

GRAPHENE NANORIBBONS

Twisted within nanotubes

Single-walled carbon nanotubes have been used as test tubes for chemical reactions in an electron microscope. It is now shown that they can also act as reactors for the synthesis of narrow, helically twisted graphene nanoribbons through electron irradiation of functionalized fullerenes.

Florian Banhart

Carbon nanotubes can in principle encapsulate almost anything that is small enough, be it liquid¹ or solid metals, inorganic materials and, more recently, organic molecules². Interestingly, fullerene molecules fit precisely into a common type of single-walled carbon nanotube³ — thus forming so-called ‘pea pods’. However, filling carbon nanotubes with graphene — nowadays the most-studied carbon structure — has seemed to be out of the question. Although a sufficiently narrow graphene nanoribbon could fit into a single-walled carbon nanotube, cutting currently available nanoribbons to the necessary width — about three hexagonal carbon rings — and fitting them inside nanotubes is far from feasible. Surprisingly, however, the synthesis of a graphene nanoribbon within a carbon nanotube is possible by adopting a different route. Reporting in *Nature Materials*, Andrei Khlobystov and co-authors show that carbon nanotubes can be used as reactors to synthesize graphene nanoribbons from functionalized fullerenes⁴.

Khlobystov and colleagues linked fullerenes to organic chains terminated by sulphur atoms. In a chloroform solution, these functionalized fullerenes can enter the hollow channel of open single-walled carbon nanotubes to create ‘pea pods’ (Fig. 1a). The authors transferred the filled nanotubes into an electron microscope and irradiated them with electrons. They observed considerable structural transformations of the encapsulated molecules, leading eventually to the formation of graphene ribbons with side bonds saturated with sulphur atoms (Fig. 1b). Graphene ribbons with open side bonds are known to be very reactive and unstable energetically, and therefore it is quite natural that the edges are saturated with other atoms. The most common edge species is hydrogen, but hydrogen is certainly unstable under electron bombardment. Sulphur atoms are difficult to remove with an electron beam and lend themselves as a more stable side termination. These sulphur-terminated carbon strips might be the narrowest graphene ribbons that have ever been made, and perhaps even

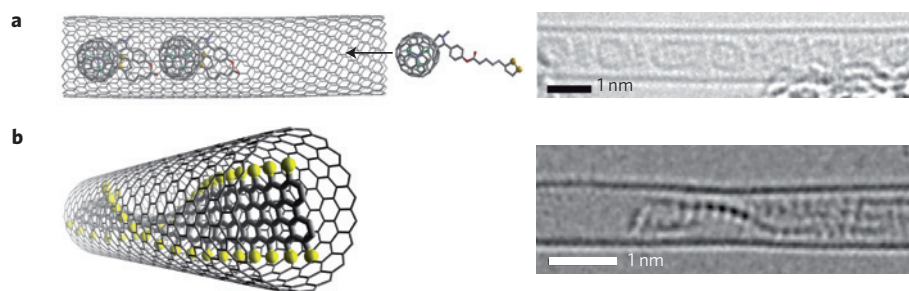


Figure 1 | Synthesis of a graphene nanoribbon within a carbon nanotube. Schemes are shown on the left and transmission electron micrographs on the right. **a**, Fullerenes functionalized with an organic molecule containing the elements H, O, N and S have exceptional affinity for the interior of the nanotube, therefore forming so-called ‘pea pods’. Images reproduced from ref. 4. **b**, By way of prolonged exposure to an electron beam or heat treatment, the functionalized fullerenes transform into a stable, helically twisted graphene ribbon with sulphur atoms (yellow) at the edges. Left image courtesy of A. Khlobystov; right image reproduced from ref. 4.

the narrowest possible graphene ribbons that are stable. In fact, this is another impressive example of the potential of carbon nanotubes as reaction vessels for the synthesis of novel and otherwise unstable structures^{2,5}. Unfortunately, details of the rapid transformation were not accessible to *in situ* observation in the microscope. This remains a challenge and could possibly be tackled by high-speed electron microscopy⁶, if the reaction could be triggered by laser pulses.

As is clearly visible in the micrograph in Fig. 1b, the nanoribbon twists around the long axis of the tube. The spiral-shaped ribbon is probably a consequence of the ribbon’s width exceeding the tube’s diameter, as the calculations by Khlobystov and colleagues show. However, twisting is not the only mechanism by which the ribbon fits into the tube. The authors also observed that the cross-section of the tube locally expands in the plane of the nanoribbon as the nanoribbon rotates. Of course, helically coiled structures inside carbon nanotubes have been previously observed⁷, and various origins of twist in nanotube-enclosed structures have been suggested, such as intercalation or entropic effects arising from inclusions or confinement, respectively, but these are probably not relevant to graphene nanoribbons. However, the chemistry at the

edge, in particular ionic repulsion, could also induce twist, even if a graphene ribbon is not encapsulated⁸. On the other hand, the growth of enclosed twisted structures could be adjusted by the inherent helicity of nanotubes if they are not of the perfect zigzag or armchair types.

The nanoribbon-in-the-nanotube system may find unexpected properties and applications. Theory predicts that the edges of graphene nanoribbons strongly influence the ribbon’s electrical properties. In fact, some of the less favourable properties of graphene, such as its missing bandgap, can be overcome by cutting graphene sheets in ribbons. Interestingly, the helical twist modifies the bandgap, as the calculations of Khlobystov and co-authors show⁴. Also, changes to the helical angle under deformation may lead to an electromechanic response of the system that could be used in switches, sensors or piezoelectric elements⁸. Moreover, large-scale synthesis could be achieved by heating, as it apparently leads to the same reaction as electron irradiation. Although Khlobystov and colleagues have shown only nanoribbons of less than 30 nm in length, there seems to be no impediment to the synthesis of longer twisted graphene ribbons with several turns. However, this would need a very careful process with a well-defined nucleation point from where

the twisting ribbon grows. Furthermore, a variety of related reactions in nanotubes can be imagined, provided that efficient uptake of precursors and a sufficient mobility inside the tubes can be achieved (at present this seems to require the presence of fullerene cages). It also remains to be seen whether the nanotube–nanoribbon system can be dismantled, and if the unconfined graphene

nanoribbons would remain stable. In any case, though, helically deformed carbon nanomaterials are no longer a chimera. □

Florian Banhart is at the Institut de Physique et Chimie des Matériaux, UMR7504 CNRS, Université de Strasbourg, 23 rue du Loess, 67034 Strasbourg, France.
e-mail: Florian.Banhart@ipcms.unistra.fr

References

1. Ajayan, P. M. & Iijima, S. *Nature* **361**, 333–334 (1993).
2. Liu, Z. *et al. Phys. Rev. Lett.* **96**, 088304 (2006).
3. Smith, B. W., Monthieux, M. & Luzzi, D. E. *Nature* **396**, 323–324 (1998).
4. Chuvin, A. *et al. Nature Mater.* **10**, 687–692 (2011).
5. Warner, J. H. *et al. ACS Nano* **5**, 1410–1417 (2011).
6. Shorokhov, D. & Zewail, A. *Phys. Chem. Chem. Phys.* **10**, 2869–3016 (2008).
7. Fan, X. *et al. Phys. Rev. Lett.* **84**, 4621–4624 (2000).
8. Gunlycke, D., Li, J., Mintmire, J. W. & White, C. T. *Nano Lett.* **10**, 3638–3642 (2010).

METALLIC ALLOYS

All particles are equal

The coarsening mechanism, by which larger droplets in a solid-state matrix consume smaller ones, can effectively be reversed in the case of core–shell precipitates, leading to a nearly monodisperse droplet size distribution.

Jeffrey J. Hoyt

Since the discovery of coarsening by the Nobel-prize-winning chemist Ostwald more than 100 years ago and the subsequent theoretical analysis by Lifshitz, Slyozov and Wagner^{1,2} 50 years ago, it has been believed that in a system consisting of second-phase droplets immersed in a supersaturated matrix, the average droplet size increases and the total droplet number density decreases over time. Indeed, the idea that larger particles grow at the expense of smaller ones is familiar to most

graduate students in materials science. Now, however, writing in *Nature Materials*³, Radmilovic *et al.* report that in the aluminium–scandium–lithium system they study, not only is coarsening quite sluggish, but it seems to happen in reverse, with the smaller particles in the distribution growing faster than the larger ones. The authors have successfully explained why this unique alloy microstructure seems to defy our textbook understanding of particle coarsening.

A finely dispersed distribution of second-phase precipitates is a very effective obstacle to the flow of dislocations through an alloy, which as a result resists plastic deformation. Precipitation hardening is in fact the main strengthening mechanism in a host of commercial aluminium alloys. There is a catch, however. If the coarsening process is allowed to continue for too long, the distance between precipitates becomes large and the barrier to plastic deformation is diminished, a phenomenon known as ‘overaging’. It would therefore be very desirable to identify mechanisms that can hinder the natural tendency to coarsen, yet maintain a narrow particle size distribution. This may lead to the development of new alloys capable of retaining desirable mechanical properties at high temperatures.

The alloy studied by Radmilovic and colleagues³ is aluminium with the addition of roughly 8.5% lithium and a smaller amount (0.11%) of scandium. A heat treatment at 450 °C leads to homogeneous nucleation of the ordered Al₃Sc phase (with a small amount of lithium) throughout the bulk, aluminium-rich matrix. A second heat treatment at a lower temperature (190 °C) creates the Al₃Li phase with the same crystal structure, but Al₃Li does not form randomly in the alloy. The interfacial energies of the system are such that Al₃Li prefers to completely wet the aluminium–Al₃Sc boundaries and effectively ‘coats’ all of the pre-existing Al₃Sc particles, leading to what is known as a core–shell precipitate structure. These Al₃Sc–Al₃Li core–shell precipitates are spherical and have practically no lattice mismatch with the surrounding aluminium phase. In other words, they satisfy quite well all of

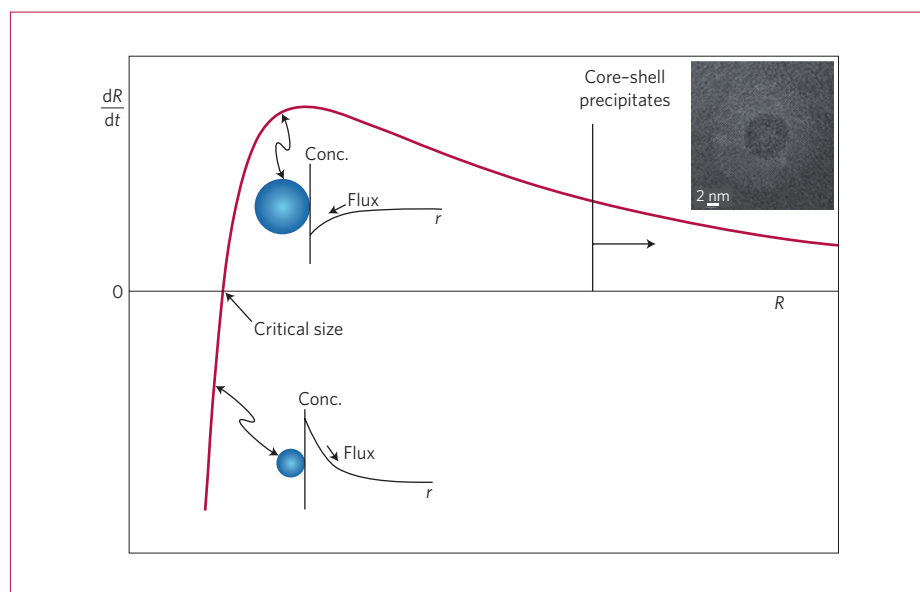


Figure 1 | Particle growth rate (dR/dt) versus particle radius (R) according to Lifshitz–Slyozov–Wagner^{1,2} theory. Insets, concentration profiles as a function of radial distance (r) surrounding two representative precipitates. Solute fluxes are directed away from the surface for small particles (bottom inset), resulting in shrinkage, whereas for large particles (top inset) growth occurs through flux towards the surface. The pre-existing core phase in the aluminium–scandium–lithium system provides the nucleation sites for the shell phase, such that all the particles lie on the downward-sloping portion of the growth-rate curve.