Carborane Thiol-modified Gold Surfaces.

A Study and Comparison of Modified Cluster and Flat Surfaces

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- Nanosize gold clusters (MPCs)
- Flat gold surfaces (SAMs)

Motivation

- 1. Electronic applications going towards capacitors with well defined monolayers of carborane molecules as dielectrics.
- 2. Investigation of molecules with high inherent dipole moment and almost spherical geometry assembled on flat gold surface.

Preparation of Au particles

AuCl₄⁻ (aq. sol.)

$$\downarrow$$
 (octyl)₄N⁺Br⁻ (Tol)
(octyl)₄N⁺ AuCl₄⁻ (Tol)
 \downarrow RSH
NaBH₄ (aq. sol.)
Au particle with modified surface

Brust, et al. Chem. Commun., 1994, 801-802

1

Thiol derivatives of $o-C_2B_{10}H_{12}$

- spherical (icosahedron)
- quasi aromatic
- more acidic then their alkane counterparts
- dipole moment
 (o-carborane ~ 4.5 D)



Size of Au particles

Average diameter was in the range from 12.3 to 2.8 nm.



SH

Desorption experiments

- in heated inlet GC/MS

Questions:

- 1. How do the molecules escape?
- 2. What is the coverage density?



Density of the carborane molecules on the particle surface.

6-7 surface gold atoms occupied by one carborane cage

Two types of samples for further investigation

- 1. Samples with the modified surface.
- 2. Samples after desorption.

XPS measurements

Observation: Au (bulk), S, Boron (carborane cage), Carbon (carborane cage)

Atomic concentration B to S

Diameter / nm	В	S
5.2	10	2.1



"Preliminary summary"

- 1. The surface is densely packed!
- 2. The desorbed samples are stable
- 3. The desorbed samples contain carborane molecules.
- 4. Two types of sulphur atoms were observed in the desorbed samples

Solid state investigation.



Colloidal solution UV-Vis (electronic) spectra



Inset: Intensity of the plasmon band is qualitatively indicative of size of the particles.

6

5

Flat surface

crystalline surface with large {111} areas

Contact angles of water

Sample	Bare Au	2 -SAM	3 -SAM	4 -SAM
angle	74 °	88°	57°	53°

The values ³ demonstrate different character of BH, CH vertices.



R. G. Nuzzo, D. L. Allara J. Am. Chem. Soc., 1983, 105, 4481

A. A. Dameron, et al. *J. Am. Chem. Soc.*, **2005**, 127, 8697-8704

7

Surface density (XPS): 8 surface Au atoms occupied by one carborane cage.





Summary: Cluster species:

- 1. Surface is densely packed. 6-7 surface gold atoms are occupied by one CB molecule.
- 2. Some CB cages appear to be incorporated inside the gold cores.
- 3. The surface molecules escape from the surface as $C_2B_{10}H_{10}$ isotopic clusters.
- 4. Sulphur atoms remain on the surface after the desorption experiments.

Flat surfaces:

- 5. Surface density on Au films: 8 surface gold atoms occupied by one CB molecule.
- 6. "Gold electrode" with passivated surfaces.
- 7. $1,12-(SH)_2-1,12-C_2B_{10}H_{10}$ forms a field of thiol groups.
- 8. The SAMs express high stability of the species.

Base, et al. Langmuir, 2005, 21, 7776-7785

Conclusion:

Carborane thiol derivatives with high inherent dipole moment assembled into monolayers on Au films exhibit interesting properties that might become important in potential nanoelectronic devices.

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