

Here are news summaries of three articles on differing ways to create graphene nanoribbons. We will explore these in this tutorial.

NANOELECTRONICS

Nanoribbons on the edge

Arrays of graphene nanoribbons are fabricated on structured silicon carbide substrates using self-organized growth, without lithography and with well-controlled widths.

John A. Rogers

Graphene is attractive for electronics because of its exceptional properties and the relative ease with which it can be integrated into transistors and circuits. In the form of large-area planar sheets, it can be processed using straightforward adaptations of methods that are already in widespread use by the semiconductor industry. However, graphene in its native single-layer form has zero electronic bandgap, which prevents transistor devices made with it from being turned off completely. This makes graphene unusable in power-efficient digital circuits (though it can still be used in radio frequency electronics)¹. Narrow graphene ribbons have

better switching capabilities, but they are difficult to manufacture owing to the very small widths that are required. Writing in *Nature Nanotechnology*, Michael Sprinkle, Walter de Heer and colleagues at the Georgia Institute of Technology and the Institut Néel in Grenoble report a clever growth technique that yields organized, aligned arrays of narrow ribbons of graphene on structured substrates of silicon carbide (SiC), with the potential to enable switching properties suitable for broad classes of electronic systems².

Early theoretical work suggested that graphene ribbons would have bandgaps

large enough to allow efficient transistor switching³. However, practical circuits require very narrow widths (less than ~10 nm), with exceptional uniformity in the lateral dimension, and well-ordered edges. Recent reports suggest that such ribbons can be achieved by ultrasonic tearing and exfoliation of larger sheets⁴, chemical ‘unzipping’ of carbon nanotubes⁵ and covalent linking of assemblies of molecular building blocks⁶. In their present state of development, however, these strategies do not offer the levels of engineering control over dimensions or spatial layouts needed for realistic applications. Lithographic

etching of large sheets represents an attractive alternative because it is able to achieve uniform, organized arrays⁷. Unfortunately, the complexity of the tools necessary for sub-10-nm patterning and an inability to control edge roughness represent significant limitations to this technique.

Sprinkle, de Heer and colleagues report progress towards a very different approach, in which ribbons are grown directly into the desired layout and with a controlled width². Their methods build on techniques that they pioneered, wherein thermal decomposition of silicon-terminated SiC wafers yields uniform sheets of graphene⁸. This team now incorporates two new steps that exploit subtle aspects of the crystalline SiC substrates. First, they etch shallow trenches into the surface of a SiC wafer along a particular crystal axis. On thermal annealing, the vertical sidewall edges of these trenches reconstruct into smooth facets, angled at $\sim 25^\circ$ above the substrate surface. The key feature of this transformation is that the depth of the trench determines the width of its facets: for example, trench depths of 20 nm yield facet widths of 40 nm. This converts the difficult problem of sub-50-nm lithography into the comparatively easy task of controlling etch depth.

The next step exploits the fact that graphene grows at different rates on different crystal faces of SiC. By orientating their trenches in an appropriate direction, Sprinkle and colleagues create facets that form graphene more quickly than surrounding regions do, possibly owing to different bonding of the silicon atoms. As a result, for short growth times, graphene forms predominantly on the facets. Combined with a fine control over facet width, this process allows the formation, in a single growth step, of organized arrays of graphene ribbons with widths that begin to

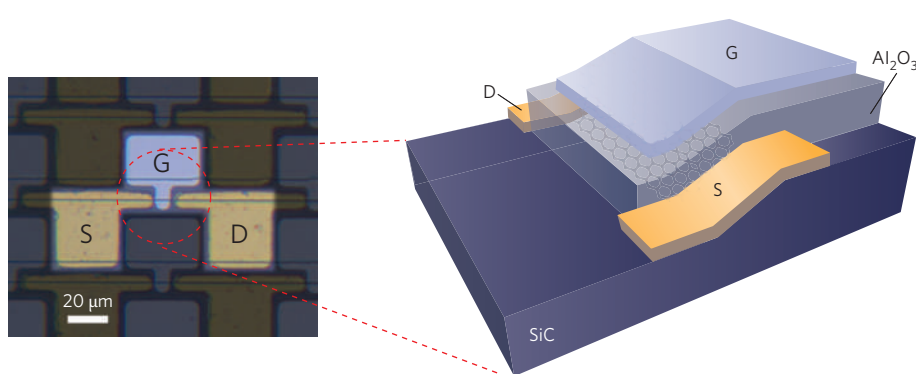


Figure 1 | An array of transistors that use graphene nanoribbons grown directly into place on the faceted step edges of a SiC wafer. Etching a shallow trench followed by annealing yields a smooth, angled facet on which graphene (shown here as a grey hexagonal lattice) grows more quickly than on adjacent surfaces (right). Adding a gate insulator (Al_2O_3) and source (S), drain (D) and gate (G) contacts completes the transistor.

approach those needed for applications in digital electronics, and with edges that are unaltered by etching processes.

The research team use their new technique² to build an array of 10,000 transistors, arranged in practical circuit geometries. Although the measured field-effect mobility is in the same range as other published ribbon devices, it is less than a tenth of the best substrate-supported graphene-sheet devices. Also, the smallest achieved widths are still much too wide for practical use, giving on/off switching ratios that are too low by several orders of magnitude. Sprinkle and colleagues suggest that these shortcomings can be addressed by optimizing their technique.

Future work in this direction looks very promising because the procedure seems to be scalable to much finer feature sizes, and optimized device designs are likely to lead to improvements. Meanwhile, other approaches to graphene ribbon fabrication are becoming more sophisticated, and techniques to produce aligned arrays of

single-walled carbon nanotubes continue to develop (also using tricks enabled by substrate crystallinity^{9–12}). The diversity of fabrication ideas together with the potential for important applications guarantees that the field of carbon nanomaterial electronics will remain an active one for years to come. □

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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 graphene⁴ (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 edges⁵. 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 reported⁹, 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) to form nanoribbons or graphene sheets (single layers of graphite). 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

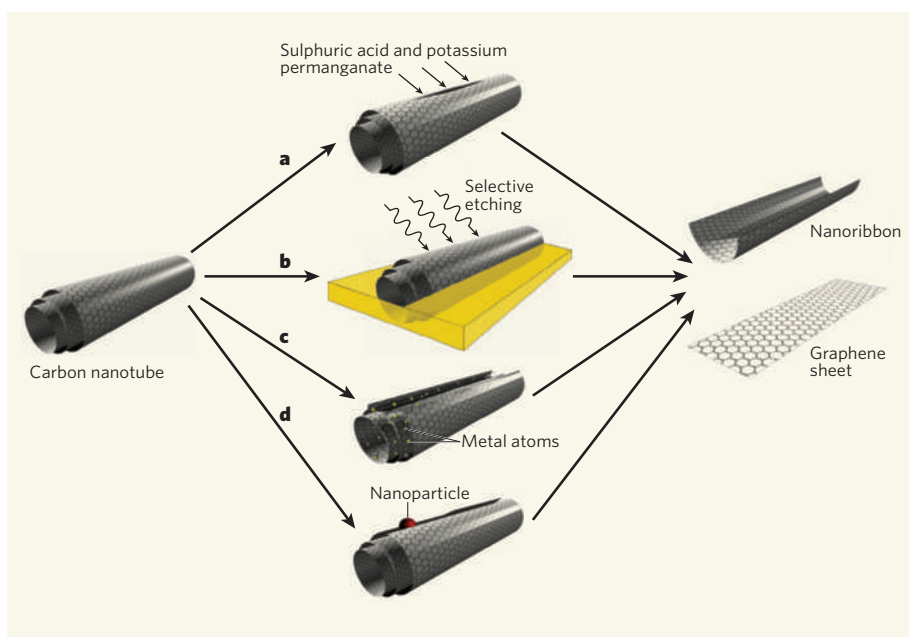


Figure 1 | Methods for unzipping carbon nanotubes. **a**, Kosynkin *et al.*⁷ report that multiwalled carbon nanotubes can be unzipped by treating them with sulphuric acid and potassium permanganate (an oxidizing agent) to form nanoribbons or graphene sheets (single layers of graphite). **b**, Jiao *et al.*⁸ describe a complementary method, in which nanotubes partially embedded in a polymer film are etched by argon plasma. **c**, Another approach¹⁰ 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.)

entangled; further experiments are therefore being done to find ways of untangling the ribbons so that they can be of practical use.

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 ribbons⁸ 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 reported¹⁰, 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 sheets¹¹. This effect could also be used to unzip multiwalled carbon nanotubes to produce nanoribbons¹², 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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GRAPHENE

Ribbons piece-by-piece

Directed assembly of molecular precursors allows the fabrication of graphene nanoribbons with atomic precision.

Michael S. Fuhrer

The exceptional electronic properties of graphene, a single-atom-thick plane of graphite, make it a promising candidate for applications from optical switches to high-frequency electronic amplifiers^{1,2}. However, graphene lacks a key attribute essential to digital electronics: graphene's bandgap, which enables the insulating 'off' state in a digital transistor, is zero. One route around this problem is to fashion graphene into strips known as graphene nanoribbons (GNRs). Narrow GNRs should have large bandgaps, and show tunable properties that depend on the direction of the ribbon relative to the graphene lattice. However, it has been difficult to achieve the atomic-scale control necessary to fabricate GNRs of precise width and direction. That has changed with a recent report in *Nature* by Jinming Cai and colleagues³ who demonstrated the assembly of atomically precise GNRs from molecular precursors on metallic substrates.

Graphene is uniquely neither metallic nor semiconducting (see Fig. 1a,b). Graphene's bandgap, the defining characteristic of a semiconductor, vanishes at two special momentum points, called Dirac points. Near the Dirac points, graphene's electronic spectrum is linear, characteristic of massless particles such as photons, and the electrons in the system are best described by the Dirac equation for massless relativistic particles, rather than the usual Schrödinger equation^{1,2}. As mentioned, although graphene is not strictly a semiconductor, it is not strictly a metal either: metals have a finite density of states at the Fermi energy, but graphene's density of states also vanishes at the Dirac points. However, when graphene is doped (and some tiny amount of doping through interaction with the environment is inescapable), the Fermi energy is moved away from the Dirac point, and graphene becomes metallic⁴. This inevitable metallic conduction prevents graphene's use as a digital switch — the current through graphene can never be turned off completely.

Physicists have long understood that this problem can be solved by cutting graphene into a GNR^{5,6}. GNRs are analogous to carbon nanotubes (CNTs), which may

be metallic or semiconducting, with semiconducting bandgaps varying inversely with the diameter of the nanotube, or in the case of GNRs, with the width of the ribbon⁶. There are, however, important differences. GNRs possess two edges, and certain edges — those with a 'zigzag' arrangement of carbon atoms — have an electronic state that has no counterpart in a CNT. Careful electronic structure calculations indicate that the zigzag edge state may be metallic, and even ferromagnetic⁷.

But the edge also brings new problems. It is a natural source of disorder, and just as the properties of GNRs are sensitive to their width and orientation, they are also sensitive to missing atoms or the presence of a chemical group bound to the edge. So far the fabrication of GNRs has relied largely on so-called top-down techniques such as nanolithography to cut a ribbon out of graphene by brute force. These GNRs, with inherent edge disorder, do indeed possess a bandgap, but the directional dependence of GNR properties appears to be confounded by disorder⁸. A number of bottom-up schemes have been

proposed for the fabrication of GNRs, such as unzipping CNT templates^{9,10} or sonicating graphene in the presence of certain polymers¹¹, but none of them have demonstrated atomic-scale level of control over the GNR structure.

Cai *et al.* have devised an ingenious scheme that can produce GNRs with atomic-scale precision³. They synthesized specifically designed molecular precursors consisting of polycyclic aromatic hydrocarbons with two well-placed binding sites, initially protected by halogens such as bromine (see Fig. 2). When deposited on a metal surface, here gold or silver, the molecules easily lose their halogens, activating the binding sites. The surface is then heated slightly; the molecules diffuse until they locate another precursor molecule and subsequently link up in a linear arrangement programmed by their active binding sites. The resulting polymer chains are heated again causing more carbon-carbon bonds to form by cyclodehydrogenation. This process produces a GNR with a predetermined structure that is well-defined.

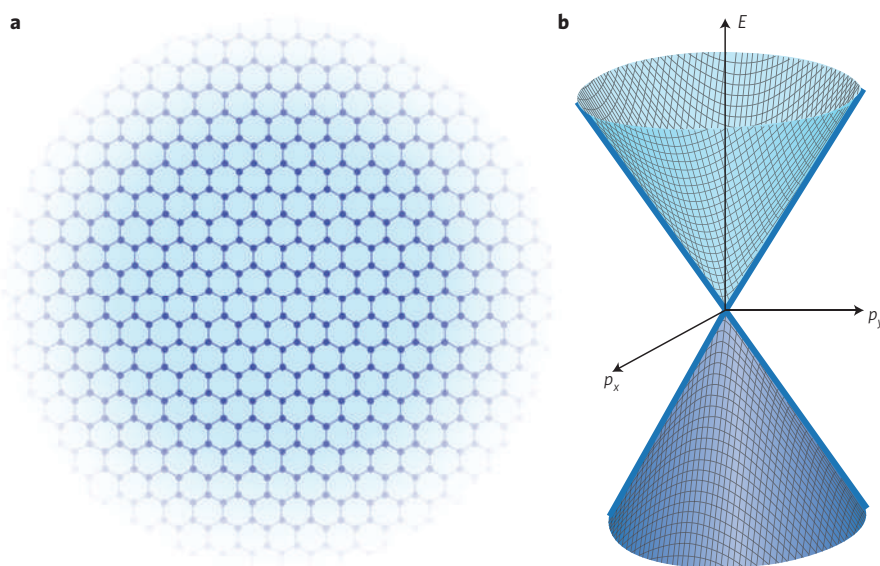


Figure 1 | Atomic and electronic structure of two-dimensional graphene. **a**, Graphene sheet. Carbon atoms are shown as blue dots. **b**, Energy (E) versus two-dimensional momentum (p_x, p_y) for electrons in graphene, showing a linear spectrum (blue lines). The conical conduction band (light blue shading) and valence band (dark blue shading) touch at the Dirac point. (A second Dirac point in graphene is not shown.)

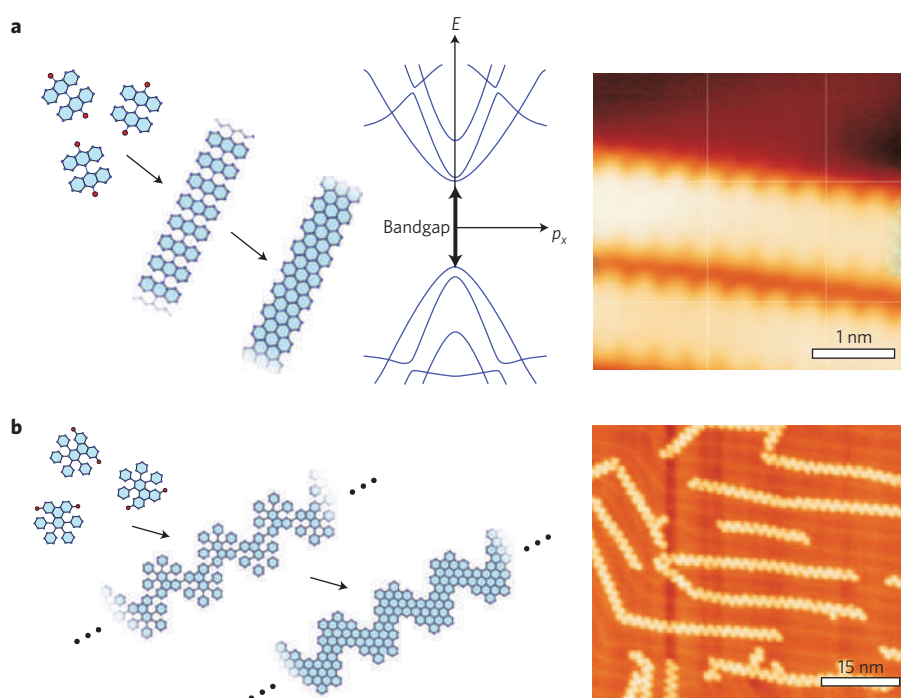


Figure 2 | Assembly of one-dimensional GNRs. **a**, Left: assembly of molecular precursors by Cai *et al.* to synthesize an $N = 7$ armchair GNR. Bromine atoms are shown in red; hydrogen atoms are not shown. Middle panel: $E(p_x)$ relationship for the $N = 7$ armchair GNR, showing several one-dimensional sub-bands separated by a bandgap. Right: high-resolution scanning tunnelling microscopy image of $N = 7$ GNR from ref. 3. **b**, Left: assembly scheme used by Cai *et al.* to synthesize a more complicated chevron GNR structure. Right: Scanning tunnelling microscopy images of chevron-type GNRs from ref. 3.

The team were able to demonstrate two GNR structures: an $N = 7$ 'armchair' ribbon just seven rows of carbon atoms wide (where N = the number of carbon atoms), and an unusual 'chevron' structure with a saw-tooth edge. Moreover, the possibility exists to adapt their scheme to a large variety of structures. Both

structures fabricated by Cai and co-workers are predicted to be semiconductors with significant bandgaps (> 1 eV; see Fig. 2a, middle panel). Using Raman spectroscopy they showed that the vibrational spectrum of the $N = 7$ armchair ribbon has the expected discrete phonon modes at the right energies. This is the first time that a discrete

spectroscopic signature of an individual species of GNR has been measured. These new modes are analogous to the radial breathing modes in CNTs, which are used to fingerprint individual CNT species.

The synthesis scheme adopted by Cai *et al.* has the significant drawback that it requires a metal surface, which precludes electronic measurements on the as-produced GNRs. However, the team have already demonstrated a rudimentary transfer of the GNRs to insulating silicon dioxide, and it is possible that their technique could be generalized to produce GNRs on insulating substrates or in solution. The controlled assembly from molecular precursors presented here thus opens a path to new research on graphene nanoribbons. □

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