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ELECTRON SPECTROSCOPY A new window opens

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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 graphene[6].

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 theory[12].

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). ❐

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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 world[1]. This is partly due to constraints imposed by the environmental cell window, which, to support a pressure 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.

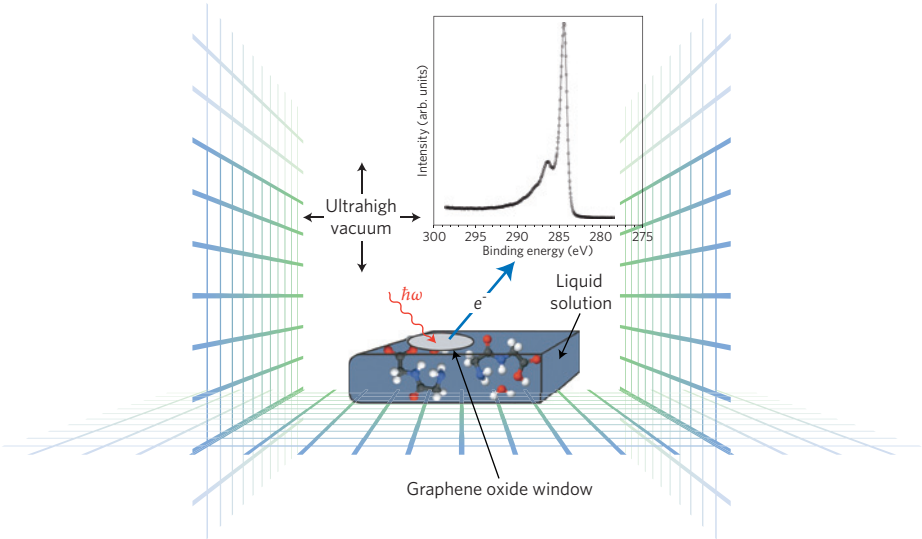

Figure 1 | Schematic diagram of an X-ray photoelectron spectroscopy (XPS) experiment with an *in situ* environmental cell. An X-ray source illuminates a sample through a thin membrane, causing it to emit photoelectrons, which exit the membrane and are analysed. A typical photoelectron energy spectrum is shown (in this case, for a carbon nanotube). The graphene oxide membrane used by Kolmakov and colleagues[2] 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).

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

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University, and colleagues from Northwestern University, Sincrotrone Trieste and TU München report a simpler approach to atmospheric-pressure XPS[2]. The key to their advance is an environmental cell window that is both thin enough to allow X-rays to enter and photoelectrons to exit, and strong enough to sustain a full atmosphere of pressure difference (Fig. 1). The window material they settled on is a nanometre-thick membrane of graphene oxide. This thickness is comparable to the elastic mean free path of photoelectrons with kinetic energy of a few hundred electron volts. And, remarkably, this thickness is sufficient to allow the membrane to be impermeable to gas and sustain a few bars of pressure difference[3,4]. These characteristics, along with the inherent chemical inertness of graphene, allow the X-ray optics and electron detection system to be kept under ultrahigh vacuum, while the sample inside the cell is kept under full atmospheric pressure. Notably, previous environmental cells used much thicker windows (0.1 μm or more), which are transparent to X-rays but not to photoelectrons with kinetic energies of less than a few thousand electron volts.

Graphene membrane environmental cells should prove particularly useful for *operando* monitoring of interfacial processes taking place in liquid, with relevance to biomedical systems, fuel cells, batteries, catalytic systems and aerosols. Existing techniques for the study of chemistry in liquid rely on microjets and droplets, which are irradiated and made to pass by a set of differentially pumped electron optics[5,6]. However, such methods require the liquid to transition from a higher-pressure to a lower-pressure area, which causes them to cool uncontrollably (typically slowing down the reaction) and to change their composition owing to altered evaporation rates. In contrast, both temperature and liquid composition can be easily controlled in an environmental cell.

Graphene-based environmental cells should also be versatile. Classical ambient-pressure XPS relies on stationary and complicated instrumentation associated with synchrotron radiation sources[1]. On the other hand, as an environmental cell allows the analytical part of the XPS setup to be under ultrahigh vacuum, it can potentially be used with any commercial electron spectrometer, with no need for expensive differentially pumped electron optics and high-flux synchrotron radiation. The sample can be kept in the cell after it has been characterized with XPS, and studied with routine electron or optical microscopes and Raman spectroscopy.

Once again, then, graphene has given established techniques a new twist. The durability of graphene oxide windows for environmental cells will need to be carefully considered, as will their reliable manufacture. If successful, they will open a new chapter in *in situ* electron spectroscopy by increasing the working pressure of ambient XPS from a few millibars to full atmospheric pressure, and by allowing controlled liquid-phase measurements. ❐

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ENVIRONMENTAL, HEALTH AND SAFETY ISSUES

Nanoparticles in the real world

Risk assessments of products containing nanomaterials require both the materials in the products and the materials emitted during their use to be analysed so that realistic exposures can be determined.

Maxine J. McCall

Over 1,300 commercially available products (ranging from textiles and cosmetics to sports goods and food containers) are identified as containing nanomaterials based on manufacturers' reports[1]. However, there are probably even more than this on markets worldwide, because labelling products as containing nanomaterials is not required. Although large international programmes (such as those coordinated by the Organisation for Economic Co-operation and Development[2]) have been organized to understand how the physical and chemical properties of nanomaterials are associated with potential toxicities, the data provided by these programmes on pristine nanomaterials may not be directly relevant to product use, because the properties of nanomaterials may change when incorporated into products[3,4]. Therefore, it is necessary to study the nature of nanoparticles in consumer products[5] to determine realistic exposures (Fig. 1).

Three recent publications add to our knowledge of real-life exposure scenarios by characterizing nanomaterials found in a range of products bought directly from stores. One report characterized nanoparticles found in sunscreens[6] and the other two described the characteristics of particles found in 15 commercially available spray products (such as hair sprays and antiperspirants) and their aerosols[7,8].

Writing in *Journal of Nanoparticle Research*, Vicki Colvin and colleagues[6] at Rice University assessed the shape, size distribution, agglomeration state, crystalline structure, elemental composition and surface area of particles found in eight commercial sunscreens labelled as containing either zinc oxide, titanium dioxide or both. To facilitate measurements, some samples were diluted with water or ethanol. The products were shown to contain either zinc oxide nanorods or titanium dioxide nanoparticles (in the rutile structure, except for one in the anatase form).

Dilution of the sunscreens was reported to break up clusters of particles, indicating that the nanoparticles were only loosely agglomerated. This suggests that rubbing sunscreen on human skin may also break up any agglomerated nanoparticles and expose the skin to dispersed nanoparticles, which may remain dispersed when released into water following swimming or bathing. This is important exposure information, because the toxicities of dispersed and agglomerated nanoparticles may differ[9]. Non-volatile organic emulsion components observed on the surfaces of nanoparticles were not characterized, but will be essential for future studies. For example, although the toxicity of uncoated zinc oxide nanoparticles to freshwater species is caused by dissolved zinc ions[10], nanoparticles with acquired sunscreen coatings may have different dissolution

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