MATERIAL WITNESS

Golden wonder

For nanotechnology, the binding of sulphur atoms to gold comes close to supplying the kind of dependable, clean linkage commonly called 'click chemistry' by organic chemists. Do you want to interface organic molecules with inorganic materials? Then give them dangling sulphur atoms and deposit them on a gold-plated surface.

This is the standard formulation for self-assembled monolayers (SAMs): films one molecule thick, typically made from alkylthiols on a gold-covered substrate. The organic molecules stick, sulphur-end down, in an orderly carpet, which might electrically insulate part of the metal surface or give a printable etch-resistant layer for patterning. A gold–sulphur linkage will also fix a molecular wire to an electrode surface.

Thiol coats are the standard way of passivating the surfaces of gold nanoparticles against colloidal aggregation. The organics can act as nanoparticle tethers, for example to create fluorescent labels for biological macromolecules. Non-toxic, corrosion-resistant and inert to most other reactions, gold is one of the key ingredients on the nanotechnological palette.

That's why the recent elucidation of the crystal structure of a thiol-protected gold nanoparticle by Roger Kornberg and his colleagues at Stanford University has caused so much excitement (P. D. Jadzinsky *et al.*, *Science* **318,** 430-433; 2007). For one thing, the work shows how surprisingly little we knew about the binding of thiol to gold. The general presumption was that the sulphur atom merely sat atop the uppermost gold layer, divalently bound to two adjacent metal atoms. The X-ray structure of Jadzinsky *et al.* reveals that, instead, pairs of thiol groups abstract a gold atom that forms a linear bridge between them while interacting weakly with the metal surface below. These gold–thiol complexes form a sort of rigid crust on the nanoparticle. It remains to be seen whether the structure persists in planar gold films, as in SAMs.

Reports of the work have struggled to do justice to all its facets, for it opens a new window on nanoparticle chemistry. That the researchers were able to obtain a crystal structure at all is because all their particles are identical, with precisely 102 gold atoms. It was not known that such a large atomic cluster could attain 'molecular' precision, rather than being simply an arbitrary aggregate.

The stability of such particles seems to come from the fact that, if each gold atom donates one valence electron, of which 44 are involved in bonding to sulphur, the 58 remaining form a closed electron shell. That makes it a kind of superatom analogue of a noble gas. Superatom clusters have been proposed as potential building blocks for new materials (P. J. Roach *et al.*, *Proc. Natl Acad. Sci. USA* **104,** 14565 (2007); A. C. Reber *et al.*, *J. Am. Chem. Soc.* **129,** 10189 (2007)).

There are doubtless other implications for the important optical and electronic properties of gold nanoparticles, and perhaps also for their site-specific binding to biomolecules to aid in structure determination — the Stanford group's original objective. Not bad for a speck of gold dust.

Philip Ball

TRANSITION METAL OXIDES

The exciting world of orbitals

Transition metal oxides show many interesting phenomena from high-T_c superconductivity to colossal magnetoresistance and multiferroicity, triggering intensive studies. However, we have barely tapped into their potential for applications.

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Oxides, often considered as synonymous with ceramics, bring terms such as china dishes or pottery to mind. However, oxides with transition metals that straddle the subtle boundary between covalent, ionic and metallic bonding show copious physical phenomena, ranging from high-T_c superconductivity in layered cuprates, colossal magnetoresistance (CMR) in perovskite manganites, to the coexistence of magnetism and ferroelectricity — termed multiferroicity. When atoms are put together to form a three-dimensional substance, the properties of the substance are governed by how quantum clouds of electrons, the orbitals, move around and interact with each other. These orbital degrees of freedom often underpin physical properties of complex oxides. The intriguing variety of orbital-related physical properties of transition metal oxides, ranging from phenomena in bulk materials to the properties of more complex structures such as phase-separated systems as well as thin films and multilayer heterostructures, were subject to intense discussions at the recent workshop, 'Orbital 2007', that was held in Stuttgart in October.

One of the most discernible electronic properties of a given material is whether it is a metal or an insulator. In the standard point of view for metals and insulators, electrons have both an itinerant tendency and mutually repulsive interactions. In the limit of strong repulsions, electrons tend to localize, inducing the well-known Mott insulating state, and spins order antiferromagnetically. Given the electron localization in Mott insulators, charge degrees of freedom are often deemed irrelevant, and only spin degrees of freedom are considered. However, as Daniel Khomskii (II. Physikalisches Institut, University of