But together with the growth of the tubular material, other carbonaceous materials are always formed and their presence has hampered the accurate characterization of the bulk properties of nanotubes. We report here a simple method to purify nanotubes which should be useful for further studies.

In the case of the arc-discharge process yielding multi-shelled nanotubes[1,2], nanoparticles are the main by-product and compose about one-third of the sample in the best preparations. To purify the nanotubes and eliminate the nanoparticles, we first tried various standard techniques such as filtration, chromatography and centrifugation of sonicated solutions of the raw material. Although these techniques will separate to some extent large clumps of material from individual nanotubes and nanoparticles, they did not separate the nanotubes from the nanoparticles.

Recently, we and others reported that nanotubes could be opened and thinned through oxidation[5,6]. The significant difference in the oxidation reaction rates of the carbon nanotube caps as compared to the cylindrical surfaces results in the production of open nanotubes during oxidation. The enhanced reactivity of the caps

results either from the strong local curvature and imperfect geometry and/or from the presence of five-membered carbon rings as discussed previously[6]. The structure (number of pentagons in a closed shell) and geometry of nanoparticles very much resembles that of the tube caps, although they are comparatively larger[7]. So nanoparticles should be similarly consumed by oxidation although at a slower rate than the highly curved (strained) nanotube tips.

Once the nanotube caps are destroyed, the tubes essentially consist of a perfect hexagonal carbon network and the reaction proceeds slowly. But in the case of nanoparticles all the concentric layers are similar in structure and etching of the layers should occur at a relatively constant rate.

The above suggests that at some point during oxidation, all the caps and nanoparticles should be destroyed, leaving only open nanometre-sized cylinders of carbon in the sample. We observe just this if the oxidation is allowed to proceed for long durations. The figure shows the dramatic improvement in the nanotube-to-nanoparticle ratio after this treatment. Note that to remove all the nanoparticles from the samples, one has to oxidize more than 99% of the material. When only about 95% of the sample is oxidized, just 10–20% of the remaining

material comprises pure nanotubes, but this still represents a substantial reduction in the proportion of nanoparticles in the total sample. In samples oxidized to a degree of less than 85%, no change in the ratio of nanoparticles is apparent relative to the original sample.

In the final purified sample, all the tubes are open and the partly removed outer layers contain reactive edges[5]. The average aspect ratios have decreased but not changed significantly (most are >100 but there are a few open cylinders with aspect ratios >20) as the tubes were originally much longer than the particles. Why more than 99% of the weight has to be burnt off to produce pure nanotubes is not clear. One possible explanation is that the oxidative species are not able to reach evenly all the parts of the sample because the ground-up nanotubes and nanoparticles are intertwined. We have tested this possibility by better dispersal of the samples before oxidation and by using flowing oxygen during the reaction. But so far we have not noticed any significant change. A more likely reason why the sample must be consumed significantly for purification is that the difference in reactivity between the nanotubes and the nanoparticles is small.

Whether this technique can be used to purify single-shell nanotubes, where soot and catalysts are major by-products[3,4], will depend very much on their relative reactivity. The single-shell nanotubes, having diameters approaching those of fullerenes, might be much more reactive, as is the case with C_{60} (refs 6,8).

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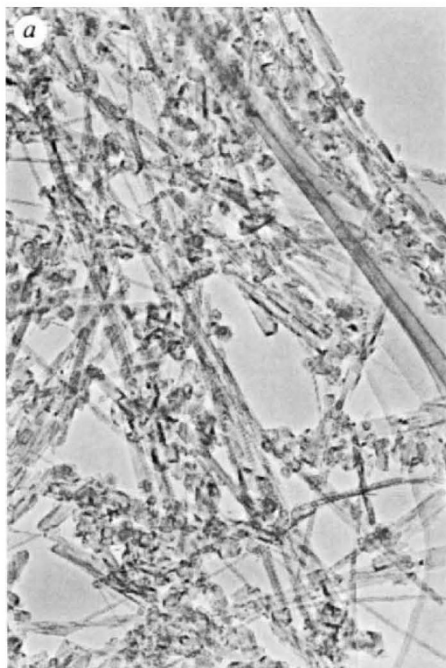
Low-magnification transmission electron microscope images of *a*, a typical nanotube sample produced by the carbon-arc method; and *b*, a purified open carbon nanotube sample. The purified sample was prepared as follows. Ground raw nanotube sample taken from the inner core of the carbon arc deposit[1,2] was placed in an oven and then the temperature was raised to 750 °C (in air or oxygen). After about 30 min, about 1% remained with the quality shown in *b*. In most tubes, the length/diameter ratios exceed 100, although there are some open cylinders with the ratio as small as 20.

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