GRAPHENE

Show of adhesive strength

The adhesion energies for atomically thin graphene membranes on silicon dioxide substrates have now been measured.

Rui Huang

Graphite is composed of layers of carbon atoms that are held together by strong covalent bonds within each graphene layer and relatively weak van der Waals forces between the layers. The mechanical properties of graphite — it is anisotropic and prone to interlayer cleavage — are closely related to the characteristics of these forces. Furthermore, according to recent work at the University of Colorado in Boulder, van der Waals forces could also be responsible for the ultrastrong adhesion between atomically thin graphene membranes and a silicon oxide substrate[1]. Writing in *Nature Nanotechnology*, Scott Bunch and co-workers report that the adhesion energy for monolayer graphene on silicon oxide is higher than that for membranes containing between two and five layers of graphene. Although the physical origin for this difference is not fully understood, the team suggests that the extreme flexibility of the monolayer graphene may be responsible.

Measurement of the interfacial adhesion energy is essential for practical applications of graphene in integrated electronic and mechanical devices. Previously, researchers at the University of Maryland estimated the graphene–SiO_2 adhesion energy to be 0.096 J m^{-2}, based on the interlayer van der Waals interaction in graphite[2], and a team at Northeastern University reported an average value of 0.151 J m^{-2} for multilayer graphene sheets (roughly five layers) on a silicon wafer, which was obtained with a nanoparticle intercalation method[3]. The values reported by Bunch and colleagues are higher — 0.31 J m^{-2} for membranes containing two to five layers of graphene — because they are based on independent measurements of the Young's modulus of the membranes[4], whereas the measurements at Northeastern University used smaller values for Young's modulus. This ability to independently measure both the Young's modulus and the adhesion energy is an important advantage of the method developed by Bunch and co-workers, which is based on the pressurized blister test (also known as the bulge test).

Pressurized blister tests are routinely used to measure the mechanical properties of thin films and also the interfacial adhesion energies between films and substrates[5]. In a typical experiment, a free-standing window of a thin film with clamped edges is pressurized from one side, and the deflection of the film is measured (often optically) from the other side. The mechanical properties of the thin film — including Young's modulus, Poisson's ratio and residual stress — are then extracted from the measurements of the deflections, based on a nonlinear mechanics model[6–9]. When the applied pressure reaches a critical value, the film starts to debond from the substrate, starting at the edges and advancing in an unstable manner if the pressure level is maintained. Measuring the critical pressure for this debonding allows the adhesion energy to be determined[10,11].

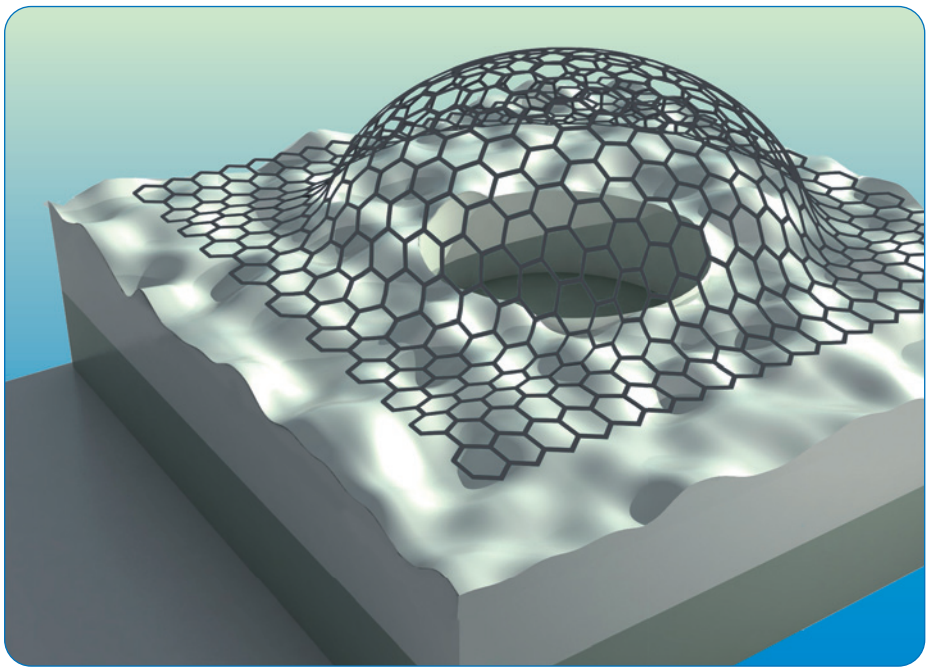

Figure 1 | Measuring adhesion at the nanoscale. In a blister test with a constant number of molecules, a graphene membrane seals gas molecules inside microcavities that have been etched in a SiO_2 substrate. The sample is then placed in a pressure chamber, and nitrogen molecules diffuse through the SiO_2 (but not through the graphene), increasing the pressure inside the microcavity until it is the same as the pressure in the chamber. When the sample is removed from the chamber, the excess of pressure inside the microcavity causes the membrane to bulge, as this artist's impression shows. Measurement of the bulge profile allows mechanical and adhesion properties of the graphene to be determined.

Over the past 30 years, different configurations of the bulge test have been developed for thin films of different materials, with thicknesses ranging from millimetres to tens of nanometres. The work by Bunch and co-workers demonstrates the application of this technique for atomically thin membranes[1].

Taking advantage of the fact that nitrogen molecules can diffuse slowly through SiO_2, but cannot pass through a graphene membrane, the researchers devised a novel blister test in which the number of molecules confined in a graphene-sealed microcavity in the substrate remained constant (Fig. 1). In contrast to the conventional constant-pressure test, the debonding at the interface grows stably

in the blister test with a constant number of molecules, which allows the radius of the blister (which is increasing) and the internal pressure (which is decreasing) to be measured continuously.

As such, these measurements provide a comprehensive data set for the mechanical and adhesion properties of graphene membranes. In particular, the adhesion energy can be determined directly from the measurable quantities, without any need to assume the value of Young's modulus (although it is necessary to assume a Poisson's ratio). Moreover, the Young's modulus of the membrane can be determined separately using the measured deflection. Furthermore, by using a different geometry for the cavity, it should also be possible to determine Poisson's ratio for the graphene membrane[9]. The robustness of this technique opens up ample opportunities for fundamental studies on the nanomechanics of graphene interacting with other materials.

The measured adhesion energy for monolayer graphene is surprisingly high (~0.45 J m^{-2}). As pointed out by Bunch and co-workers, this may be attributed to the flexibility of monolayer graphene. It has been predicted that the bending modulus of monolayer graphene is two orders of magnitude lower than that of bilayer graphene[12], which could lead to monolayer and multilayer graphene membranes having different morphologies on the SiO_2 substrate and, hence, different adhesion energies.

Theoretical models have predicted that graphene membranes supported on a surface can undergo a transition between a highly conformal morphology and a non-conformal morphology, depending on the surface roughness and the bending modulus of the membrane[13,14]. The adhesion energy, as measured by the blister test, tells us about the microscopic interactions between graphene and the substrate. As monolayer graphene conforms much more closely to the substrate surface than membranes containing two to five layers, the measured adhesion energy is expected to be higher. A more quantitative analysis may be required to confirm this explanation, and to provide a better understanding of the effects of surface forces, roughness and the intrinsic mechanical properties of graphene on interfacial adhesion.

Ultimately, for graphene to be integrated into devices, its adhesive interactions with other materials (such as metals and polymers) will have to be studied in detail. Both experimental techniques and theoretical models are needed to uncover the physical mechanisms that may result in different levels of adhesive interactions[15]. The impacts of the adhesive interactions on the fabrication, performance and reliability of graphene devices will also have to be examined, as has happened with thin-film devices. ❐

Rui Huang is in the Department of Aerospace Engineering and Engineering Mechanics, University of Texas at Austin, Austin, Texas 78712, USA.
e-mail: ruihuang@mail.utexas.edu

References

1. Koenig, S. P. *et al. Nature Nanotech.* **6,** 543–546 (2011).
2. Ishigami, M. *et al. Nano Lett.* **7,** 1643–1648 (2007).
3. Zong, Z. *et al. J. Appl. Phys.* **107,** 026104 (2010).
4. Lee, C. *et al. Science* **321,** 385–388 (2008).
5. Freund, L. B. & Suresh, S. *Thin Film Materials* (Cambridge Univ. Press, 2003).
6. Vlassak, J. J. & Nix, W. D. *J. Mater. Res.* **7,** 3243–3249 (1992).
7. Williams, J. G. *Int. J. Fracture* **87,** 265–288 (1997).
8. Wan, K. T. *et al. Thin Solid Films* **425,** 150–162 (2003).
9. Xu, D. & Liechti, K. M. *Exp. Mech.* **50,** 217–225 (2010).
10. Gent, A. N. & Lewandowski, L. H. *J. Appl. Polymer Sci.* **33,** 1567–1577 (1987).
11. Allen, M. G. & Senturia, S. D. *J. Adhesion* **25,** 303–315 (1988).
12. Koskinen, P. & Kit, O. O. *Phys. Rev. B* **82,** 235420 (2010).
13. Li, T. & Zhang, Z. *J. Phys. D* **43,** 075303 (2010).
14. Aitken, Z. H. & Huang, R. *J. Appl. Phys.* **107,** 123531 (2010).
15. Sabio, J. *et al. Phys. Rev. B* **77,** 195409 (2008).

BIOMATERIALS

A natural source of nanowires

Fibrous proteins from bacteria can be used to make biofilms with electrical conductivities that are comparable to those measured in conducting polymers.

Fang Qian and Yat Li

The discovery of conducting polymers[1] in the mid-1970s led to the development of a variety of organic electronic and optoelectronic devices, including light-emitting diodes, transistors and solar cells. If we consider conducting polymers to be 'synthetic organic metals', we can ask if the discovery of 'natural organic metals' could have similar consequences. Biological proteins are obvious candidates for 'natural organic metals'. If we could understand long-range charge transport in these materials, then we might be able to introduce metal or semiconducting biomaterials[2] to electronic devices and open up new opportunities in bioelectronics, bioenergy and medical applications.

Pilin nanofilaments (pili) — also known as microbial nanowires — are a class of fibrous proteins found in sediment bacteria, and researchers have been investigating charge transport in these quasi-one-dimensional biomaterials for a number of years. The first step was taken by Derek Lovely, Mark Tuominen and co-workers at the University of Massachusetts in 2005, when they used an atomic force microscope with a conducting probe to measure the conductance maps of pilin nanofilaments taken from *Geobacter sulfurreducens* on a graphite electrode[3]. The researchers found that the pili were conducting in the radial direction, which indicated that they might be involved in extracellular electron transfer.

A year later, Yuri Gorby, of the Pacific Northwest National Laboratory, and co-workers examined the pilin nanofilaments produced by the MR-1 strain of *Shewanella oneidensis* with a combination of scanning tunnelling microscopy and spectroscopy[4]. The scanning tunnelling microscopy images (based on tunnelling current) showed that these pili were also highly conducting in the radial direction, which suggested that radial conductivity might be a generic feature of the pili from certain types of bacteria. However, the measurement techniques available at the time were not able to quantitatively investigate the conductivity of pili along their length. Now, writing in *Nature Nanotechnology*, Tuominen, Lovely and co-workers report that films made of pili taken from *G. sulfurreducens* exhibit metallic-like conductivities and are able to conduct an electric current over centimetre distances[5].

The UMass team designed a unique microbial fuel-cell reactor with a split