to obtain an image, the technique uses radio waves whose energy is less than a billionth of that of the X-rays used for diffraction studies or the electrons used in an electron microscope. MRI is itself based on nuclear magnetic resonance (NMR), which exploits the intrinsic and plentiful nuclear magnetic spins present in all substances. These nuclear magnets oscillate at a precisely measurable frequency that is determined by fields generated by neighbouring atoms, and by an externally applied field. Hence, these nuclear magnets are embedded, microscopic probes that reveal details of their host's electronic, magnetic and structural properties. Detailed information obtained from NMR has been extensively used for tasks ranging from identifying organic molecules to illuminating subtle features of exotic superconductors.

For imaging, the external field is arranged to vary controllably across the sample, so that the frequency of the nuclear magnetic oscillation will reveal its precise location. This mechanism underlies non-invasive, three-dimensional MRI of regions deep within a sample. Rather than scattering energetic particles, MRI uses low-energy radio waves to excite the nuclear spins so that their oscillation frequency can be measured. A benefit of using magnetic resonance for imaging is that these magnetic resonance signals allow spatially resolved NMR experiments and characterization that enrich the images with detailed microscopic information.

However, the weak interaction that makes MRI so non-invasive is also its Achilles heel: the interaction of the detector with the spin is so small that, in conventional approaches, many spins (10^{12}–10^{18}) are needed to provide a large enough signal to tease out information about the materials. The dimensions of the resolvable volume are limited by the need to detect the weak oscillatory signal of the few spins in the small-volume elements that make up the image. This limits conventional MRI to volumes of several cubic micrometres, and so reduces the usefulness of the technique in solid-state physics, or molecular or cell biology.

In 1991, John Sidles[2] proposed a system for mechanically sensing the weak force that a microscopic ferromagnet exerts on the nuclear magnetic moment in a sample. Tiny forces, he suggested, can be measured by placing the sample under investigation on a compliant cantilever. By observing the slight resulting deflection of the cantilever using, for example, an optical interferometer, extraordinarily small forces can be detected[3]. Force-detected MRI, dubbed magnetic resonance force microscopy (MRFM), has rapidly improved in sensitivity and spatial resolution[4–6]: it has been used to observe a single electron spin[7] and for highly sensitive nuclear-spin detection[8]. MRFM is also a practical materials probe that has been applied to major problems in science[9,10] and technology[11]. Beyond this, it has been shown that techniques used in conventional pulsed NMR are effective for force-detected magnetic resonance[12].

Rugar and colleagues' imaging of individual virus particles[1] is a striking advance in MRFM capability that demanded exceptional detection sensitivity. In particular, the ferromagnetic probe must be brought within tens of nanometres of the cantilever-mounted virus. At these distances, the cantilever experiences many other forces from the nearby surfaces — including, for example, van der Waals forces that are typically thousands to millions of times larger than the nuclear magnetic forces to be measured, and dissipative, electrostatic cantilever-surface forces that produce noise that obscures the signal.

The authors' success is the fruit of a decade of work developing ultrasensitive force-detection techniques. They include excitation techniques[13], which manipulate the spins to produce a distinctive force signal that can be picked out from the background forces, and a nanofabricated antenna[14] that produces a strong radio-frequency magnetic excitation field sufficiently localized that it doesn't disturb the cantilever (the nuclear magnetic forces generate cantilever deflections only at the sub-angstrom level). Finally, the work shows that the noisy signals can be deconvolved into images.

The MRFM procedure will not meet all imaging needs. It is a demanding technique that must be performed in a vacuum and at low temperature. This is a limitation that is shared by electron microscopy of biological specimens, which is nonetheless a highly successful imaging tool. The detection sensitivity of MRFM is improving rapidly, and its history indicates that these capabilities, now at the cutting edge, will soon be routine for MRFM practitioners. But it will be some time before those capabilities can be exploited by the wider microscopy community.

That said, the demonstration[1] of the imaging of viral particles at a resolution down to 4 nanometres heralds the emergence of a new microscope for investigating native biological specimens that will compete with, and complement, electron microscopy and NMR spectroscopy. It uniquely combines non-destructive imaging with the capability of imaging individual copies of specimens such as proteins. The approach is also likely to find wide application beyond biology, in investigations of the chemical and elemental make-up of nanostructures in the physical and materials sciences. ■

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MATERIALS SCIENCE

Nanotubes unzipped

Mauricio Terrones

Nanotubes are single sheets of graphite rolled up into a cylinder. But no one thought that nanotubes could be cut along their axis and flattened out to make such sheets. Until now.

The discovery of buckyballs and carbon nanotubes in the 1980s and early 1990s[1–3] launched the field of carbon nanoscience, and spawned intensive research into the synthesis and applications of these structures. For a long time, it seemed as if the landscape of the carbon nanoworld contained only round objects — spheres and tubes. But in the twenty-first century, flat forms of carbon gained prominence with the discovery of graphene[4] (single layers of graphite) and graphene nanoribbons[5,6]. To realize the practical potential of these newcomers, methods for their mass production are sorely needed. In this issue, two possible solutions are reported — by Kosynkin *et al.*[7] (page 872) and Jiao *et al.*[8] (page 877) — in which nanotubes are 'unzipped' and rolled open to produce nanoribbons.

Graphene is a metal-like conductor, but nanoribbons can generally be either metallic or semiconducting depending on the patterns formed by their edges[5]. Furthermore, nanoribbons less than 10 nanometres wide are expected to be semiconductors, independent of their edge patterns. Narrow nanoribbons are thus excellent candidates for use in electronic devices, such as field-effect transistors, which form the basis of microchips in computers. A thorough exploration of the chemical and mechanical properties of nanoribbons will undoubtedly suggest other applications for these structures, perhaps as sensors, catalysts, scaffolds for tissue regeneration or components of composite materials.

Existing methods for making nanoribbons involve chemical synthesis, cutting graphene sheets into ribbons, or using ultrasound to break up graphene that has had its surface modified by the non-covalent binding of polymer molecules. But these methods produce only minute quantities of nanoribbons. A technique for producing bulk quantities has been reported[9], which involves depositing volatile carbon precursors onto a substrate where they react to form nanoribbons that are metal conductors. Nevertheless, alternatives to this chemical vapour deposition method still need to be developed that produce large-scale amounts of semiconducting nanoribbons.

Kosynkin *et al.*[7] report an extremely simple, efficient and potentially scalable technique for making graphene sheets and nanoribbons. The authors' starting materials are multiwalled nanotubes consisting of 15–20 concentric cylinders, with diameters of 40–80 nanometres. The method involves treating the nanotubes with concentrated sulphuric acid followed by potassium permanganate (an oxidizing agent) at room temperature, and finally heating them at 55–70 °C (Fig. 1a). This process chemically unzips the nanotubes, forming nanoribbons up to 4 micrometres long, with widths of 100–500 nanometres and thicknesses of 1–30 graphene layers. The products are highly soluble in water and in polar organic solvents, which is crucial if the nanoribbons are to be used in composite materials or for biological applications.

The chemical mechanism of the unzipping process probably involves the oxidation of carbon–carbon double bonds in the nanotubes. But it could also be that sulphuric acid molecules insert themselves between the concentric cylinders of the nanotubes — a similar 'intercalation' occurs when graphite is treated with sulphuric acid and potassium permanganate to peel off graphene sheets. The mechanism of Kosynkin and colleagues' technique thus needs clarification, and should stimulate further experiments.

The authors found that their nanoribbons were poor conductors, because the edges of the structures hold many oxygen-containing chemical groups that disrupt the flow of charge carriers. Kosynkin *et al.* therefore removed these groups by treating their products with a reducing agent, or by heating (annealing) the products in hydrogen. The wide nanoribbons thus produced were metallic conductors, similar to those grown by chemical vapour deposition. The authors also showed that their chemically reduced nanoribbons are in principle suitable for making field-effect transistors. Another benefit of the annealing process is that it could improve the reactivity and smoothness of the nanoribbons' edges.

Kosynkin and colleagues also used their method to unzip single-walled carbon nanotubes to yield narrow nanoribbons. Unfortunately, the resulting products become entangled; further experiments are therefore being done to find ways of untangling the ribbons so that they can be of practical use.

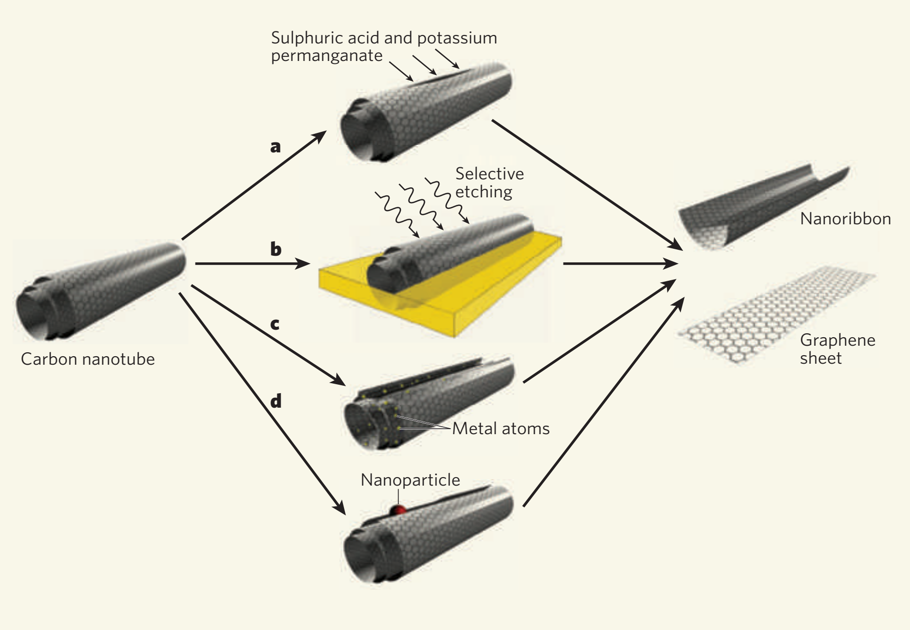

Figure 1 | Methods for unzipping carbon nanotubes. **a**, Kosynkin *et al.*[7] report that multiwalled carbon nanotubes can be unzipped by treating them with sulphuric acid and potassium permanganate (an oxidizing agent) to form nanoribbons or graphene sheets (single layers of graphite). **b**, Jiao *et al.*[8] describe a complementary method, in which nanotubes partially embedded in a polymer film are etched by argon plasma. **c**, Another approach[10] is to insert alkali-metal atoms between the concentric cylinders of a multiwalled carbon nanotube, which causes graphene sheets to peel off. **d**, A method still to be explored would use catalytic metal nanoparticles to cut along the length of a nanotube like a pair of scissors. (Graphic by A. R. Botello-Méndez.)

The authors' technique works well with nanotubes that have many structural defects on their surfaces (such as those made by chemical vapour deposition). But it is less effective with more crystalline nanotubes produced by other methods, such as laser ablation or arc discharge. Fortunately, Jiao *et al.*[8] describe an alternative approach for unzipping highly crystalline multiwalled carbon nanotubes. They partially embedded tubes in a polymer film, and then etched them with argon plasma (Fig. 1b). The film was then removed using solvent vapour, and the resulting nanoribbons were heated at 300 °C to remove any residual polymer.

The thicknesses of Jiao and colleagues' nanoribbons typically ranged from one to three graphene layers, depending on the plasma etching conditions. The ribbons were also narrower (10–20 nanometres wide) than those of Kosynkin *et al.*[7]. As expected, Jiao and colleagues' narrow ribbons[8] were semiconductors (unlike Kosynkin and colleagues' wider ribbons, which were metallic conductors).

The two reports[7,8] break new ground in the bulk fabrication of nanoribbons. An alternative method for unzipping multiwalled carbon nanotubes has also just been reported[10], in which alkali-metal atoms intercalate between the concentric cylinders of the nanotubes. The atoms are then washed out, which causes the tubes to open along their axes (Fig. 1c). Furthermore, catalytic particles of metals such as iron and nickel can cut through graphene sheets[11]. This effect could also be used to unzip multiwalled carbon nanotubes to produce nanoribbons[12], and should be explored further (Fig. 1d).

More research is, however, needed to find ways of efficiently unwrapping single- and double-walled nanotubes, in order to carefully control the widths and edge patterns of nanoribbons. Once bulk quantities of nanoribbons are available, their toxicological effects and possible biological applications can be studied. And, last but not least, the potentially unusual magnetic and catalytic properties of these materials can finally be explored. ■

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