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

\[
\text{AuCl}_4^- \quad \text{(aq. sol.)} \\
\downarrow (\text{octyl})_4\text{N}^+\text{Br}^- \space (\text{Tol}) \\
(\text{octyl})_4\text{N}^+ \text{AuCl}_4^- \space (\text{Tol}) \\
\downarrow \text{RSH} \\
\text{NaBH}_4 \quad \text{(aq. sol.)} \\
\text{Au particle with modified surface}
\]


Thiol derivatives of \(\alpha\text{-C}_2\text{B}_{10}\text{H}_{12}\)

- spherical (icosahedron)
- quasi aromatic
- more acidic than their alkane counterparts
- dipole moment (\(\alpha\text{-carborane} \approx 4.5 \text{ D}\))

Size of Au particles

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

XPS measurements

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

Atomic concentration B to S

<table>
<thead>
<tr>
<th>Diameter / nm</th>
<th>B</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>10</td>
<td>2.1</td>
</tr>
</tbody>
</table>

XP spectra of S 2p electrons

Two types of samples for further investigation
1. Samples with the modified surface.
2. Samples after desorption.
“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.

Proposed model:

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

crystalline surface with large \{111\} areas

Contact angles of water

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bare Au</th>
<th>2-SAM</th>
<th>3-SAM</th>
<th>4-SAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>angle</td>
<td>74 °</td>
<td>88 °</td>
<td>57 °</td>
<td>53 °</td>
</tr>
</tbody>
</table>

The values demonstrate different character of BH, CH vertices.

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

Electrochemical investigation:
Au electrode: bare versus modified surface


XP spectra of S 2p electrons

![S 2p spectra](image)

- **S 2p**
- **Au₂S**

**BINDING ENERGY (eV)**

**INTENSITY (arb.units)**

1. modified Au core
2. modified Au core
3. Au film
4. modified Au core
5. thiol

- thiolate
- Au film
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 \( \text{C}_2\text{B}_{10}\text{H}_{10} \) 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.
7. 1,12-(SH)\(_2\)-1,12-C\(_2\)B\(_{10}\)H\(_{10}\) forms a field of thiol groups.
8. The SAMs express high stability of the species.

Conclusion:

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

Research team:

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