

The third issue concerned the choice of organisms in the experiment. What are the criteria for choosing the organism and which outcomes should be measured after particle exposure? These choices depend largely on whether one is studying the mechanism of toxicity or performing a risk-assessment analysis.

In general, well-studied and well-characterized organisms such as *Daphnia* (a type of water flea found in freshwater lakes, acidic swamps and rivers), fish and algae are used as representatives of the major trophic levels. However, whether other ecologically relevant organisms should be examined is still largely questioned. Until we know the environmental concentrations of ENPs and where they eventually end up, it remains difficult to extrapolate data from laboratory

experiments to the larger ecosystem. Despite this, the information from these microcosm studies is important for feeding quantitative parameters into modelling studies such as those discussed by Bernd Nowack² from EMPA and Martin Scherlinger from ETH Zurich. The bottom line is that different organisms have different levels of sensitivity. Most of the current literature looks at exaggerated concentrations of exposure but as more is known about the real quantities of ENPs in the environment, a lower and wider range of concentrations will need to be examined.

On a final note, more sensitive imaging and detection tools are now in demand amongst environmental toxicologists. Taking advantage of knowledge and tools from surface chemistry, analytical chemistry,

toxicology and ecotoxicology in a concerted approach will build a solid framework for understanding the impact of ENPs on the environment and designing safer materials for the future.

References

1. Boxall, A. B. A., Tiede, K. & Chaudhry, Q. *Nanomedicine* **2**, 919–927 (2007).
2. Mueller, N. C. & Nowack, B. *Environ. Sci. Technol.* (in the press).
3. http://www.empa.ch/plugin/template/empa/*60627/---/1=1
4. Smith, C. J., Shaw, B. J. & Handy, R. D. *Aqua. Toxicol.* **82**, 94–109 (2007).
5. Zhu, X. S. et al. *J. Environ. Sci. Heal. A* **43**, 278–284 (2008).
6. Hund-Rinke, K. & Simon, M. *Environ. Sci. Pollut. Res.* **13**, 225–232 (2006).
7. Lovern, S. B., Strickler, J. R. & Klaper, R. *Environ. Sci. Technol.* **41**, 4465–4470 (2007).
8. Benn, T. M. & Westerhoff, P. *Environ. Sci. Technol.* doi:10.1021/es.7032718 (2008).
9. Brunner, T. J. et al. *Environ. Sci. Technol.* **40**, 4374–4381 (2006).
10. Moore, M. N. *Environ. Int.* **32**, 967–976 (2006).

ELECTRONIC MATERIALS

Making graphene for macroelectronics

Techniques for creating ultrathin films of reduced graphene oxide with large areas could prove useful in flexible electronics and other applications.

John A. Rogers

is in the Department of Materials Science and Engineering, University of Illinois, Urbana, Illinois 61801, USA.

e-mail: jrogers@uiuc.edu

Carbon is special. Not only is it the atomic building block for all known forms of life, it also provides exceptionally good charge transport characteristics when configured into single-walled carbon nanotubes (SWNTs)¹ or graphene². Unfortunately, as with diamond, carbon in these forms is special for another reason: it is extremely difficult to synthesize, manipulate and process in ways that allow it to be integrated into devices on large scales.

Graphene has spectacular electronic properties, and finding a reliable method to create films that contain just a few sheets of graphene by depositing them from solution could lead to applications such as radiofrequency (RF) devices that might be able to outperform those based on inorganic compound semiconductors, or large-area electronic systems that are less expensive than those based on amorphous silicon. Writing on page 270 of this issue, Goki Eda, Giovanni Fanchini and Manish Chhowalla of Rutgers University describe some important first steps that could lead to these capabilities³.

Research such as theirs is a natural step forward from the discovery of new materials and the characterization of their mechanical, electronic and other properties. For example, SWNTs can now be configured into arrays that are suitable for use as high-performance thin-film semiconductors in RF electronics^{4,5}. Such films, or analogous ones formed with flakes of graphene, could also be useful in systems where areal coverage is more important than RF performance.

Existing electronics of this type use amorphous silicon on glass substrates and are mostly found in displays. In the future, such 'macroelectronic' circuits⁶ might be printed onto plastic substrates to reduce costs and make the devices flexible. Films of SWNTs or graphene offer the possibility of giant improvements (many orders of magnitude) in electrical properties over the amorphous silicon used today, as well as alternatives based on organic polymer and small molecule thin film semiconductors. A number of promising techniques already exist for depositing ultrathin or even sub-monolayer assemblies of SWNTs from solution^{7–9}, and now Eda and co-workers have reported some of the first results for graphene, in the form of reduced graphene oxide^{10–12}.

The Rutgers team starts by using a combination of oxidation and sonication to exfoliate bulk pieces of highly ordered pyrolytic graphite into single-layer flakes of graphene oxide (GO) suspended in water. Passing this suspension through a filter with a pore size of ~25 nm creates the GO films in a process that has a useful self-limiting character. In this process, GO flakes pushed against the filter form flat platelets that block the pores, stopping further flow and thus preventing the build-up of thick multilayer deposits. The films produced by this process are remarkably flat, and their thickness can be controlled so that they contain between one and five layers (Fig. 1).

Eda and co-workers show that these films can be transferred from the filters to target substrates, such as glass or plastic, over large areas in a procedure that is almost 100% efficient. Although such GO films have modest electrical properties, they can be converted to a graphene-like material, which the authors refer to as reduced graphene oxide, by treatment with hydrazine and annealing at low temperatures (around 200 °C) that are compatible with many plastics. The resulting films contain several layers and are electrically conducting. Moreover, one- and two-layer samples exhibit charge-transport characteristics that can be modulated by an applied electric

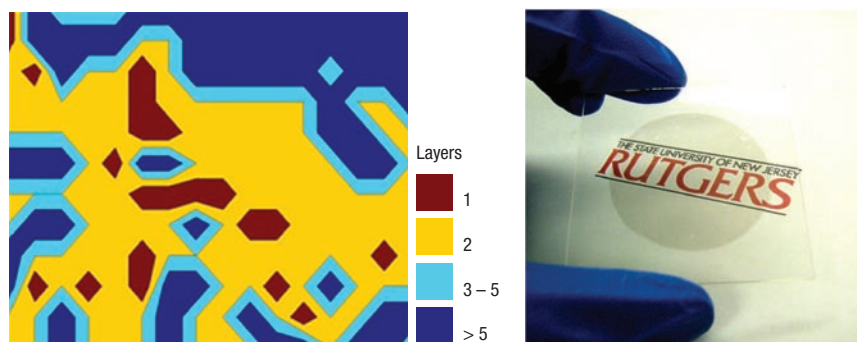


Figure 1 A colour-coded Raman map (left) showing the number of layers in an ultrathin film of reduced graphene oxide⁹. The image is 15 µm across. The film is transparent, as can be seen in the photograph on the right.

field, which is the basis for a field-effect transistor (FET).

A big advantage of these materials is that it is remarkably straightforward to integrate them into devices: they can be processed using standard photolithographic and related planar-fabrication techniques, much like standard thin-film electronic materials. Of the many devices that could be fabricated to demonstrate the usefulness of this approach, the Rutgers team makes FETs

and solar cells on plastic substrates: in the former application the reduced graphene oxide acts as a semiconductor, whereas in the latter it is used as a transparent conductor (Fig. 1). When processed with existing procedures the transistors show electrical properties that are similar to some of the best organic semiconductors, but with ambipolar characteristics (that is, involving both holes and electrons) and low on/off switching ratios (possibly because of their ambipolar character).

Although these demonstrations are noteworthy, there is plenty of room for improvement. In particular, although the films show interesting transport properties, they are much worse than those of individual sheets of pristine graphene. Spectroscopic data indicates that this might be caused by irreversible modifications in the graphene during the process of exfoliation. Electrical measurements also show that individual flakes of reduced graphene oxide have much better transport properties than the films, which again suggests that there is a lot of scope to optimize both the exfoliation stage and the process used to make the films. These and other topics provide excellent motivation for further study of this promising and unusual class of thin-film electronic material.

References

1. Chau, R. *et al.* *IEEE Trans. Nanotechnol.* **4**, 153–158 (2005).
2. Geim, A. K. & Novoselov, K. S. *Nature Mater.* **6**, 183–191 (2007).
3. Eda, G., Fanchini, G. & Chhowalla, M. *Nature Nanotech.* **3**, 270–274 (2008).
4. Kocabas, C. *et al.* *Proc. Natl Acad. Sci. USA* **105**, 1405–1409 (2008).
5. Kang, S. J. *et al.* *Nature Nanotech.* **2**, 230–236 (2007).
6. Reuss, R. *et al.* *Proc. IEEE* **93**, 1239–1256 (2005).
7. Meitl, M. A. *et al.* *Nano Lett.* **4**, 1643–1647 (2004).
8. Wu, Z. C. *et al.* *Science* **305**, 1273–1276 (2004).
9. Zhou, Y., Hu, L. & Grüner, G. *Appl. Phys. Lett.* **88**, 123109 (2006).
10. Gijie, S., Han, S., Wang, M., Wang, K. L. & Kaner, R. B. *Nano Lett.* **7**, 3394–3398 (2007).
11. Wang, X., Zhi, L. & Mullen, K. *Nano Lett.* **8**, 323–327 (2007).
12. Ruoff, R. *Nature Nanotech.* **3**, 10–11 (2008).

ELECTRON MICROSCOPY

New directions for chemical maps

A new generation of scanning transmission electron microscopes will allow researchers to study the composition and bonding of all the atoms in a solid material.

Leslie J. Allen

is in the School of Physics, University of Melbourne, Victoria 3010, Australia.

e-mail: lja@unimelb.edu.au

In 1959, during his famous and remarkably prescient talk “There’s Plenty of Room at the Bottom”¹, Richard Feynman highlighted the crucial role that better electron microscopes would play as the subject that we now call nanotechnology developed and the need to “see where the atoms are” increased. He also pointed out that the use of stationary and axially symmetric electric fields as lenses in electron microscopes always led to severe aberrations, as had been shown in a theorem published by Otto Scherzer in 1936. This limited the useful aperture of the lenses in

electron microscopes and seemingly ruled out the possibility of imaging samples with atomic resolution. “Why must the field be symmetrical?” Feynman asked. “I put this out as a challenge: is there no way to make the electron microscope more powerful?”

Scherzer had actually figured out the solution to the problem in 1947, when he showed that the aberrations could be corrected by adding electric fields that are not cylindrically symmetric, such as quadrupole and octupole fields, to the system. However, technical challenges meant that the first aberration-corrected electron microscopes did not appear until about a decade ago. Since then, seeing columns of atoms using ‘Z-contrast’ imaging in an aberration-corrected scanning transmission electron microscope (STEM) has become

routine for reasonably heavy atoms². In these experiments an Ångström-sized probe is scanned across the sample and electrons that have been thermally scattered through large angles are detected in an annular detector. This scattering scales roughly as the square of the atomic charge, Z , but unambiguously identifying the atoms responsible for the scattering is not straight forward. Imaging lighter atoms is also difficult.

By using electron energy-loss spectroscopy (EELS) in tandem with Z-contrast imaging, chemical mapping is possible and local bonding in the specimen can also be explored. For example, one might find that a significant number of electrons lose about 450 eV of energy when they pass through the sample. This corresponds to the minimum energy needed to ionize an