

MATERIALS SCIENCE

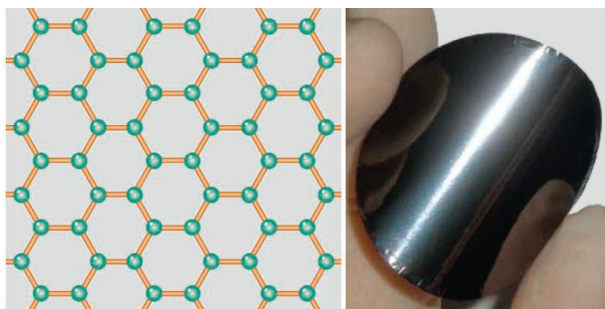
Graphene-Based Materials

Dan Li¹ and Richard B. Kaner²

Graphenes—mono-layers of carbon atoms arranged in a honeycomb network (see the figure, left panel)—are prevalent in many carbon-based materials. For example, graphite can be considered as stacks of graphene layers. Although the weak interactions that hold the graphene sheets together in graphite allow them to slide readily over each other, the numerous weak bonds make it difficult to separate the sheets. When physicists recently managed to isolate individual graphene sheets from mechanically cleaved graphite, they discovered unusual electronic properties arising from confinement of electrons in two dimensions (1). Researchers are now making rapid progress toward creating processable graphene.

Apart from its electronic properties, graphene displays several other unusual attributes. Graphene is a giant aromatic macromolecule that conducts both electricity and heat well in two dimensions. The theoretical specific surface area of individual graphene sheets (2) is more than double that of the finely divided activated carbon used in water purification. Their mechanical strength is comparable to that of carbon nanotubes—which can be considered graphene with a twist. Furthermore, recent studies (2–9) suggest that the production cost of graphene sheets in large quantities could be much lower than that of carbon nanotubes. Graphene sheets are thus attractive as atomically thin yet robust components for nanoelectronic and nanoelectromechanical devices (1, 10) and as nanoscale building blocks for new materials.

To create useful graphene-based materials, graphene sheets must be available in large quantities. Approaches for producing graphene



Simple structure, great potential. (Left) In graphene, carbon atoms (green dots) are bonded together through sp^2 hybridization (orange lines). (Right) Shiny and flexible graphene paper is formed by controlled restacking of graphene sheets (8).

sheets include mechanical cleavage of graphite (1), epitaxial growth (11), bottom-up organic synthesis (12), and chemical exfoliation of graphite (2–9). Given that graphite is relatively inexpensive and available in large quantities, the top-down method—splitting graphite into individual sheets mechanically or chemically—has received the most attention with respect to large-scale production of graphene.

High-yield direct exfoliation of graphite, however, has so far remained a challenge. Many researchers are now focusing on derivatives of graphite, especially graphite oxide (2–9). The latter is hydrophilic and has a larger interlayer distance than graphite; it can readily exfoliate into individual graphene oxide sheets in water and forms stable dispersions after ultrasonication. Subsequent deoxygenation via chemical reduction can restore electrically insulating graphene oxide to conductive graphene (3–5). Rapid thermal expansion can also cause graphite oxide to delaminate, but many of the resultant sheets are crumpled and wrinkled (2).

In all synthetic routes, keeping the graphene sheets individually separated is the most important and challenging part. Bulk graphene sheets—if left unprotected—will spontaneously agglomerate and even restack to form graphite. Chemical functionalization or the use of dispersants is generally needed to prevent agglomeration (4–7). The graphite oxide synthetic route is especially attractive for stabilizing individual sheets in solution. The oxygen-containing groups that exist in graphite oxide (carboxyl and hydroxyl) provide reactive sites for chemical modification using known carbon surface chemistry. Chemical attachment of

Advances in synthesizing graphene offer opportunities for making novel materials for nanoelectronics and many other applications.

appropriate organic groups onto graphite oxide surfaces not only leads to physical separation of the resultant graphene sheets, but also makes it possible to directly form stable graphene dispersions during the synthetic process (5, 7), something that has been difficult to accomplish with carbon nanotubes.

Chemical conversion from graphene oxide leaves residual oxygen-containing groups and makes the resulting graphene surfaces negatively charged when dispersed in water. By controlling the colloid chemistry, graphene sheets can form stable aqueous colloids via electrostatic repulsion without the need for foreign polymeric or surfactant dispersants (8). By alternately immersing a substrate into a negatively charged graphene colloid and a positively charged polycation solution, graphene sheets can be integrated with other functional materials at a molecular/nanometer scale to create multifunctional graphene-based composites (8).

Successful dispersion of graphene enables the use of low-cost solution processing techniques to fabricate various potentially useful graphene-based materials. For example, graphene films can be made by drop-casting, spraying, electrostatic adsorption, filtration, and dip- or spin-coating of graphene or precursor dispersions (6–9, 13–17). Chemically functionalized graphene can be readily mixed with other polymers in solution, producing a new class of electrically conductive nanocomposites at relatively low cost (5).

Dispersion of graphene in solution facilitates assembly of the atomically thin sheets into highly ordered macroscopic architectures that are otherwise difficult to make. Ruoff and co-workers have shown that, under a directional flow induced by vacuum filtration, graphene oxide sheets in solution can interlock in a near-parallel manner, yielding a paper-like material that is remarkably stiff and strong—much stronger than its nanotube counterpart (13). Analogously, we have shown that filtration of chemically reduced graphene colloids readily yields ultrastrong, electrically conductive, thermally stable graphene paper (see the figure, right panel) (8).

Graphene sheets can be further modified by engineering their shape, size, and chemical structure. For example, Dai and co-workers have used controlled ultrasonication of thermally expanded graphite to produce graphene

¹ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW 2522, Australia. E-mail: danli@uow.edu.au ²Department of Chemistry and Biochemistry, Department of Materials Science and Engineering, and California NanoSystems Institute, University of California, Los Angeles, CA 90095, USA. E-mail: kaner@chem.ucla.edu

nanoribbons less than 10 nm wide. Transistors based on these nanoribbons exhibit high on/off ratios (18).

Facile synthesis and solution-processing of chemically derived graphene facilitates not only the fabrication of graphene-based nano-electronic devices (14, 15, 18), but also the exploration of its use in many other areas—for example, as transparent electrodes for solar cells (16). Nonetheless, research toward the application of graphene-based materials has just begun. Many challenges and opportunities remain. For example, to enable applications in batteries and supercapacitors, in separation technologies, and as supports for catalysts, the hierarchical structure of graphene

assemblies must be controlled to make the surface of individual sheets maximally accessible. Additionally, graphene synthesis through chemical conversion from graphite introduces a considerable amount of defects, reducing electrical conductivity. New strategies are needed to produce more conducting yet processable graphene.

References

1. A. K. Geim, K. S. Novoselov, *Nat. Mater.* **6**, 183 (2007).
2. M. J. McAllister *et al.*, *Chem. Mater.* **19**, 4396 (2007).
3. S. Stankovich *et al.*, *Carbon* **45**, 1558 (2007).
4. S. Stankovich *et al.*, *J. Mater. Chem.* **16**, 155 (2006).
5. S. Stankovich *et al.*, *Nature* **442**, 282 (2006).
6. S. Niyogi *et al.*, *J. Am. Chem. Soc.* **128**, 7720 (2006).
7. Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.* **130**, 5856 (2008).

8. D. Li, M. B. Mueller, S. Gilje, R. B. Kaner, G. G. Wallace, *Nat. Nanotechnol.* **3**, 101 (2008).
9. G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **3**, 270 (2008).
10. J. S. Bunch *et al.*, *Science* **315**, 490 (2007).
11. C. Berger *et al.*, *Science* **312**, 1191 (2006); published online 12 April 2006 (10.1126/science.1125925).
12. J. S. Wu, W. Pisula, K. Mullen, *Chem. Rev.* **107**, 718 (2007).
13. D. A. Dikin *et al.*, *Nature* **448**, 457 (2007).
14. S. Gilje, S. Han, M. Wang, K. L. Wang, R. B. Kaner, *Nano Lett.* **7**, 3394 (2007).
15. C. Gomez-Navarro *et al.*, *Nano Lett.* **7**, 3499 (2007).
16. X. Wang, L. J. Zhi, K. Mullen, *Nano Lett.* **8**, 323 (2008).
17. H. A. Beceril *et al.*, *ACS Nano* **2**, 463 (2008).
18. X. Li, X. Wang, L. Zhang, S. Lee, H. Dai, *Science* **319**, 1229 (2008); published online 23 January 2008 (10.1126/science.1150878).

10.1126/science.1158180

PLANETARY SCIENCE

Is Mars Geodynamically Dead?

Matthias Grott

The temperature of a planet's interior is one of the key factors controlling the amount of geodynamic activity at its surface. Planetary scientists can estimate interior temperatures if they can assess the deformability of the planetary surface, which is greater when interior temperatures are higher (warm rocks will more easily deform than cold ones). Mass loading by glaciers and mountains deflects the surface, and this deformation can be used to estimate the elasticity of the surface layer when the load was emplaced. On Mars, the polar caps are a geologically recent load. On page 1182 of this issue, Phillips *et al.* (1) report that the amount of deflection caused by the polar caps leads to unexpected constraints on the current thermal state of the planet.

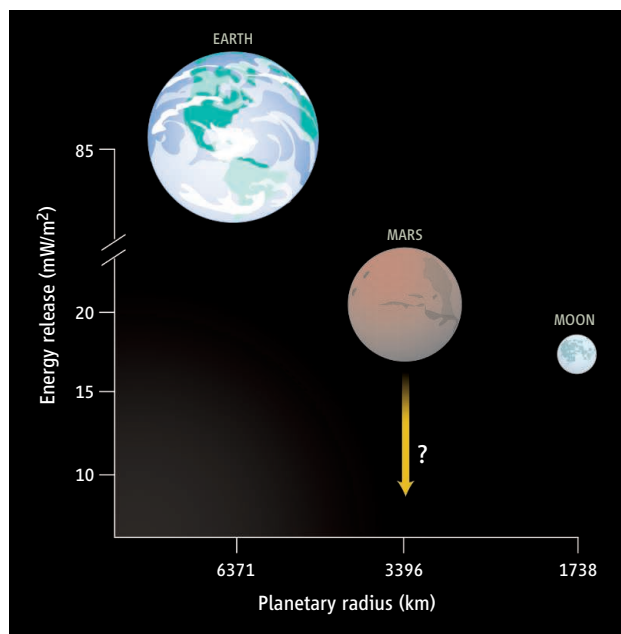
To investigate the ice-hidden planetary surface, the authors used radar-sounding data of the northern polar cap obtained by SHARAD, the shallow-radar instrument onboard the Mars Reconnaissance Orbiter, which has orbited Mars since 2006. The radar-wave travel times can be converted into distances by assuming that the polar cap consists of water ice and dust. The vertical deformation of the surface was extremely small—less than 100 m—and requires that the surface be very stiff to support these loads. The elastic lithosphere thickness, a measure of the surface's resistance to flexure, needs to be greater than 300 km at the poles today. This value is

almost twice as great as previously estimated from other measures of deformation and theoretical considerations (2, 3). Because the stiffness of the rocks is connected to temperature, Phillips *et al.*'s findings imply that the martian interior is extremely cool.

The observation that Mars' northern polar cap barely deforms its crust implies that its planetary interior is colder than expected.

This result is surprising. First, the temperatures in the interior of terrestrial planets should be proportional to their radius if they started with the same amount and distribution of radioactive, heat-producing elements and then cooled through surface losses (see the figure). In this case, Mars would be expected to plot between Earth and the Moon. However, the new estimates imply that the martian heat flow, a measure for the temperatures in the planetary interior, is below even that of the Moon, even though Mars is about twice the diameter. Either there is a large degree of compositional heterogeneity among the terrestrial planets, or heat transport is very inefficient inside Mars.

Second, theoretical considerations of the planet's thermal evolution have unanimously concluded that Mars should have retained more internal heat than is consistent with the observed stiff lithosphere (4, 5). This discrepancy could be resolved if the amount of radioactive elements in Mars (potassium, thorium, and uranium) were smaller



A colder Mars. The energy release at a planetary surface is a measure for the temperatures in the planetary interior. Large planets, which have a lower surface-to-volume ratio, should be warmer than small ones if they contain equal concentrations of heat-producing elements. The average heat flow of Earth is 87 mW/m², and the lunar heat flow determined by the Apollo experiments is 18 mW/m² (9). Mars was expected to release 20 mW/m², but the value inferred from Phillips *et al.*'s findings would be much lower.