teration in apoptosis? The authors point out that cells with diminished capacity to undergo apoptosis have a selective advantage. New episodes of Sun exposure gradually weed out the *p53*-positive, apoptosis-competent cells while the apoptosis-impaired cells survive and replace their normal counterparts. Thus, UV is doubly effective as a carcinogen (see figure).

But why is *p53* such a favoured target for mutation? There are several possibilities, one of which emerges from the work of Ziegler *et al.* They find that cells heterozygous for *p53* mutations (one mutant allele and one wild-type allele) are intermediate between wild-type and homozygous mutant cells with respect to apoptotic competence. This suggests that *p53* mutations are co-dominant for apoptosis; that is, a single inactivating mutation promotes survival of the heterozygote over the wild type.

A second explanation may be that, for the price of inactivating one gene, *p53* mutations have two important consequences; namely, deregulation of the cell cycle and reduced apoptosis. A third explanation is that somatic *p53* mutations may seldom or never compromise the viability of the cell, whereas mutations in other tumour-suppressor genes or oncogenes may do so. If most cancer genes can be altered only at specific times in tumour formation, and only in certain combinations without simply killing the cell, they may appear to have undergone mutation less frequently than *p53*.

Other issues are raised by the new work. Inactivation of *p53* does not completely abolish the cells' capacity to undergo apoptosis. What pathway (or pathways) is responsible for this residual apoptotic behaviour? Actinic keratoses, the precursors of squamous cell carcinomas, frequently contain *p53* mutations; yet these lesions regress spontaneously in the absence of UV exposure. Are cells with *p53* mutations at a selective disadvantage without UV? The skin, like the colon, is an attractive model in which to study cancer. In future studies, it will be important to extend to other tissues the concept of p53 as a bona fide growth regulator highlighted by Ziegler and colleagues' informative analysis of skin tumorigenesis. □

Alexander Kamb is at Myriad Genetics Inc., 390 Wakara Way, Salt Lake City, Utah 84108, USA.

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CARBON NANOTUBES

The continuing saga

Rodney S. Ruoff

CARBON nanotubes have attracted intense scrutiny since their discovery[1] in 1991. The empty core at the centre of a nanotube begs to be filled, and the low-melting-point metals lead and bismuth were induced several years ago to part-fill this centre core[2]; but the approach used has not been extended to high-melting-point metals, and the quantities of partially filled nanotubes produced were microscopic. Two considerable advances in the filling of the core volume in nanotubes with different metals have now been reported — one on page 761 of this issue[3], the other a few weeks ago[4]. Guerret-Piécourt *et al.*[3] have used direct synthesis in a direct-current (d.c.) carbon arc maintained in gaseous helium to which is added a metal. Tsang *et al.*[4] treated nanotube material with nitric acid to open the tubes, with filling achieved from metal ions present in solution.

There are currently two types of nanotubes, different in appearance and in their mode of production. Multi-walled nanotubes occur inside a growth that builds up on the cathode of a d.c. carbon arc operated in a helium atmosphere[1]. Single-walled nanotubes have been produced in the 'soot' that emanates from carbon arcs; these develop only when certain elements such as iron or cobalt are added to the carbon arc[5,6]. Both Guerret-Piécourt *et al.* and Tsang *et al.* use multi-walled nanotubes; filling the single-walled variety remains on the horizon.

Using approaches similar to that on page 761, other groups have seen evidence of encapsulation of carbides of yttrium[7] and gadolinium[8] in nanotubes culled from the cathode growth from a typical d.c. arc. Although these results are tantalizing, the yield of partially filled nanotubes has been small, the encapsulate being a minor product alongside empty nanotubes, nested polyhedra which may be empty or partially filled, and other forms of carbon such as particles of graphite and amorphous material[8]. One might have asked, before this week's paper, whether direct production in the d.c. arc was really a suitable approach for filling carbon nanotubes with metals, although it has given high yields of filled or partially filled carbon polyhedra for certain elements[9,10].

But the new work shows that a variety of elements can partially fill nanotubes grown in such a way, and that some of the filled sections are around a micrometre in length. I suggest that a critical factor is the maintenance of an especially stable arc for long periods during the arc run, and that previous researchers who have not seen such yields were working with arcs that were not particularly stable. Smalley has suggested that empty nanotubes grow on the cathode in a d.c. carbon arc (no metal present) because of very large electric fields at their tips, which serve to keep the tips open as carbon cation species are 'guided' to the open tips along the field lines[11].

Achievement of particularly stable arcs (uniform and non-fluctuating electric field at the cathode surface) is in a sense a defeat of the 'cathode spot' phenomenon, where the electric field is concentrated particularly on one spot on the cathode for a short time, and then hops to a different spot; this is deleterious to uniform growth of nanotubes. Videotapes taken in our laboratory clearly show that the current path in a typical d.c. arc hops back and forth over the cathode and anode carbon electrode surfaces. Active feedback in controlling the current and voltage of the arc can hold an arc in stable operation[12]. An alternative method, initiating a glow discharge between graphite electrodes with a tesla coil coupled to a tungsten wire held close to the electrode pair, allows a stable current to be maintained and improves nanotube yields[13]. The yields of filled nanotubes in ref. 3 are in the 1–5 per cent range as estimated from transmission electron micrographs. If this method were to be combined with deliberate design of very stable arcs or glow discharges, it should be possible to improve yields and to study in detail the mechanism for filling.

Typical multi-walled nanotubes as currently produced are closed off or capped at the ends. The positive curvature of the end closure is achieved by pentagon insertion into the hexagonal bonding network, and the pentagon locations are probably more reactive. Proof of a faster rate of oxidation, and subsequent removal of the pentagons and capped portion, comes from the work of Tsang *et al.*[4] who report a simple chemical method for opening nanotubes in a selective manner with boiling concentrated nitric acid. One can then imagine filling them with different solutions and depositing the solute of interest. Solvent removal could leave a residue which might itself be a metal, or on further treatment be converted to a metal.

An important aspect of solution-based filling is that a wide variety of compounds could probably be incorporated. For example, it is difficult to imagine *in situ* arc production of filled nanotubes with encapsulated NaCl or CdSe crystals, but solution-based filling should be possible. Control of encapsulate stoichiometry should be much greater with precipitation from solution than by arc methods. Be-

cause the nitric acid treatment can be scaled up, the availability of open nanotubes is limited only by the availability of the capped feedstock. Ebbesen and coworkers, and Hwang, have also obtained good tube-opening results with a solution of potassium permanganate in acidic solution (T. Ebbesen, K. C. Hwang, personal communication).

Selective removal of tube tips by nitric acid shows that the pentagon carbon atoms and the carbon atoms under strain at the tips are reactive but that the hexagonal network of sp^2-bonded carbon on the tube sides is not, on the timescale of treatment used in ref. 4. The ability of nitric acid to chew selectively along a line of pentagons, 'drilling' inwards through a series of corners in a nested polyhedral particle (R. S. R. and S. Subramoney, unpublished results) without destroying the hexagonal sheets, may lead to new recipes for carbon-coated nanocrystals where the nanocrystals are formed by techniques analogous to those used by Tsang *et al.* to fill nanotubes.

One aspect of ref. 4 deserves special scrutiny. One could infer from the procedures used that the final volume filling of NiO on conversion of a nickel precursor is determined by the concentration of nickel nitrate solution used. Straightforward calculation shows that a volume filling of only 0.27 per cent would result. But the lengths given as typical are 20 nm for NiO crystallites and 200 nm for nanotubes and the NiO crystallite fills the nanotube essentially completely over its 20-nm length[4]. So the filling cannot simply be a question of the bulk solution concentration. The roughly 10 per cent filling with NiO means that the nickel nitrate precursor (a solid) must essentially completely fill the tube (taking account of molecular weights and respective densities). How does nearly 40 times 'too much' NiO end up, following calcination, in the nanotube, or how could the tube be filled completely with a solid precursor? I leave it to the reader to ponder the implications of precipitation of solids inside the nanotubes when the bulk solution outside them is subsaturated.

We may speculate about possibilities that filling from solution can offer. One may think of the internal volume of a nanotube as a test tube for studying chemical reactions, or the thermodynamics or kinetics of phase transitions, in small spaces. For an ionic solution, is the concentration of ions in the solution *inside* the tube the same as in the bulk solution, or do unusual concentration gradients develop? If one forces a non-wetting liquid[14] such as mercury into a tube with high pressure, will it stay in the tube when pressure is released? If so, and the filled tube is cooled to below the superconducting transition temperature of bulk Hg (about 4 K), perhaps interesting phenomena will be observed. At room temperature, will encapsulated Hg be a liquid? For the chemist chef who desires peas-in-a-pod, can opened nanotubes be filled with C_{60}?

One wonders, too, how enclosed nanocrystals whose expansion is limited radially will melt. Topological constraints may govern phase transitions; for instance, preliminary theoretical efforts show that argon will have difficulty forming a complete solid phase inside some tube geometries even though the temperature is below the bulk freezing value, because of the difficulty of growing a non-frustrated cylindrical crystal inwards from the inner tube perimeter to the centre (M. Maddox and K. E. Gubbins, personal communication). The dynamics of water or of a long-chain polymer inside nanotubes could be fascinating and could be studied by NMR.

One wants to believe in quantum wires based on long nanotubes that have been completely filled with conducting metals, and progress in improving yield and quality of nanotubes continues at a good rate. But in my opinion this is a more distant goal than immediate studies of incorporating materials of relatively short length into opened nanotubes, and investigating their various properties. Progress in fundamental areas and in applications that do not rely on perfect filling should come first, such as studies of the thermodynamics and dynamics of solutions or solids inside nanotubes, and new catalysts.

But if we may dream of nanowires, how about taking a scanning probe microscope nanotip that is a carbon nanotube, clipping off its end by a wet chemical etch, and dipping it into an appropriate solution to produce a magnetic encapsulate such as Fe or Ni at the tip end? Perhaps such a tip could detect atom-specific magnetic resonance of biomolecules on surfaces. □

Rodney S. Ruoff is in the Molecular Physics Laboratory, SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025, USA.

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DAEDALUS

Celestial graffiti

LAST week Daedalus proposed the scanning electron telescope. It was an orbiting launcher for strong electron and positive-ion beams (both together, to maintain overall charge-neutrality). The beams were to be aimed at planetary targets, so that earthbound telescopes could study the luminosity of their impact. He now proposes aiming the beams down towards the Earth.

When high-energy particles hit the high atmosphere, they excite an auroral glow. The shifting, filmy, magical curtains of the polar aurora are produced by the impact of solar-wind particles on the air molecules about 150 kilometres up. The molecules luminesce as they decay back to their ground state. Aurorae can have many colours: red (the 'proton glow' from protons in the solar wind), and yellow, green and violet from various spectral bands of electron-excited nitrogen and oxygen molecules.

A powerful, narrow particle beam directed from above should create a very bright 'point-aurora' at its site of impact. The colour and intensity of the auroral glow could be controlled by varying the energy and particle density of the beam. The positive and negative beams would create point-aurorae of different colours, which could be scanned independently around the sky. The application is obvious: celestial colour television. From space, it should be possible to scan a picture over the atmosphere 100 kilometres across and 150 kilometres up, and visible over an area the size of central Europe.

In the daytime, the brightest auroral picture would be imperceptible. Celestial television will come into its own at night. Low-orbit satellites will speed across the heavens trailing huge pictures in their wake, like publicity banners behind an invisible plane. Geosynchronous satellites will paint a stable frame that will fill the same chunk of sky night after night. At first Daedalus hoped for educational programmes, with leading astronomers pointing out planets and constellations to the upgazing masses. But the dream soon faded. He now expects the sky to fill up rapidly with the usual trash, advertisements and all. One consolation is that the pictures would be silent. Aurorae make no noise of their own, and even the radio emission from particle impact would be hard to modulate into a useful soundtrack. Furthermore, the Earth's ever-changing magnetic field will sabotage the line-scan, making the images wobble unsteadily. With luck this undignified wavering will discourage the more pompous nonsense, leaving the sky to the likes of Tom and Jerry. David Jones