

to the external field and, instead of being reduced, the splitting of the two lines in the PL is now increased. In fact, Makhonin *et al.* could observe the nuclear spin while rotating coherently by varying the length of the NMR pulse. By further controlling the phase of the oscillating field, rotations about different axes were achieved, thus allowing full control of the nuclear spin.

The reconfigurable and strong local field that was achieved is useful for performing quantum gate operations for quantum computation¹². The rotations of the collective nuclear spin can be carried out on timescales shorter than the nuclear decoherence time and therefore in a coherent manner. Thus, one can

foresee the creation of non-classical states of the nuclear environment¹³, as well as entanglement between an electron spin and an entire collection of nuclear spins. Of course, once these goals are reached, the nuclear spins will have been promoted from mere environment to part of the actual system. Finally, whereas a single nuclear spin is clearly a microscopic object ruled by quantum mechanics, a collection of a million nuclear spins lies somewhere between the known quantum and classical regimes. Hence, controlling these nuclear spins coherently and observing their behaviour may also help our fundamental understanding of the boundary between the quantum and classical worlds. □

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X-RAY IMAGING

A coherent look at stress

Molecular ligands are widely used to functionalize gold nanoparticles, but their influence on the particle structure has been difficult to probe. Coherent X-ray diffraction has now reached sufficient sensitivity to resolve adsorption-induced near-surface stress in a single nanocrystal.

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Gold nanoparticles have already been used — unconsciously, of course — in ancient times. One of their first applications in coloured glass exploited their optical properties, which show a change of apparent colour from gold to red as their size is reduced down to the nanometre scale. Recently, interest in these materials has been exploding, as, although occasionally overestimated or mystified, the opportunities they offer are indeed breathtaking. Possible applications of gold nanoparticles (AuNPs) and gold nanostructures in general range from their use in sensors to exploiting near-field optical effects, such as antenna effects for field enhancement¹ or microscopy beyond the diffraction limit².

In many cases, in particular if the particles are to be dissolved or processed without aggregating, or if a specific surface functionality is desired, they are coated with an organic layer³. For AuNPs, the use of thiols, which incorporate sulphur as a linking group, is the most common and most successful strategy for functionalization. For extended gold surfaces (bulk crystals or thin films) this scheme has been employed in a vast number of studies⁴. By virtue of the thiol anchor, a broad variety of functionalities can be attached to a gold surface to render it sticky or non-sticky, hydrophilic or hydrophobic, to give just a few examples.

Although this recipe has been employed widely, the structure of many AuNPs and their magic coatings has remained surprisingly elusive even today. Writing in *Nature Materials*, Moyu Watari *et al.* now report that they have successfully resolved the structure and the surface strain in a single AuNP using coherent X-ray scattering⁵.

When it comes to the crystallographic characterization of bulk crystals and their surfaces, which, interestingly, Watari's

co-author Ian Robinson pioneered among others, we are spoiled by the possibility to almost routinely solve such questions with a mouse click, provided the materials are sufficiently well defined and extended⁶. However, some AuNPs are not crystalline at all, and even for those that are it is not obvious how conventional X-ray diffraction techniques would reveal this structure, let alone subtleties such as surface strain. A conventional diffraction approach on an ensemble of unaligned AuNPs would face difficulties to resolve the issues addressed by Watari *et al.*, and it lacks the required surface sensitivity for these systems.

The approach developed by Watari *et al.* circumvents part of the classical phase problem of crystallography. In a previous project the authors studied already bare, that is, uncoated, NPs using coherent X-ray scattering⁷. This technique has become possible with the development of modern highly coherent X-ray sources, that is, synchrotrons, and now also X-ray lasers. The idea is that if the sample is bathed in a coherent beam of X-rays, the usual (incoherent) averaging is avoided, and more information, including the relative scattering phase of rather distant regions within the sample, can be extracted. In essence, this is the result of the oversampling of the diffraction pattern, which can be further processed and inverted to obtain

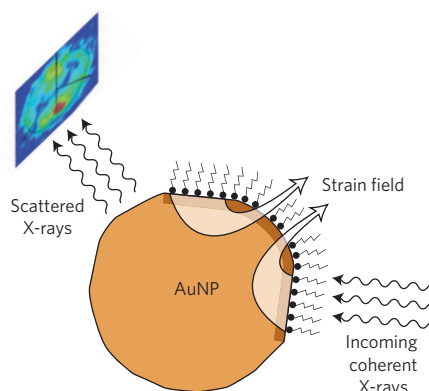


Figure 1 | Schematic of the experiment by Watari *et al.*⁵. The particle is bathed in a coherent beam and the relative scattering phase of rather distant regions within the sample is measured. The results can be analysed to obtain an extremely detailed real-space picture, including surface strain.

a real-space image of the property under investigation. Obviously, the inversion algorithm and the data analysis in general are key for this method. In the present study, Watari *et al.* have employed coherent X-ray scattering to characterize AuNPs coated with self-assembled monolayers (see Fig. 1). It turns out that coherent X-ray diffraction is extremely sensitive to displacements of the atoms from their equilibrium structure, and that even the small contribution of chemically induced strain on the near-surface region can be visualized through difference maps. Such maps are basically the comparison between an unperturbed and a perturbed system and suitable to identify localized small changes.

They find that the structure of a single 300-nm-diameter faceted gold nanocrystal

changes profoundly after the adsorption of thiols. The changes require large stresses comparable to those observed in cantilever measurements. Watari *et al.* conclude that the stress generated by thiol adsorption on gold has a fundamentally different nature in the curved, nominally spherical, regions of the crystal surface than its flat facets. This seems to be a major step, considering that already the interface structure, that is, the binding geometry, of thiols on flat surfaces has been a subject of substantial controversy.

The characterization of the atomic-level structure should bring us one step further in our understanding of nanoparticles. At the same time, it is a beautiful demonstration of the power of coherent X-ray diffraction, which is still seen as a specialist technique

and some distance away from being applied routinely. With the increasing availability of coherent sources, in particular the new X-ray lasers, more exciting applications of this technique lie ahead. □

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A QUICK FIX

Delicately patterned micro- and nanostructures can be produced without the need for laborious fabrication, by relying on physical forces to organize materials spontaneously into intricate forms. The capacity of soft materials such as surfactants and block copolymers to self-organize into regular patterns has been long recognized^{1–3}, and superlattices and other regular arrays in two and three dimensions can be produced from the microphase separation of block copolymers^{4–6}. Many of these approaches recognize the precedence of nature, which uses the same parsimonious principles to make elaborate micropatterns such as exoskeletons⁷ and photonic crystals^{8,9}.

Not all of the rich patterns generated spontaneously by physical forces are long-lived, however, which may limit opportunities for exploiting them in technologies. Fluids are particularly apt to display transient patterned instabilities that are gone in an instant. Yet an instant is more or less all it takes to 'freeze' such structures in a method described by Grilli *et al.*, who have used rapid heat curing of a liquid polymer to create a range of transparent microstructures that might find uses in optics¹⁰.

The researchers have focused primarily on the 'beading' of a liquid filament — a variant of the Rayleigh instability studied since the late nineteenth century. This describes the way a column of liquid will become

spontaneously unstable to undulatory perturbations that break it up into a string of roughly spherical droplets, often of alternating size. The instability can be seen in a narrow liquid jet, and it is responsible for the way the glue coating the threads of a spider's web forms a string of beads. Dew does likewise, decorating the web with a beautiful array of droplets.

Grilli *et al.* induce the patterning artificially by using an electrohydrodynamic method¹¹ in which a strong electric-field gradient produces instabilities in a dielectric fluid, here the molten polymer polydimethylsiloxane. In a typical example, a thin liquid bridge is formed by using the field between two plates to draw up a droplet of polymer sitting on the lower plate. The bridge drains to a very narrow column that then bunches into 'beads on a string.' A hot-air jet cures the structure within seconds, before it can fragment. The result is a string of linked, transparent, spherical or lenticular beads just a few or a few tens of micrometres across. These can be used as, for example, one-dimensional arrays of optical resonators, with optical properties tunable by mixing fluorescent particles into the liquid polymer.

Other 'frozen' instabilities that may be created this way include 'axicons': conical structures with a needle tip at their apex, which might be used as elements for optical tweezers with a



PHILIP BALL

large depth of focus, or as the tips of near-field optical microscopes.

The idea of using the self-organizing forces in liquids to create devices too small to be easily fabricated by hand is actually a very old one. It is how Antoni van Leeuwenhoek made the tiny lenses for the microscopes that enabled him to launch the field of microbiology, by rapidly cooling molten glass into tiny spherical beads. □

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