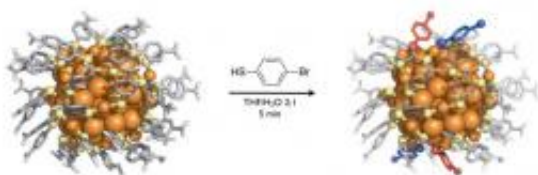


New structural information on functionalization of gold nanoparticles

August 2 2012



This is a visualization of the atomic structure of the Au₁₀₂(p-MBA)₄₄ particle (left) and the partially ligand-exchanged Au₁₀₂(p-MBA)₄₀(p-BBT)₄ (right). The exchanged ligand bromo benzene thiol (p-BBT) is schematically shown in the middle and the observed ligand exchange sites by red and blue on the right. Credit: None

Nanometre-scale gold particles are currently intensively investigated for possible applications as catalysts, sensors, biolabels, drug delivery devices, biological contrast agents and as components in photonics and molecular electronics. The particles are prepared in a solution from gold salts and their reactive gold cores can be stabilized with various organic ligands. Particularly stable particles can be synthesized by using organothiol ligands that have a strong chemical interaction to gold, producing precise compositions in the size range of 1 to 3 nanometres. Modification of the protecting molecular overlayer is a key step in almost all applications. A detailed structural atomistic understanding of the processes of the exchange reaction has been lacking.

Now, professors Chris Ackerson in the Colorado State University in Ft. Collins, USA, and Hannu Häkkinen at the Nanoscience Center of the University of Jyväskylä, Finland, report the first structural study on the atomistic processes of a ligand-exchange reaction of a well-defined gold nanoparticle that has 102 gold atoms and 44 ligand sites in the molecular overlayer. The study was published in the *Journal of the American Chemical Society* on 21 July 2012 [1]. Prof. Häkkinen's work is funded by the Academy of Finland and prof. Ackerson's work is funded by the Colorado State University and the American Federation for Aging Research.

The studied particle has a chemical formula of $\text{Au}_{102}(\text{p-MBA})_{44}$ and it was made by using a water-soluble thiol (para – mercapto benzoic acid, p-MBA) as the stabilizing molecule. The X-ray crystal structure of this particle was first reported as the cover article of *Science* in 2007 by the group of Roger D. Kornberg from Stanford University [2]. Häkkinen led an international team of researchers that published a theoretical analysis of this and other thiol-stabilized gold nanoparticles in 2008 in the *Proceedings of the National Academy of Sciences* [3].

In the new study, Ackerson's group succeeded in making heterogeneous crystals of samples of Au_{102} particles that had undergone a ligand-exchange reaction where the p-MBA thiols in the molecular overlayer had been partially exchanged to a similar thiol containing a Bromine atom, the so-called para – bromo benzene thiol (p-BBT), under a fast 5-minute reaction. The analysis of the heterogeneous crystals showed which ligand sites in the overlayer are the most likely to be changed during the short reaction time, i.e., from which sites the exchange process starts. Surprisingly, only 4 sites out of the 44 possibilities showed occupation by the exchanged ligand (see Figure). Theoretical analysis performed by Häkkinen's group gave insight into the atomistic details of possible reaction mechanisms. Evidence from experiment and theory indicates that the $\text{Au}_{102}(\text{p-MBA})_{44}$ nanoparticle has a thiol

overlayer where almost every thiol ligand site has its own reaction rate due to a highly heterogeneous structure of the overlayer. "The Au₁₀₂(p-MBA)₄₄ nanoparticle has a structure reminiscent of a protein, with a rigid inorganic gold core analogous to the alpha-carbon backbone of a protein [core](#) and chemically modifiable functional groups in the low-symmetry molecular overlayer", says prof. Ackerson. "When ligand exchange reactions are better understood, we hope to fully control the surface functionalization of the Au₁₀₂ and similar water-soluble gold nanoparticles. The implications in biology for a fully controllable synthetic surface the size of a protein are profound", says prof. Häkkinen.

More information: 1. C.L. Heinecke, T.W. Ni, S.A. Malola, V.P. Mäkinen, O.A. Wong, H. Häkkinen and C.J. Ackerson, "Structural and theoretical basis for ligand exchange on thiolate monolayer protected gold nanoclusters", J. Am. Chem. Soc., published online July 21, 2012 (pubs.acs.org/doi/abs/10.1021/ja3032339).

2. P.D. Jadzinsky, G. Calero, C.J. Ackerson, D.A. Bushnell and R.D. Kornberg, "Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution", Science 318, 430 (2007) (www.sciencemag.org/content/318/5849/430.abstract).

3. M. Walter, J. Akola, O. Lopez-Acevedo, P. D. Jadzinsky, G. Calero, C. J. Ackerson, R. L. Whetten, H. Grönbeck, H. Häkkinen, "A unified view of ligand-protected gold clusters as superatom complexes", Proc. Natl. Acad. Sci. (USA) 105, 9157 (2008) (www.pnas.org/content/105/27/9157).

Provided by Academy of Finland

Citation: New structural information on functionalization of gold nanoparticles (2012, August 2)
retrieved 25 April 2024 from
<https://phys.org/news/2012-08-functionalization-gold-nanoparticles.html>

This document is subject to copyright. Apart from any fair dealing for the purpose of private study or research, no part may be reproduced without the written permission. The content is provided for information purposes only.