

showing instead non-directional rotation at a much higher speed of rotation.

The directional rotation is provoked by the chirality of the STM tip (Fig. 1c)⁵. In particular, the differences observed for enantiomers on electrical excitation with the same STM tip are attributed to non-identical tip–molecule interactions. The intramolecular vibrational energy redistribution from the high-energy C–H stretch modes to the lower-energy rotational states is a complex process, and depends both on the symmetry of the tip and molecule. Efficient coupling leads to many rotational events of larger hop angles.

Inefficient coupling however results in slower, but directional, hopping. By using different STM tips, both enantiomers are also found to sometimes exhibit no directionality, which would be expected for the interaction of enantiomers with an achiral probe.

The molecular motor created by Sykes and colleagues is far from a practical machine — its maximum directionality is 5% at a rotation hop rate of ~50 Hz. However, the creation of functional molecular motors is stimulating to both scientists and the wider public. Moreover, the work illustrates how these motors can be addressed individually, and

highlights the importance of the symmetry of nanoscale contacts. □

Steven De Feyter is at the Department of Chemistry, Katholieke Universiteit of Leuven (KU Leuven), B-3001 Heverlee, Belgium.
e-mail: Steven.DeFeyter@chem.kuleuven.be

References

1. Koumura, N. *et al.* *Nature* **401**, 152–155 (1999).
2. Hernandez, J. V. *et al.* *Science* **306**, 1532–1537 (2004).
3. Stipe, B. C. *et al.* *Science* **279**, 1907–1909 (1998).
4. Tierney, H. L. *et al.* *Nature Nanotech.* **6**, 625–629 (2011).
5. Tierney, H. L., Murphy, C. J. & Sykes, E. C. H. *Phys. Rev. Lett.* **106**, 010801 (2011).

GRAPHENE OPTOELECTRONICS

Plasmons get tuned up

Plasmons in graphene nanoribbons have widely tunable frequencies and interact strongly with light.

Farhan Rana

Plasmons are collective oscillations of electrons^{1,2} that can be localized at the surface of a conductor or found in the bulk of a material. Moreover, the wavelength of the electromagnetic field associated with a plasmon can be orders of magnitude shorter than the wavelength of light with the same frequency. This means that plasmons can be used to control electromagnetic radiation at the nanoscale^{1,2}. They are also key to the response of electrons in solids to external fields, and to the functioning of metamaterials in applications such as negative refraction, superlensing, and cloaking^{3,4}.

Traditionally, metals such as gold and silver have been used to support surface plasmons and create subwavelength devices that work in the visible and near-infrared frequency range^{3,4}. However, there are two fundamental problems with using metals for plasmonics. First, since the electron charge density in metals cannot be varied, the plasmon frequency cannot be tuned. Second, the plasmon scattering time in metals is usually very short (typically tens of femtoseconds), so the plasmons quickly decay. The solution of these two problems represents a long-sought-after goal for the plasmonic research community.

Writing in *Nature Nanotechnology*, Feng Wang and colleagues⁵ at the University of California, Berkeley and the Lawrence Berkeley National Laboratory now report a structure based on graphene — a two-dimensional membrane of carbon atoms arranged in a honeycomb lattice⁶ — that supports plasmons with widely tunable frequencies and reduced loss (Fig. 1).

Electrons in graphene have demonstrated high room-temperature mobility⁷, and their density can be controlled by doping or by gating, from very low ($\sim 10^{10} \text{ cm}^{-2}$) to very high ($\sim 10^{14} \text{ cm}^{-2}$) values. As a result, plasmon frequencies can be tuned from $\sim 1 \times 10^{12} \text{ Hz}$ (1 THz) to $\sim 2 \times 10^{14} \text{ Hz}$, the latter being in the near-infrared. Furthermore, plasmons in graphene couple more strongly to interband electronic transitions than do free photons, and they have a large oscillator strength, which is a measure of their robustness against decay into other excitations. These properties have motivated recent investigations of graphene for use in plasmonic and metamaterial devices^{8–11}.

The large oscillator strength of graphene plasmons should lead to pronounced peaks in absorption at certain frequencies, if the coupling between the plasmons and the incident electromagnetic radiation can be made strong enough. However, this coupling is usually weak owing to the large difference in the wavelengths of the plasmons and the radiation for the same frequency. Wang and his colleagues overcame this obstacle by patterning their graphene into an array of ribbons, each just a few micrometres wide. This patterning accomplished two things. First, plasmons confined to a structure that is comparable in size to the plasmon wavelength can couple well to light incident normally. The total force exerted by the light field on a free plasmon mode will, in general, be zero, because the force on the positive and negative lobes of the plasmon mode will cancel. But if the plasmon mode is confined to a ribbon with a width that is an odd multiple of a half-

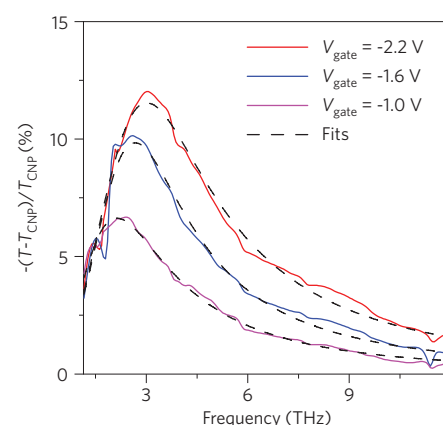


Figure 1 | Transmission spectra of a graphene nanoribbon array show plasmon resonances that are tunable with the carrier density as the gate voltage (V_{gate}) is varied. The transmission spectra obtained in the absence of carrier density in graphene (at the charge neutrality point, T_{CNP}) is subtracted and also used to normalize the data shown. Figure adapted from ref. 5.

wavelength, then this cancellation does not occur and the mode can be excited.

Second, unlike surface plasmons in metals, plasmons in bulk graphene have a frequency that depends strongly on wavelength. Plasmon confinement thus allows the selection of only those resonant plasmon modes that have a wavelength compatible with the dimensions of the confining structure.

The Berkeley team used light to excite plasmon modes in the ribbons, and

measured resonances in the absorption spectra that corresponded to the frequency of the confined plasmon modes. The polarization dependence of the absorption and the change in the plasmon frequency with the ribbon width confirmed that the measured resonances did indeed result from energy absorption by plasmons. Although the resonances were broad, indicating a large plasmon scattering rate, much smaller scattering rates should be possible, as demonstrated by electron transport measurements in graphene⁶.

The most interesting aspect of this experiment is the ability to tune the plasmon frequencies from ~1.5 THz to ~6 THz by changing the electron density in graphene using an ion-gel top gate. Wang

and colleagues were also able to verify that the electron density dependence of the plasmon frequency is exactly as predicted by theory¹².

The graphene-ribbon array made by Wang and colleagues is, in some sense, a simple metamaterial, because its functionality derives from patterning at a spatial scale below the wavelength of light. These results open the door to a variety of devices tunable all the way from the near- to far-infrared, including metamaterial devices (such as modulators, filters, polarizers, retarders, cloaking devices and superlenses), plasmonic devices (including biological and chemical sensors) and optoelectronic devices (oscillators, amplifiers, photodetectors, interconnects and switches). □

Farhan Rana is in the School of Electrical and Computer Engineering, Cornell University, 223 Phillips Hall, Ithaca, New York 14853, USA.
e-mail: farhan.rana@cornell.edu.

References

1. Barnes, W. L., Dereux, A. & Ebbesen, T. W. *Nature* **424**, 824–830 (2003).
2. Maier, S. A. *Plasmonics: Fundamentals and Applications* (Springer, 2007).
3. Veselago, V. G. *Sov. Phys. Uspekhi* **10**, 509–514 (1968).
4. Shalaev, V. M. *Nature Photon.* **1**, 41–48 (2007).
5. Ju, L. *et al. Nature Nanotech.* **6**, 630–634 (2011).
6. Geim, A. K. & Novoselov, K. S. *Nature Mater.* **6**, 183–191 (2007).
7. Orlita, M. *et al. Phys. Rev. Lett.* **101**, 267601 (2008).
8. Vakil, A. & Engheta, N. *Science* **332**, 1291–1294 (2011).
9. Jablan, M., Buljan, H. & Soljacic, M. *Phys. Rev. B* **80**, 245435 (2009).
10. Rana, F. *IEEE Trans. Nanotechnol.* **7**, 91–99 (2008).
11. Rana, F. *et al. Phys. Rev. B* **84**, 045437 (2011).
12. Hwang, E. H. & Das Sarma, S. *Phys. Rev. B* **75**, 205418 (2007).

ELECTRON SPECTROSCOPY

A new window opens

Graphene membranes allow measurements of surface chemistry under realistic conditions.

Dmitry Zemlyanov

Understanding the chemical reactions involved in fields such as catalysis, biochemistry and materials science often requires the ability to observe reactions on surfaces under realistic conditions. For decades, surface science has relied on electron spectroscopy for this task. These measurements have a high surface sensitivity, because the photoelectron elastic mean free path is too short for the sample bulk to contribute a significant signal. This short mean free path, however, also impedes the movement of photoelectrons through liquids and gases, making electron microscopy under realistic conditions difficult.

In a standard electron spectroscopy measurement, the sample is kept under ultrahigh vacuum and illuminated with an X-ray beam, causing it to eject photoelectrons; the energy of these photoelectrons is then measured. A recent innovation is ambient-pressure X-ray photoelectron spectroscopy (XPS), which can be used to study liquid and solid surfaces at up to a few millibars of pressure. A differentially pumped electron lens system keeps the electron beam and optics in vacuum, while the sample is at *operando* (or realistic) conditions inside a specially designed environmental cell. However, the instrumentation required is state-of-the-art, and is available at only a few laboratories around the world¹. This is partly due to constraints imposed by the environmental cell window, which, to support a pressure

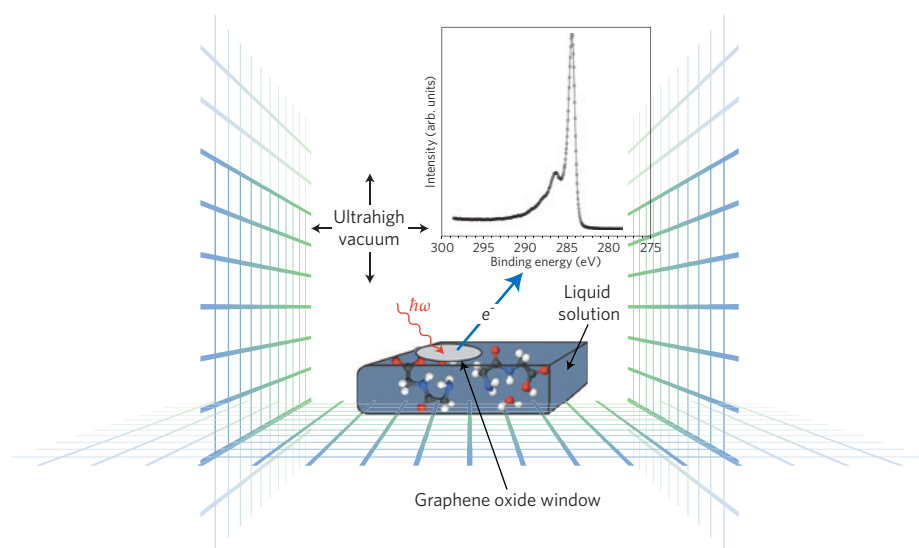


Figure 1 | Schematic diagram of an X-ray photoelectron spectroscopy (XPS) experiment with an *insitu* environmental cell. An X-ray source illuminates a sample through a thin membrane, causing it to emit photoelectrons, which exit the membrane and are analysed. A typical photoelectron energy spectrum is shown (in this case, for a carbon nanotube). The graphene oxide membrane used by Kolmakov and colleagues² allows X-rays and photoelectrons to pass through while withstanding a large pressure difference between the sample (which is at close to atmospheric pressure) and the electron and beam optics (which are under ultrahigh vacuum).

difference, must be relatively thick. This in turn requires high-intensity X-ray fluxes, typically available only at synchrotrons. At the same time, full atmospheric pressure can not be reached, because the photoelectrons have

to travel through a gas to reach the entrance of the electron optic, and the elastic mean free path of the electron at 1 atm is only ~1 μm.

Now, writing in *Nature Nanotechnology*, Andrei Kolmakov from Southern Illinois