

MSNs and the green fluorescent protein (GFP) marker encoded in the DNA was expressed in the cells and detected by microscopy. Delivery is efficient because the minimum amount of DNA required to detect marker expression was 1,000-fold lower than that required when using conventional methods to deliver DNA into protoplasts. It seems that using MSNs as a means to deliver DNA in this way should gain popularity for protoplast-based gene expression studies.

Although delivering material into protoplasts is important, it is not a particularly common approach in plant biotechnology because the cell walls must first be removed. A popular tool used to deliver materials into plants with intact cell walls is the 'gene gun'. The carrier particles, usually coated with DNA, enter the cells through the walls by bombardment using high-pressure gases or, less commonly, explosive rounds. Despite the destructive nature of this method, recovery is efficient enough to allow the DNA to be expressed in the plants.

Given the physical properties of the plant cell wall, which provides the strength required for plants to grow up to 130 m high⁸, particles that can

penetrate this barrier must exceed some momentum threshold. Particles used for bombardment are typically made of gold (around 0.6 μm in diameter) because they readily adsorb DNA and are not toxic to cells. MSNs, being much smaller (and lighter) are not effective in delivering DNA to intact plant cells. However, Torney and colleagues found that capping the MSNs with gold nanoparticles increases their momentum after acceleration by the gene gun. Their experiments showed that the plasmid DNA delivered using gold-capped MSNs was successfully expressed in intact tobacco and maize tissues.

The advantage of using MSNs with the gene gun is that both the DNA and small effector molecules can be delivered at the same time (Fig. 1b). Here, plasmid DNA carrying a regulated version of the GFP marker is adsorbed on the MSN surface and the small effector molecules that activate GFP expression (in this case β -oestradiol) are contained inside the gold-capped structure. After bombardment into the plant cell, the effector molecules are released from the gold-capped structure (Fig. 1c) by incubating the plant tissues on media containing dithiothreitol — a chemical

that reduces the disulphide bonds that attach the gold caps to the MSNs. GFP expression is only observed under these conditions.

This work stimulates a number of questions. What might be the effect of including combinations of effector molecules within the MSNs, and/or combinations of plasmid DNA on their surfaces? Can MSNs be designed to uncage under more selective conditions (for example, using laser light or in response to chemical changes in the plant cells)? Can MSNs be designed so they can be recapped? Answering these questions is by no means easy, but the promise shown by MSNs in general, and this work in particular, suggests many more breakthroughs will emerge in this area.

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STRUCTURAL PROPERTIES

Magic nanoclusters of gold

A combination of theory and experiment is shedding new light on the structural and electronic properties of gold nanoclusters, including cage-like structures that contain other atoms.

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Gold is widely used to build nanostructures because it is relatively chemically inert, although gold clusters can become quite reactive as they get smaller. Indeed, positive gold ions can react with noble gases, and gold particles just a few nanometres in diameter can act as catalysts in many reactions, as can single gold atoms bound in suitable complexes¹.

Because the shape and electronic structure of gold nanoparticles play such an important role in determining their

chemical reactivity, significant effort has been devoted to understanding how these structural properties evolve with size. These studies reveal that gold can adopt a wide variety of structures. For example, particles that contain fewer than about twelve atoms prefer to form flat flakes, whereas more spherical structures are stable when the total number of valence electrons in the cluster (each gold atom contributes about one) is equal to or near the value of 2, 8, 18, 32, 50, 72, ..., $2(L+1)^2$ electrons, where L is an integer. These 'magic numbers' may look familiar: they are the number of electrons necessary to fill, respectively, the s , p , d , f and g orbitals of atoms.

Clusters with 18 electrons ($L=2$), in which the first s , p and d orbitals are filled, are surprisingly robust². However, the total

kinetic energy of the electrons in the cluster increases as each new atomic-like orbital is added, and a stable state is only reached again when the orbital is filled. For example, the next magic number after 18 is 32, which corresponds to filling the valence f shell of the cluster. However, gold atoms do not have valence electrons in the f shell and it may not be possible to form clusters that stabilize the 32-electron state. Theorists have therefore looked for examples formed from slightly heavier elements, such as lead, which can contribute two valence electrons per atom. Indeed, one prediction suggests that Pu@Pb_{12} (a shell of 12 lead atoms around a central plutonium atom, may be a candidate³).

Just as in real atoms, the s , p and d orbitals of clusters do not have to fill sequentially and more complex filling

arrangements can occur. For instance, the 20 electrons in the compound Si@Au_{16} fill two s orbitals, one p and one d orbital⁴. Also, the same electron count can be satisfied by two different filling arrangements, giving rise to so-called 'false magic numbers'³. In addition, certain highly symmetric geometric structures are associated with particular numbers of atoms. For example, Au_{20} is a tetrahedron and Au_{32} is predicted to be an empty icosahedron.

Given the complexity of possible structures with increasing cluster size, a systematic comparison between theoretical predictions and precise measurements of the structure of gold clusters is strongly needed. Two recent papers appearing in *Angewandte Chemie International Edition* make this important contribution.

Building on earlier work in which they were able to form stable gold cages of 16 to 18 atoms⁵, Lai-Sheng Wang at Pacific Northwestern National Lab and colleagues from Washington State University and the University of Nebraska have looked at new ways to stabilize clusters of gold near the magic number of 18 valence electrons by filling the centre of the cage with a copper atom⁶.

To make the cage-like clusters, they laser-evaporated a Au/Cu alloy. After the clusters were ionized to have a negative charge, and selected for a specific mass, they were studied with photoelectron spectroscopy, which gives a sensitive fingerprint of the electronic and geometric structure of the cluster. In this way, the group was able to confirm the presence of Cu@Au_{16}^- (Fig. 1a) and Cu@Au_{17}^- . There are 18 and 19 valence electrons associated with these clusters, respectively, indicating that the copper transfers its single valence electron to the surrounding Au.

This new work rounds out the experimental evidence for both 'empty' gold cages Au_{16}^- and Au_{17}^- (ref. 5), and cages filled with one Cu atom⁶. Moreover, it provides important insight into how the Cu dopant affects the properties of the cluster. Taking the work a step further and filling the gold shells with magnetic atoms would open a number of applications and may pave the way to investigating the magnetic properties of other types of metal clusters^{7,8}. In addition, Wang's group suggests that this strategy could also be a way to tune the catalytic properties of gold nanoparticles.

The question of what happens for larger clusters is still open. Although it has been possible to make hollow 32-atom gold nanospheres surrounded by an organic thiolate shell⁹, less is known about pure clusters of this size. The experimental and theoretical study

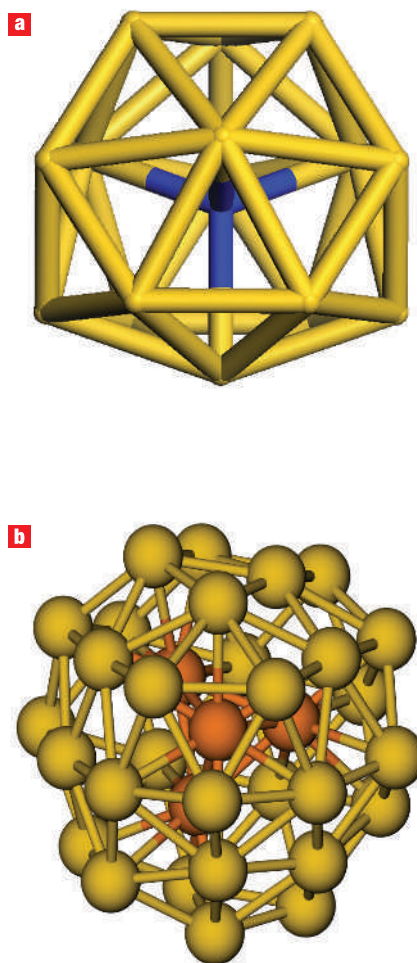


Figure 1 Two types of stable gold clusters. **a**, Copper-gold clusters, Cu@Au_{16}^- , consisting of one copper atom (indicated schematically in blue) surrounded by a cage of sixteen gold atoms, have 18 valence electrons. Gold clusters with this 'magic number' of electrons tend to be very stable as it corresponds to filling the atomic-like s , p and d orbitals associated with the cluster⁶. **b**, Larger clusters with 34 atoms, Au_{34}^- , are also found to be stable, but have a much lower structural symmetry¹⁰.

from Detlef Schooss and colleagues at the Research Center in Karlsruhe, Germany is a serious effort to better understand the geometrical structure and electronic properties of large pure gold clusters¹⁰. In particular, one question that has particular relevance to how chemical bonds are formed in clusters is whether gold clusters larger than about 20 atoms adopt structures with high or low symmetry.

Using time-dependent density functional theory, the group calculated the energy required to form different configurations — or isomers — of gold, all with the same number of atoms. To test these predictions, Schooss and colleagues

captured gas-phase particles of Au_{34}^- in a 'magnetic bottle' and used a technically challenging measurement called trapped ion electron diffraction to determine the structure. Like the Wang group, they also used photoelectron spectroscopy to measure the electron binding energies for the clusters, and compared them with theoretical calculations for different types of structures.

The main conclusion of the work from Karlsruhe is that the Au_{34}^- cluster with the lowest calculated energy also has a very low symmetry, a result that is supported by the structural measurements. The best way to describe the low-symmetry structure is as a sort of truncated and deformed version of bulk gold (Fig. 1b), which has a face-centred cubic lattice structure. Another similarity to bulk gold is that the surface of the 34-atom particle is restructured, meaning it develops a structure that is distinct from the interior. Schooss and colleagues suggest that this reconstruction helps to minimize the surface energy while keeping bond distances at the interior of the cluster close to those found in bulk gold.

A chiral molecule, such as a helix, has the property that it cannot be projected onto its own mirror image, and this is the case for the Au_{34}^- clusters studied by the German group. Interesting effects can be observed with chiral molecules, such as the polarization of light that passes through them. For this to be possible with the Au_{34}^- gold clusters, however, the gas-phase mixture would have to contain more molecules of one chirality than its mirror image (they tend to form in equal amounts), a separation that is not easy to achieve in a magnetic trap. Moreover, it is not so surprising that Schooss and colleagues find these clusters are chiral as many low-symmetry clusters have this property.

Yet, what is clear from the useful conclusions of this work, as well as those of the Wang group, is that the multitude of possible structures for gold can only be resolved by a careful comparison of theory and experiment.

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