METAL NANOCRYSTALS

Deforming like liquid droplets

Metallic nanocrystals can be deformed pseudoelastically at room temperature without generating dislocations.

Claude R. Henry

The properties of materials often change drastically when their size is decreased to the nanometre range. For example, as the surface-to-volume ratio of a material is increased, typically its melting temperature depresses and its chemical reactivity tends to increase. Also, as the size of a crystal shrinks down to submicrometre sizes, it becomes more difficult to deform it plastically (that is, the material becomes harder). This occurs because of the increasing difficulty for dislocations in the crystal to nucleate and move as crystal size is decreased. Yet Ju Li, Ze Zhang, Litao Sun and colleagues report in *Nature Materials* that a 10-nm silver nanocrystal can be deformed at room temperature in the absence of any dislocation activity[1] by compressing or stretching it using the tip of a scanning tunnelling microscope located inside a high-resolution transmission electron microscope (TEM), which allows for the deformation of the nanocrystal to be visualized at atomic resolution.

Li and co-authors used a set-up where the nanocrystal was partially bonded to a tungsten tip that approached a counter ZrO_2 surface (Fig. 1a). The authors observed that when the nanocrystal was compressed against the oxide, it continuously flattened (Fig. 1b–d), and that it continuously elongated when the tip was retracted (Fig. 1e,f; during tip retraction, the contact area between the top of the nanocrystal and the oxide surface decreased until complete detachment). They also observed that when the nanocrystal detached from the surface it rapidly recovered the original facetted shape. Visualization of the lattice planes in the TEM images demonstrated that, during the whole process, the nanocrystal remained as a perfect single crystal — that is, it did not contain dislocations. Importantly, the authors demonstrated that the nanocrystal deformed by surface diffusion, as indicated by the growth of atomic planes on its external surface. They confirmed this by means of molecular dynamics simulations (Fig. 1g).

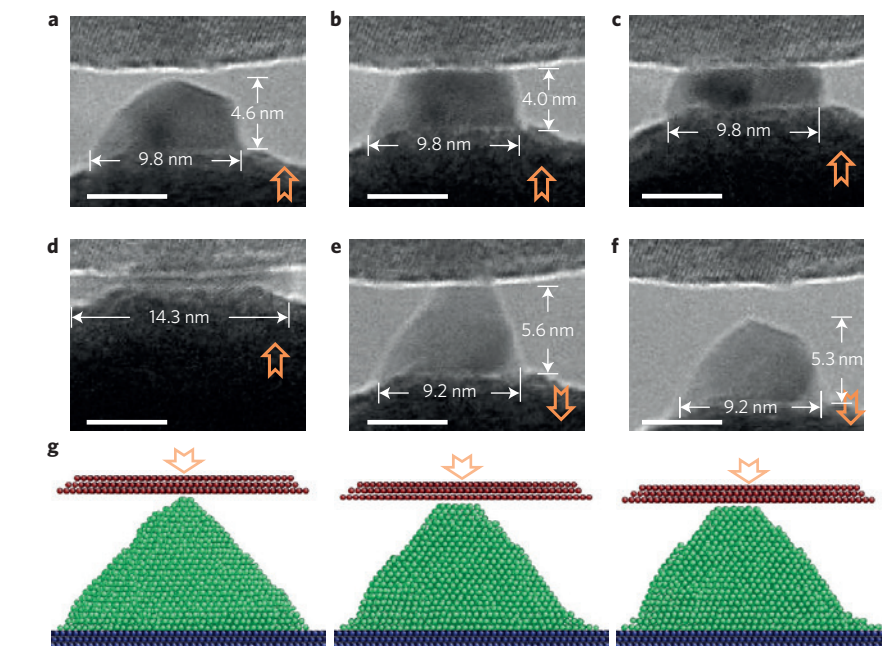Surface diffusion as a deformation mechanism is of a different nature than

Figure 1 | Pseudoelastic deformation of a silver nanocrystal[1]. **a–f**, A silver nanocrystal that underwent a compression (**a–d**) and stretching (**e,f**) cycle almost recovered its initial size (**a**). Scale bars, 5 nm. **g**, Simulation of the compression process, showing that changes in nanoparticle shape occur in the absence of dislocation activity and are driven by surface diffusion. The orange arrows indicate the movement direction of the tungsten tip.

classical plastic deformation, which involves the nucleation and migration of dislocations. In fact, nanocrystal deformation in the experiments by Li and colleagues was not purely elastic but pseudoelastic, and differed fundamentally from classical plastic deformation by the fact that in the absence of any applied constraint the nanocrystal returned spontaneously to its rest shape (to minimize its total surface and interface energy). Phenomenologically, the nanocrystal behaved like a liquid droplet, yet remained a crystalline solid. The rest shape of the nanocrystal must be the crystal's equilibrium (Wulff's) shape, which at low temperature is a polyhedron.

Remarkably, Li and collaborators show that the nanocrystal shape-relaxation time is short, of a few seconds at room temperature (in a macroscopic sample, relaxation would be too slow

to be observed in any reasonable time at temperatures far from the crystal's melting point). As relaxation time is proportional to the nanocrystal size to the fourth power and inversely proportional to the surface-diffusion coefficient[2], it strongly increases with cluster size and decreasing temperature. Reversible shape relaxation has also been recently observed by means of an environmental TEM in Au and Pt nanoparticles during exposure to oxygen, carbon monoxide or hydrogen[3–5] (basically, gas adsorption, which varies for different crystal facets, changes surface-energy anisotropy and thus the crystal's equilibrium shape). For a 4-nm gold nanocrystal, the relaxation time was about 10 s (ref. 6), in fairly good agreement with Li and co-authors' silver nanocrystals. However, the electron beam in the TEM can increase the rate of atomic surface diffusion on gold nanoparticles[7,8]. To

minimize potential electron-beam effects, the authors ran the full deformation cycle with the electron beam off, and turned it on at the end of the process to image the final shape, which they showed to be identical to that before the deformation process started. They also show that, at low current, heating effects are small. Although these experiments do not definitely rule out all potential electron-beam effects on the surface-diffusion process, the authors have taken great care to reduce the beam current to values that are low enough for the influence of the beam on surface diffusion to be negligible[7].

Li and colleagues' findings have consequences for basic science and for the practical use of nanocrystals — for example, as used in nanoelectronic devices. On the one hand, their experimental approach should make possible the systematic study of the relaxation time of nanocrystals of different sizes as they recover their equilibrium shape at room temperature. Such a study would serve as a test of the power-law dependence of relaxation time on nanocrystal size[1]. On the other hand, nanocrystals can temporarily suffer stresses that irreversibly change the nanocrystal's shape, potentially causing device failure. Also, nanocrystal shape can evolve rapidly under varying chemical conditions, such as changes in the composition of its immediate environment. This could cause device damage but could also be an advantage in gas-sensing devices, as shape changes induced by gas adsorption may cause changes in electrical conductivity.

All in all, Li and colleague's results highlight that crystals at the nanoscale can deform like liquids. □

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ELECTRON MICROSCOPY

Shape of a crystal from one image

Aberration-corrected electron microscopes are now being exploited to achieve quantitative atomic-resolution information about surface morphology from a single image.

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In 1994, Hÿtch and Stobbs[1] pointed out the existence of a large contrast mismatch between high-resolution electron microscopy images that were obtained using conventional transmission electron microscopy (CTEM) and simulations, a mismatch known as the Stobbs factor. This was also the case for images obtained with scanning transmission electron microscopy (STEM), where a fine probe is raster-scanned across the specimen to form an image. Despite the substantial improvements in resolution offered by the advent of aberration-corrected electron microscopy in the years following[2], it was not until 2008 in the case of STEM[3] and 2009 for CTEM[4] that quantitative imaging was demonstrated, overcoming the problems related to the Stobbs factor. This quantification capability in STEM imaging has led to counting of atoms in a gold foil[5] and to locating impurity atoms in three dimensions[6,7]. Now, a further major advance in quantitative imaging has been made using CTEM. Writing in Nature Materials[8], Jia and co-workers demonstrate the experimental reconstruction of the three-dimensional (3D) shape of a thin magnesium oxide crystal with single-atom precision from only one image. The reconstruction procedure is able to reveal the surface morphology of the crystal with atomic resolution with the benefit of detecting adsorbed impurity atoms.

The approach used by Jia and co-workers differs fundamentally from the standard 3D reconstruction approach used in tomography, which relies on the combination of the information gathered by different views (or 2D projections) of the object being imaged. The difference is that Jia and colleagues make efficient use of the fact that electron diffraction is intrinsically a 3D process. Figure 1 illustrates[8] how this 3D information can be used: a magnesium dioxide crystal is illuminated from the top by the CTEM electron beam. The structural information about the distribution of atoms in each column of the crystal is encoded in how the illumination above that atomic column interacts with it, leading to subtle variation in contrast as one moves from column to column (Fig. 1, labels i,j). The instrumentation produced TEM images with an absolute greyscale and a good signal-to-noise ratio. The spatial variations in the images were then compared with simulations. A structure refinement iterative procedure was used to find the best fit between a structure model and the experimental image. A statistical confidence check provided precise quantitative statements about the uniqueness of the final 3D structure model. In this way it was possible to gather information on column positions, number of atoms in a column and the species of the top-most atom, as well as on how a column is located along the optical axis, thus determining the surface morphology of the crystal (Fig. 1). In fact, it was even possible to identify sites that appeared 'half-occupied' (brown and cyan in Fig. 1), most likely due to impurity carbon atoms. Additionally, the results show that single-atom sensitivity is not only obtainable for high nuclear charge elements but also for light chemical elements, such as oxygen. This is of considerable practical relevance because oxygen plays a key role as an anionic constituent in many technologically important materials.

Several factors contributed to the success of the approach used by Jia and colleagues[8]. Carefully chosen imaging conditions were used to provide strong localized image contrast. A good signal-to-noise ratio in the recorded image data was essential to clearly distinguish between candidate structures that, as can be seen in simulations, have small differences in intensity. These imaging conditions require