

Carborane Thiol-modified Gold Surfaces. A Study and Comparison of Modified Cluster and Flat Surfaces

Tomáš Baše,^a Zdeněk Bastl,^b Zbyněk Plzák,^a Tomáš Grygar,^a Jaromír Plešek,^a and Michael J. Carr^c

^a The Institute of Inorganic Chemistry, 250 68 Řež near Prague, and ^b J. Heyrovský Institute of Physical Chemistry, Dolejškova 3, 182 23 Prague 8, of the Academy of Sciences of the Czech Republic and ^c the School of Chemistry of the University in Leeds, LS2 9JT England, UK;
E-mail: tbase@iic.cas.cz, zdenek.bastl@jh-inst.cas.cz

Both colloidal gold particles and gold films are known for centuries. In the times of the Roman Empire gold colloids were used for decorative purposes. Later, in 1856, Michael Faraday gave the Bakerian lecture on the experimental relations of gold to light. In the context of gold surface chemistry we here present a new study from the areas recognized as monolayer protected clusters¹ and self-assembled monolayers.²

For the first time, we report on carborane thiol modifications of both gold cluster and flat surfaces. Four different *ortho*-carborane thiol derivatives³ were used to modify the surfaces of gold nanoparticles and macroscopic gold films. The novel materials engendered from these modifications are extraordinarily stable species with surfaces that support self-assembled monolayers of 1-(HS)-1,2-C₂B₁₀H₁₁, 1,2-(HS)₂-1,2-C₂B₁₀H₁₀, 1,12-(HS)₂-1,12-C₂B₁₀H₁₀, and 9,12-(HS)₂-1,2-C₂B₁₀H₁₀. Surprisingly, characterization of these materials revealed that a number of molecules of the carborane thiol derivatives are incorporated inside the gold nanoparticles (Figure 1). We studied this structural feature using a number of techniques, including X-ray photoelectron spectroscopy (XPS), and UV-Vis and IR spectroscopies.

Thermal desorption experiments show that carborane molecules detach and leave the nanoparticle surface mostly as 1,2-C₂B₁₀H₁₀ clusters, leaving sulfur atoms bound to the gold surface. The surfaces of both the gold nanoparticles and the flat gold films are densely packed with carborane thiolate units. One carborane cluster molecule occupies an area of 6-7 surface gold atoms of the nanoparticle and 8 surface gold atoms of the flat film. XPS data showed that molecules of 1,12-(HS)₂-1,12-C₂B₁₀H₁₀ bind to the flat gold surface with only one half of the thiol groups due to the steric demands of the icosahedral carborane skeleton. Modification of flat surfaces is shown schematically in Figure 2. Electrochemical measurements indicate complete coverage of the gold surfaces modified with the carborane thiol molecules.

The major aims of this study are to provide a detailed view of the structural features of the carborane thiol-modified gold nanoparticles, discuss the gold cluster-flat surface analogy, and investigate the bonding of the carborane thiol derivatives to the gold surfaces. The described materials may find use as tiny dielectric layers with oriented inherent dipole moment in capacitors, or as building blocks for another “bottom-up” modification for further studies of biological as well as technical character.

This work is a part of Řež-Leeds Anglo-Czech Polyhedral Collaboration (ACPC) and was supported by the following grants of the GAAV: B4032302, K4040110, T400400413 and the UK EPSRC: L/49505, R/61949.

References:

- ¹ M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, R. Whyman, *J. Chem. Soc., Chem. Commun.*, **1994**, 801.
- ² R. G. Nuzzo, D. L. Allara, *J. Am. Chem. Soc.*, **1983**, 105, 4481.
- ³ J. Plešek, S. Heřmánek, *Collect. Czech. Chem. Commun.* **1980**, 45, 1775; J. Plešek, S. Heřmánek, *Collect. Czech. Chem. Commun.* **1981**, 46, 687.

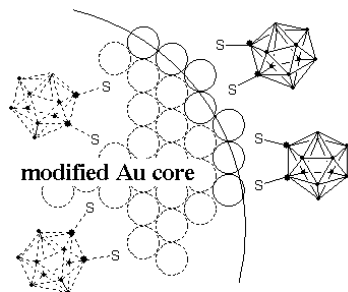


Figure 1

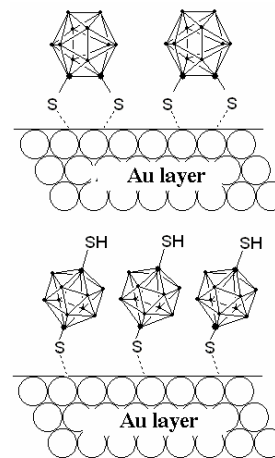


Figure 2