Researchers unlock key to nanocluster formation

Cordelia Sealy

Metal nanoparticles are intriguing for many applications because their unique properties differ from both the atomic and macro level. But although such nanoparticles or nanoclusters have been fabricated in the lab for decades, exactly how this process takes place has remained something of a mystery.

Now researchers from the University of Pittsburgh think that they may have unlocked the key to metal nanocluster formation — and it all depends on the energy balance between the core and the shell [Taylor and Mpourmpakis, *Nature Communications* (2017) 8:15988, doi: 10.1038/ncomms15988 http://dx.doi.org/10.1038/ncomms15988].

Colloidal Au nanoclusters can be synthesized in a range of different sizes and shapes, which determine their physical and chemical properties. The process relies on ligand molecules that bind the metal atoms together to form a core, while simultaneously providing an outer shell (Fig. 1). But only some clusters of certain sizes are thermally stable — dubbed 'magic number' nanoclusters.

"Even though there is extensive research into the experimental synthesis of metal nanoclusters, there really isn't a rational explanation of why metal nanoclusters are formed at specific sizes," says researcher Giannis Mpourmpakis.

Two theories have been proposed to explain why some clusters are stable and others are not. The 'divide and protect' and 'superatom' theories are based on different basic assumptions and while they work for some clusters of up to a few hundred atoms, they cannot predict all the possible stable nanoclusters. As a result, Mpourmpakis and his colleague Michael G. Taylor, point out that nanocluster predictions differ from those actually synthesized.

Now the two have come up with what they hope is a more successful model of nanocluster formation based on the energy of the metal core and the ligand shell. The 'thermodynamic stability' theory suggests that nanoclusters will only be stable (and therefore possible to synthesize) if the cohesive energy of the core is balanced by the core-to-shell binding energy.

"The novelty of our contribution is that we have revealed that for experimentally synthesizable nanoclusters there has to be a fine balance between the average bond strength of the nanocluster's metal core and the binding strength of the ligands to the metal core," explains Mpourmpakis.

The theory can predict not only which thiolated Au nanoclusters will be stable and experimentally accessible, but other metals-ligand combinations as well. In addition, because the model is based on the energy of the core and shell, the predictions can be correlated to the size and shape of nanoclusters as well.

"By relating the interaction energy of these atoms with the structural characteristics of the nanoclusters, we can now design previously undiscovered nanoclusters in the computer that can be potentially experimentally synthesized in the lab," says Mpourmpakis.

Such 'designer' nanoclusters could be used to biolabel individual cells or carry out targeted drug delivery, as well as facilitate catalytic reactions, say the researchers. The findings could also help understand the fabrication of other nanomaterials such as semiconductor nanocrystals and quantum dots.

"We are currently developing similar theories that are applicable to bimetallic nanoclusters, as well as to other classes of nanoparticles, with a focus on introducing a framework to design and test the stability of nanoparticles *in silico* and guide experimental research, avoiding trial-and-error experimentation in the lab," Mpourmpakis told *Nano Today*.

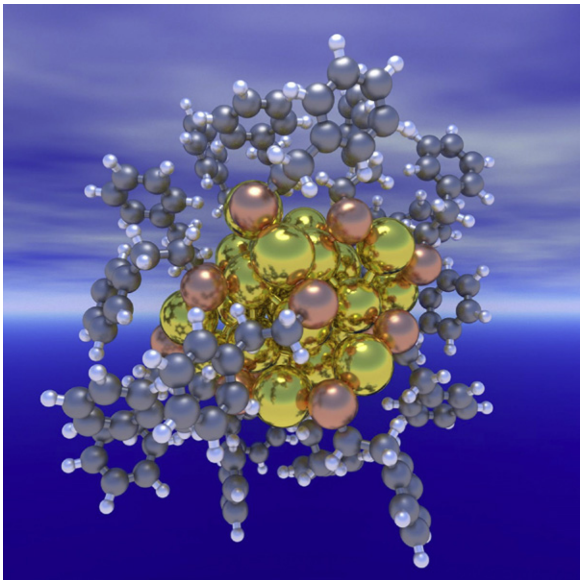

Fig. 1 Au_{25} nanocluster stabilized by 18 thiolate ligands.

Asaph Widmer-Cooper of the University of Sydney notes that the new thermodynamic model appears to work for a range of atom types, as well as correctly predicting the stability of Au-thiolate clusters ranging in size from 18 to 133 Au atoms, including several clusters that were not predicted to be especially stable by the well-known superatom theory.

"This is an intriguing model and it will be interesting to see how well it works for much larger nanoparticles and for ligands other than thiolates," he says.

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Fluorine holds magnetic attraction for boron nitride

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Fluorine transforms the two-dimensional, ceramic insulator hexagonal boron nitride (h-BN) into a wide-bandgap semiconductor with magnetic properties, a team of researchers have discovered [Radhakrishnan et al., *Science Advances* **3** (2017) e1700842, http://dx.doi.org/10.1126/sciadv.1700842].

Two-dimensional materials like h-BN — also know as 'white graphene' — have attracted great interest in recent years as novel electronic materials. But while functionalization of these materials has become an indispensible tool for tailoring their physical and chemical properties, fluorinating two-dimensional materials had required specialized instruments.

Now researchers from Rice University, together with colleagues from the Indian Institute of Science, University of Houston, Louisiana State University, Baker Hughes' Center for Technology Innovation, University of Toronto, and Air Force Research Laboratories at Wright-Patterson, have developed an easy and straightforward way of fluorinating h-BN.

"The simple solvothermal method involves Nafion, a fluoropolymer," says researcher Chandra Sekhar Tiwary. "Nafion acts as the fluorinating agent by degrading at the synthesis temperature to produce fluorine free radicals, which break the B-N bonds to form B-F and N-F bonds."

In its normal state, h-BN is a chemically inert, thermally conductive, layered ceramic made up of B and N atoms arranged in alternating positions in a hexagonal lattice. But the addition of F, and creation of B-F and N-F bonds, changes the bandgap of h-BN and introduces defect states (Fig. 1). Moreover, the F atoms alter the spin of electrons in the N atoms and their magnetic moments. The randomly angled spins create pockets of magnetism.

"Magnetic centers introduced by fluorination give ferromagnetic behavior at room temperature, while the low temperature measurements reveal signatures of unconventional magnetism," explains Tiwary.

This unconventional or 'frustrated' magnetism arises from the change in charge density on the N atoms produced by the introduction of the F atoms.

"There has been a lot of effort to try to modify the electronic structure [of h-BN], but we didn't think it could become both a semiconductor and a magnetic material," says Pulickel M. Ajayan. "This is something quite different, nobody has seen this kind of behavior in h-BN before."

The researchers believe fluorinated-BN (FBN) could be useful for spintronic applications, where the material's high thermal conductivity should be a boon for high power electronic devices. FBN could also represent an attractive replacement for GaN in compact lasers, since the level of fluorination could be used to tune the emission wavelength.

"The versatility of the method lies in its ability to fluorinate other two-dimensional materials, as well, which is now being pursued," adds Tiwary. "Moving forward, the work is branching out in all different directions, looking at a variety of applications."

Hexagonal-BN is currently widely studied and increasingly useful because of its insulating properties and