

formation of hollow tubes of CA extending over micro- or millimetre scales.

So how does this system differ from a classical chemical garden? Most remarkable is the exquisite degree of control over the system and the homogeneity of the microtubes. Once growth of the tube has started, the diameter remains constant and materials with diameters in the range 20 to over 100 micrometres have been obtained. The tube diameter can be controlled by adjusting the concentration of C in the bulk solution, with lower concentrations leading to larger diameters. The chemical integrity of the material has been established and it was found that the microtubes are essentially homogeneous CA. These are critical differences from the classical chemical garden in which typical bulk growth is non-homogeneous and often has a macroscopic dendritic appearance. Furthermore, silicate-based chemical gardens tend to have rather inhomogeneous constitution, arising from local pH gradients associated with the bulk transfer of material in the alkaline solution.

Mechanical control of chemical reactions is a relatively rare phenomenon, but in this study a beautiful example is presented. If a growing microtubule is punctured somewhere along its length, growth along the original vector ceases and a new branch starts at the puncture point as a new jet of saturated solution is created. This branch then continues to grow until the POM is depleted or another mechanical event occurs. In another remarkable observation, the direction of growth of the microtubes can be controlled by the application of an external potential. The origin of this effect

is a little obscure because the potentials applied are relatively modest, but the approach offers the promise of subtle control over the topology and topography of the microtubes.

POMs are of current interest as redox catalysts and photocatalysts and have potential applications as electronic materials⁴ as well as possessing established biological activity^{3,5}. So, what does the future hold for these unusual constructions? In all honesty, one can only speculate as to the potential, but immediate thoughts spring to the design of microfluidic systems through chemical growth. Although the necessary degree of architectural control has yet to be established, fluorescent dyes injected into the microtubes are seen to flow in confined channels, indicating that the tubes are hollow and structurally robust. The availability of POM-based microtubes now offers the possibility of designing microfluidic systems in which the catalytic functionality of the material can be used within the tubes, where the surface-to-volume ratio is high.

So far, nothing is known of the electrical properties of the materials, but if they could be tuned to give semiconducting properties, numerous applications are possible. If growth can be maintained through changes in the bulk solution component, it might be possible to construct novel heterojunctions. However, the chemical nature of the material offers, in my opinion, the potential for a whole series of new technologies. As mentioned previously, the cations selected show biological activity against cancer cell lines

and it might be possible to topically target cell clusters. If it proves possible to control the size of microtubes to engineer smaller diameters, it might even be possible to use the biologically active tube material directly in an intracellular fashion.

Applications of this nature depend critically on the reproducibility and scalability of the synthesis and the ease of harvesting and fabrication of the nanotubes. So far, only the first of these four issues has been addressed but the future looks rich for chemically designed microtubes. However, the long-term importance of the work by the Glasgow group will, perhaps, be to raise awareness of the simple osmotic-pressure-driven growth of both soft and hard condensed materials under ambient conditions. The incorporation of organic components, in this case cations, raises an almost infinite variety of materials classes that might be addressed by simple combinations of cationic and anionic materials reacting to form insoluble species. □

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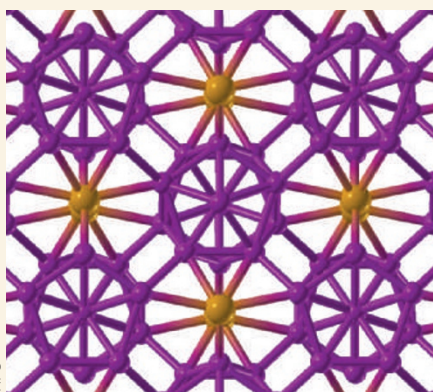
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ELEMENTAL ALLOTROPES

More on boron



Although boron has been known since 1808, a reasonably pure form was only isolated in 1909; its full phase diagram

is still not well understood and its stable phase at normal conditions is yet to be established experimentally. Now, Artem Oganov, from ETH Zurich and Moscow State University, with colleagues from across the world, has discovered a new form of boron at high pressure (pictured; *Nature* **457**, 863–867; 2009).

All currently known structures of boron contain icosahedral clusters of 12 boron atoms and this is no exception. What makes the new form particularly interesting is that it features pairs of boron atoms as well. The B₁₂ clusters (purple in the figure) and B₂ pairs (orange) are arranged in a rock-salt-type lattice, with the B₁₂ clusters taking the place of the cubic-close-packed anions and the pairs

fitting in the octahedral spaces. This results in a more dense structure than those with just clusters, hence why it is formed at high pressures.

Charge transfer between the clusters and the pairs results in the compound having a small but not insignificant ionic character. This ionicity affects its dielectric, electronic and optical properties and 'boron boride' represents the first example of ionic bonding observed in pure elements, as well as helping to fill in the phase diagram for such a well-known element.

Read even more about boron on page 92 in this month's 'In your element'.

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