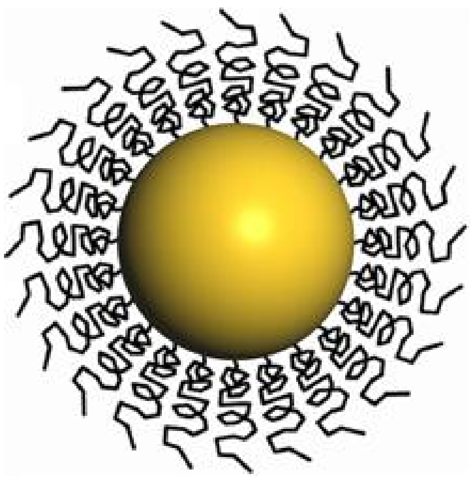
A hot bath for gold nanoparticles

August 2 2011, By Carol Kiely



A schematic diagram shows a gold nanoparticle stabilized with polyvinyl alcohol (PVA) ligands.

Gold nanoparticles, says Chris Kiely, are fast becoming some of the most effective diplomats of the nanoworld.

They facilitate a wide range of chemical reactions between molecules that would not normally interact or would do so only at much higher temperatures.

And in most cases, they effect a single favorable outcome with few, if any, unwanted side reactions.

In short, says Kiely, a professor of materials science and engineering, the nanoparticles are extremely good catalysts.

Conventional methods of preparing gold nanoparticles, however, alter the morphology and catalytic activity of the particles.

Now, an international team of researchers has developed a procedure that enhances the surface exposure of gold nanoparticles and their catalytic activity over a range of reactions.

A new procedure improves on convention

The team reported its results in July in *Nature Chemistry* in an article titled “Facile removal of stabilizer-ligands from supported gold nanoparticles.”

Its members include Kiely and Graham Hutchings, a chemist at Cardiff University in Wales in the U.K., who have studied nanogold together for more than a decade.

“In industry,” says Kiely, “the most common way of preparing gold nanocatalysts is to first impregnate a nanocrystalline oxide support, such as titanium oxide (TiO2) with chloroauric acid. A reduction reaction then converts the acid into metal nanoparticles.

“Unfortunately, this leads to a variety of gold species being dispersed on the support, such as isolated gold atoms, mono- and bi-layer clusters, in addition to nanoparticles of various sizes.”

An alternative technique that allows more precise control over particle size and structure, is to pre-form the gold nanoparticles in a colloidal solution before depositing them onto the support.

The disadvantage to this method is that during fabrication the nanoparticles are coated with organic molecules – ligands – that prevent them from clumping together. Once they are deposited onto a support, these ligands tend to impair the nanoparticle's catalytic performance by blocking the approach of molecules to active sites on the metal surface.

A milder form of ligand removal

Previous methods for stripping away these ligands have involved heat treatments of up to 400 degrees C.

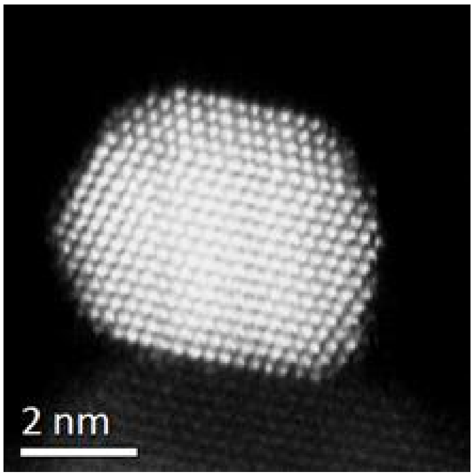
"At these temperatures the morphology of the nanoparticles changes and they begin to coalesce," says Kiely. "There is also significant decrease in their catalytic activity."

The Kiely-Hutchings team developed a milder alternative for removing the ligands from polyvinyl alcohol-stabilized gold nanoparticles deposited on a titanium oxide support – a simple hot water wash.

Graduate student Ramchandra Tiruvalam used Lehigh's aberration-corrected JEOL 2200 FS transmission electron microscope to examine the catalysts before and after washing and to compare them with those that had undergone heat treatment to remove the ligands.

"Hot water washing had very little effect on particle size," says Kiely, who directs Lehigh's Nanocharacterization Laboratory, "and while the particles retain their cub-octahedral morphology, their surfaces appear to become more distinctly faceted. This is presumably due to some surface reconstruction occurring after losing a significant fraction of the protective PVA ligands."

"Heating the samples to 400 degrees C was also effective at removing the ligands but the average particle size increased from 3.7 to 10.4nm," says Kiely. "There was also tendency for the particles to restructure and develop flatter, more extended interfaces with the underlying TiO_2 support."



A micrograph taken by Lehigh's high-angle annular dark field (HAADF) scanning transmission electron microscope (STEM) shows a gold nanoparticle on a TiO_2 support after a hot water wash.

For the oxidation of carbon monoxide to carbon dioxide, catalysts prepared by this colloidal/hot water wash displayed more than double the activity of conventional gold/TiO_2 catalysts. This particular reaction is crucial for the removal of carbon monoxide from enclosed spaces such as submarines and space craft, prolonging the life of fuel cells, and extending the usable lifetime of a firefighter's mask.

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Tiruvalam is now a research scientist with Haldor Topsoe, a catalyst company in Copenhagen, Denmark.

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