PRESS RELEASE

Self-assembly of gold nanoparticles into small clusters

Berlin, 4.8.2014

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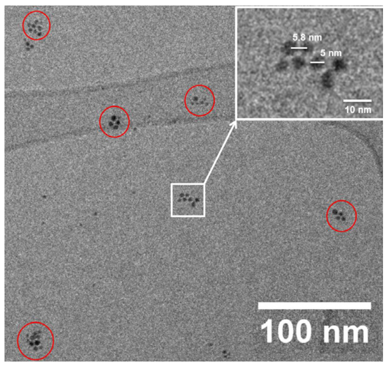
Researchers at HZB in co-operation with Humboldt-Universität zu Berlin (HU, Berlin) have made an astonishing observation: they were investigating the formation of gold nanoparticles in a solvent and observed that the nanoparticles had not distributed themselves uniformly, but instead were self-assembled into small clusters. This was determined using Small-Angle X-ray Scattering (SAXS) at BESSY II. A thorough examination with an electron microscope (TEM) confirmed their result. "The research on this phenomenon is now proceeding because we are convinced that such nanoclusters lend themselves as catalysts, whether in fuel cells, in photocatalytic water splitting, or for other important reactions in chemical engineering", explains Dr. Armin Hoell of HZB. The results have just appeared in two peer reviewed international academic journals.

"What is special about the new process is that it is extremely simple and works with an environmentally friendly and inexpensive solvent", explains Professor Klaus Rademann from HU Berlin. The solvent actually consists of two powders that one would sooner expect to find in agriculture than in a research laboratory: a supplement in chicken feed (choline chloride, aka vitamin B), and urea. British colleagues discovered a few years ago that mixing the two powders forms a transparent liquid able to dissolve metal oxides and heavy metals, called deep eutectic solvent (DES). The researchers in Berlin then positioned above the solvent gold foil that they could bombard with ions of noble gas in order to detach individual atoms of gold. This is how nanoparticles initially formed that distributed themselves in the solvent.

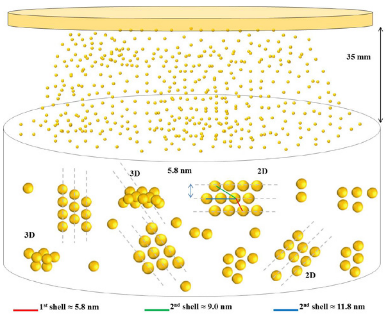
Two surprising results: Nanoparticles stay small and form clusters

The longer the bombardment (sputtering) of the gold foil lasted, the larger the nanoparticles could become, the scientists reasoned. However, this was not the case: the particles ceased growing at five nanometres. Instead, an increasing number of nanoparticles formed over longer sputtering times. The second surprise: these nanoparticles did not distribute themselves uniformly in the liquid, but instead self-assembled into small groups or clusters that could consist of up to twelve nanoparticles.

These kinds of observations cannot be easily made under a microscope, of course, but require instead an indirect, statistical approach: "Using small-angle X-ray scattering at BESSY II, we were not only able to ascertain that the nanoparticles are all around five nanometres in diameter, but also measure what the separations between them are. From these measurements, we found the nanoparticles arrange themselves into clusters", explains Hoell.



Cryogenic TEM micrograph of gold nanoparticles (Au-NP) in DES-solvent. Sputtering duration 300 s. Red circles show the different domains of self-assembled Au-NPs. The inset shows an enlarged image of one particular domain of self-assembled Au-NPs.
Image: HU Berlin/HZB



Model of the self-assembly mechanism
Image: HU Berlin/HZB

Coherent picture by simulations, small angle scattering and electron microscopy

“We ran computer models in advance of how the nanoparticles could distribute themselves in the solution to better understand the measurement results, and then compared the results of the simulation with the results of the small-angle X-ray scattering”, explains Dr. Vikram Singh Raghuwanshi, who works as a postdoc at HU Berlin as well as HZB. An image from the cryogenic transmission electron microscope that colleagues at HU prepared confirmed their findings. “But we could not have achieved this result using only electron microscopy, since it can only display details and sections of the specimen”, Hoell emphasised. “Small-angle X-ray scattering is indispensable for measuring general trends and averages!”

Solvent is crucial

It is obvious to the researchers that the special DES-solvent plays an important role in this self-organising process: various interactions between the ions of the solvent and the particles of gold result firstly in the nanoparticles reaching only a few thousand atoms in size, and secondly that they mutually attract somewhat – but only weakly – so that the small clusters arise. “We know, however, that these kinds of small clusters of nanoparticles are especially effective as catalysts for chemical reactions we want: a many-fold increase in the reaction speed due only to particle arrangement has already been demonstrated”, says Rademann.

Research on catalytic performance planned

Dr. Raghuwanshi will give a talk on these results, as well as providing a preview of the catalysis research approaches now planned, at the International conference, IUCr2014, taking place from 5-12 August 2014 in Montreal, Canada.

In the coming year, HZB will incidentally be one of the hosts of the 16th International Small-Angle Scattering Conference, SAS2015.

Publication

Langmuir: http://pubs.acs.org/doi/pdf/10.1021/la500979p
Royal Society of Chemistry: http://pubs.rsc.org/en/content/articlehtml/2014/cc/c4cc02588a