Carboranethiol-Modified Gold Surfaces. A Study and Comparison of Modified Cluster and Flat Surfaces

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Received April 27, 2005. In Final Form: June 21, 2005

Four different carboranethiol derivatives were used to modify the surfaces of gold nanoparticles and flat 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-C8B10H14, 1,2-(HS)-1,2-C8B10H14, 1,-12-(HS)-1,12-C2B10H10, and 9,12-(HS)-1,2-C8B10H14, respectively. Surprisingly, characterization of these materials revealed that a number of molecules of the carboranethiol derivatives are incorporated inside the nanoparticles. This structural feature was studied using a number of techniques, including X-ray photoelectron spectroscopy (XPS), UV–vis, and IR spectroscopies. Thermal desorption experiments show that carborane molecules detach and leave the nanoparticle surface mostly as 1,2-C8B10H14 isotopic 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 carboranethiolate units. One carborane cluster molecule occupies an area of six to seven surface gold atoms of the nanoparticle and eight surface gold atoms of the flat film. XPS data showed that molecules of 1,12-(HS)-1,12-C2B10H10 bind to the flat gold surface with only half of the thiol groups due to the steric demands of the icosahedral carborane skeleton. Electrochemical measurements indicate complete coverage of the modified gold surfaces with the carboranethiol molecules.

Introduction

The modification of the surfaces of gold nanoparticles and macroscopic gold surfaces represents a chemical tool frequently used in the preparation of materials with properties that reflect a transitional phase between the molecular and bulk level. Generally, there is a high interest in the fabrication of such materials for application in fields ranging from those in biological to technical sciences and other related areas.1–5 These materials, which are called monolayer protected clusters (MPCs)6–8 and self-assembled monolayers (SAMs),9–15 have so far been studied especially with a series of alkanethiol compounds. Both MPC and SAM systems remain at the center of interest for many research groups due to their unique and tunable properties effectuated by their small dimensions and adjustable chemical composition.

Alkanethiol species are described in the literature as binding to gold surfaces as alkanethiolate units.14 The adsorption of these thiol derivatives provides highly ordered monolayer films with well-defined structure, thickness, and wetting properties. It was shown that the alkanethiolate moieties pack densely on gold surfaces of both nanoparticles and flat coatings.7,9,10 The molecular packing of the films has been studied using several techniques, e.g., electron microscopies, XPS, and infrared spectroscopy. On X-ray exposure, the alkanethiolate units may connect together to form disulfides.16

Herein we report a study of Au surfaces modified with carboranethiol molecules, which are substantially more acidic17 than their alkane counterparts and, in some cases, possess a distinct and inherent molecular dipole moment.18 The almost spherical shape and quasi-aromatic character

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Carboranethiol-Modified Gold Surfaces

Langmuir, Vol. 21, No. 17, 2005

Figure 1. (a) Idealized space filling schematic of carborane clusters centered on 6-fold surface units of gold atoms. Dimensions: A, ~ 7 Å; B, 2.8 Å. The real geometry of carborane clusters (dashed circles) is approximately that of a regular icosahedron. (b) Side-on view of the carborane molecules bound to the substrate surface via one and two B–Au links, respectively. Hydrogen atoms associated with the carborane have been omitted for clarity.

of carboranethiols make these species also rather unique. We characterized these carborane–thiol MPCs and SAMs using a number of methods, which led to the revealing of several significant differences from the alkanethiol-modified gold surfaces reported previously. On the basis of these revelations we here propose a special model for the new nanoparticle species that has some carboranethiol derivatives located inside the metal core as well as on its surface. The gold nanoparticles, which represent a colloidal system, can be viewed as a model for the modified flat films that were investigated for electronic applications exploiting preorganized monolayers of compounds with a distinct dipole moment. These monolayers may have interesting properties when used as dielectric layers in capacitors. Both modified Au colloids and Au films are described here with respect to their complementary character to each other. The major aims of this study are to provide a detailed view of the structural features of the carboranethiol-modified gold nanoparticles, discuss the gold cluster–flat surface analogy, and investigate the bonding of the carboranethiol derivatives to the gold surfaces. Moreover the present study introduces an interesting basis for comparison with the previously studied alkanethiol-modified gold surfaces.

As a preliminary view, we wish to show a possible packing of a flat gold surface with carboranethiol derivatives. Figure 1 is a schematic representing the approximate area of gold surface that is covered per carborane cluster along the Au(111) lattice plane. A hexagonal overlayer (dashed circles) is placed on the gold(111) surface,19–21 with one carborane cluster per seven surface gold atoms. This model is discussed further at later stage in this article with respect to the experimental results and the similarities between cluster and flat gold surfaces.

Experimental Section
Carboranethiol Derivatives and Other Materials. Carboranethiol derivatives 1-(HS)-1,2-C2B10H11 (1), 1,2-(HS)2-1,2-C2B10H12 (2), 1,12-(HS)2-1,12-C2B10H12 (3), and 9,12-(HS)2-1,2-C2B10H10 (4) (Figure 2) were prepared according to the procedures reported in the literature.17–22 All these thiol compounds were purified by both sublimation and crystallization techniques as described in the literature, and were isolated in a crystalline form. All compounds were found to be >98% pure as verified by

The following techniques: nuclear magnetic resonance spectroscopy (1H and 13C NMR), gas chromatography–mass spectrometry (GC–MS), elemental analysis (EA) and induced coupled plasma (ICP) spectrometric analysis.

HAuCl4·3H2O (99.9%) was purchased from Aldrich. 1,2-C2B10H12 (99.0%) and 1,12-C2B10H12 (99.0%) for the synthesis of the thiol derivatives were received from Katchem Ltd. (Czech Republic). NaBH4 was received from OY Finn. Chem. Ltd. (Finland). Gold(1) sulfide (Au2S) (99.9%) was received from Aldrich and gold(III) sulfide (Au2S3) (99.9%) from Alfa Aesar (Germany). All solvents were purchased as analytical grade from Lachema Ltd. (Czech Republic). Toluene was additionally distilled on a Vigreux Column. For UV–vis measurements methanol of HPLC quality from Aldrich was used.

Self-Assembly of the Carboranethiol Derivatives on Gold Nanoparticles. The established two phase liquid–liquid method28 was used. This method, which generally leads to gold nanoparticles soluble in nonpolar environments, was first described in 1994 by Brust, Schiffrin, and co-workers.

Preparation. HAuCl4·3H2O (355.3 mg; 0.9 mmol) was dissolved in 30 mL of distilled water and added to a vigorously stirred toluene solution (90 mL) of tetraoctylammonium bromide (2.1876 g, 4 mmol). The reaction mixture was stirred for 2 h; all tetrachloroauric anion was transferred into the toluene phase, which subsequently turned a deep red color. The o-carboranethiol derivative (1 or 2) was added in solid form as one portion (for amount see Table 1) followed by the linear addition over 10 min of a freshly prepared aqueous solution (20 mL) of sodium tetrahydroborate (378.4 mg, 10 mmol). The toluene phase turned a deep violet color and gas evolution was observed. The reaction mixture was stirred for 5 h at 30 °C in an oil bath. The toluene phase was separated and the solvent evaporated under reduced pressure until approximately 10 mL of the volatiles remained in the flask. This solution was mixed with methanol (200 mL) and stored in the freezer (−20 °C) over two nights. During this time a black waxy material precipitated. The excess solvent was decanted and the solid was additionally dried under reduced pressure. The crude product was subsequently dissolved in a small amount of acetone and purified by chromatography on a silica gel column with acetone as the eluting agent. Thus, the tetraoctylammonium bromide, which was used as the transferring reagent, was completely removed from the surface of the gold nanoparticles. All samples had the appearance of black waxy materials before chromatography and that of a loose black-gold powder after purification. The smaller the amount of the thiol used in the reaction, the more aureate the appearance of the product observed. Typically 60–80 mg of the pure product was obtained in one batch. The pure products were soluble in acetone and methanol, giving violet colored colloidal solutions. This procedure failed with 4; under the same conditions only a gold sponge was obtained.

Desorption. Desorbed samples were prepared by heating MPC materials under vacuum (~ 0.1 Torr) in a heated inlet placed in a GC oven of a GC–MS instrument. For details concerning the GC–MS instrument see “Heated Inlet GC–MS” in General Methods. Desorption process was monitored by MS analysis of the gaseous phase evolving from the samples. The time dependency of the desorption experiments, presented in Figures 5 and 6, was obtained by using the following experimental setup: 35 °C (0 min), linear increase of temperature by 20 °C/
min up to 280 °C (12.25 min), and 280 °C kept for additional 17.75 min. These desorption conditions were the same for preparation of all desorbed samples. The desorbed species were soluble in acetone and methanol, giving dark violet colored colloids.

Preparation of Au Films. Au films were prepared by the evaporation of gold (99.99%, Safina Ltd., Czech Republic) onto freshly cleaved mica wafers (1.5 × 1.5 cm) at a substrate temperature of ~300 °C under a vacuum of ~3–4 × 10⁻⁸ mbar. Gold was evaporated from a resistively heated tungsten boat with a deposition rate of 0.5 Å/s. The thickness of the Au films, monitored with a quartz crystal oscillator, was typically 140 nm. The deposition was carried out in a Pfeiffer PLS 570 high-vacuum evaporator equipped with an oil-free pumping system and a liquid N₂ Meissner trap (with a normal base pressure of about 1 × 10⁻⁸ mbar). After deposition, the wafers were left to cool to 30 °C, and the vacuum chamber was filled with nitrogen of technical purity. By flame annealing Au(111) terraces can be easily obtained.

The following procedure was used: the Au film was placed into the flame until dark red glowing appeared. The film was taken out for ~30 s and the whole procedure was repeated three times. The Au film samples were stored under argon atmosphere at room temperature for 1 h before use for further experiments.

Using atomic force microscopy (MM AFM, Nanoscope IIIa, Digital Instruments), Au(111) terraces of about 100–200 nm in diameter were observed separated by rough boundaries.

Table 1. Data for the above Experimental Procedure

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<td>1:0.75</td>
<td>1:1</td>
<td>1:1.25</td>
<td>1:1</td>
</tr>
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<td>2-MPCs (2)</td>
<td>2-MPCs (3)</td>
<td>2-MPCs (4)</td>
<td>2-MPCs (5)</td>
<td>2-MPCs (6)</td>
<td>1-MPCs (7)</td>
</tr>
</tbody>
</table>

* M: the amount of the thiol derivative used in the synthesis reaction. Ratio: mole ratio of HAuCl₄·3H₂O:thiol derivative.

Figure 3. TEM picture of the 2-MPCs (6) and the desorbed sample (top right inset) with the inset electron diffraction pattern (top left) and histogram showing size distribution of the nanoparticles (bottom right).

Figure 4. Relation between the average particle diameter (\(D/\)) and the mole ratio \(2:HAuCl_4\) used in the synthesis reaction.

Figure 5. Total ion current profile of the desorbing molecules from 2-MPCs, obtained with a temperature program starting at 35 °C (0 min) followed by 20 °C/min increase to 280 °C (12.25 min), where it was held to the end of analysis.

Figure 6. Desorption curves of samples obtained in the synthesis reaction with the mole ratio HAuCl₄·3H₂O:2 (a) 1:0.1–1.1, (b) 1:1.15 and (c) 1:1.35.

For comparison, we also used commercially available gold films from Dr. Dirk Schröer (Arrandee, Werther, Germany). These Au films were ~250 nm thick deposited on a borosilicate glass with a chromium interlayer (~2.5 nm) for better adhesion of gold to glass. The flame annealing was done in the same way as described above.

Self-Assembly of the Carboranethiol Derivatives on Flat Gold Surfaces. There are two procedures that we used to obtain SAMs of the thiol derivatives on Au films. First: The \(\alpha\)-carboranethiol derivatives were adsorbed onto the gold flat surface by the immersion of freshly prepared and hydrogen-flame annealed gold coatings in 10 mL of acetone solution of \(2\) (0.21 g; 10 mmol) and subsequent multiple rinsing with pure solvent. Second: The freshly prepared hydrogen-flame annealed gold coatings were exposed to vapors of the volatile thiol derivatives \(3\) or \(4\) overnight. The excess of the thiol derivative deposited on the Au surface (observed in XP spectra) was removed by rinsing the wafer with pure hexane. The latter procedure eliminates any need for long exposure of the Au film to a solvent and thus significantly reduces adsorption of impurities from the solvent. Additionally, we found that the thiol derivative \(3\) reacts with acetone solvent to produce undesirable side-products that
are organic in composition and that unwantedly adsorb to the Au film.

**General Methods. Transmission Electron Microscopy.** TEM images were recorded on a Philips EM 201 with an accelerating voltage of 80 kV. Samples were prepared by dropcasting single drops from a 1 mg/mL gold nanoparticle in acetone solution onto standard carbon-coated (20–30 nm) Formvar films on copper grids (600 mesh) followed by evaporation in air. Process Diffraction software was used for analyzing selected area electron diffraction patterns. The data were assigned according to the JCPSD PDF-2 database.

**Heated Inlet GC—MS.** MS experiments were performed on a MAGNUM GC—MS ion trap system (Finnigan MAT). A heated inlet device setting developed by Spectronex AG, Basel, Switzerland, was used. The gaseous desorbed molecules, vaporized in a high-temperature environment of the GC oven, were transported into the ion trap by using the pressure gradient between the sample crucible (~10−1 Torr) and the ion trap manifold (~10−5 Torr). Samples were introduced as solids with typical quantities 15–40 mg. The transfer line was heated to 280 °C. The ion trap operated in electron ionization (EI) mode and was tuned using default software settings (Magnum 2.4, Finnigan MAT) to obtain suitable mass calibrations, filament emission current, multiplier voltage, and AGC (Automatic Gain Control) settings. The total loss of mass during desorption experiments was determined using microbalances.

**X-ray Photoelectron Spectroscopy.** The photoelectron spectra were measured using an ESCA 310 (Scintia, Sweden) electron spectrometer equipped with a high-power rotating anode, wide-angle quartz crystal monochromator, and a hemispherical electron analyzer. The analyzer was operated in a fixed-angle transmission mode. Al Kα radiation was used for electron excitation. All measurements were performed with an electron analyzer pass energy of 300 eV and an analyzer entrance slit of 0.8 mm. With these settings the full-width at half-maximum (fwhm) of Au 4f7/2 photoemission line of bulk Au standard was 0.65 eV. A drop of the metal colloid solution in acetone was deposited on a clean Cu surface and dried. The spectra were recorded at room temperature. The background was the bare gold substrate. The results were confirmed by attenuated total reflection (Smart Performer accessory) IR measurements with ZnSe crystal using the same spectrometer.

**Electrochemical Measurements.** Voltammetric curves were obtained using a μAutolab potentiostat (EcoChemie, The Netherlands). A three-electrode cell was used that consisted of a saturated calomel reference electrode (SCE), Pt-plate counter electrode, and a working electrode. In the case of nanoparticle samples and gold sulfides, the working electrode was a paraffin-impregnated graphitic rod and the samples were deposited mechanically on the basal surface of the rod (voltammetry of microparticles); An aqueous solution, deaerated with flushing with N2 gas, of sodium acetate—acetic acid (total acetate 0.2 M, acetate-to-acetic acid 1:1) was used as the electrolyte. In the case of Au-films (bare or modified with 2, 3, or 4) on mica, the plates were used as a working electrode and they were connected to the potentiostat with a crocodile clip; the measurements were performed in a N2(g) flushed—deaerated aqueous solution of K2[Fe(CN)6] (1 mM), K3[Fe(CN)6] (1 mM), and KCl (100 mM). The scanning was performed from the open-circuit potential toward negative potentials and cycled between −0.5 and +0.8 V/SCe using linear polarization at a scan rate of 100 mVs.

**Elemental Analysis.** Elemental analysis of the MPC materials were done using an iCP-OES spectrometer, made by Hilger-Thermo Electron Corp. with the IRRIS Intrepid II XSP, equipped with an ultrasonic CETAC Inc. nebulizer, model U5000 AT. The measurements were done in axial plasma mode.

**Contact Angles.** Contact angles of water were measured at 22 °C on a CAM-MICRO contact angle meter. The following technique was used: Approximately, a 1 mL drop of distilled water was formed at the end of a needle attached to a 50 mL syringe. The needle was lowered until the drop touched the surface, followed by the raising of the needle. The drop detached itself from the needle tip. An average of six measurements of stable static drops was done for a bare gold surface and gold surfaces modified with 2, 3, and 4.

### Results and Discussion

**Size of the Modified Gold Nanoparticles.** The structural questions that concern the dimensions and elemental composition of modified gold nanoparticles are fundamentally related to the ultimate understanding of these materials. Using the two phase liquid–liquid method we prepared a series of nanoparticles with average diameters from 2.8 to 12.3 nm (Table 2). The gold cores were modified with 2 and, for comparison, in one case with 1. TEM investigations provided information about the size distribution of the gold cores (Figure 3) and to follow the dependency of the average core size on the molar ratio HAuCl4·3H2O: 2 (Figure 4). It is shown that the average size of the nanoparticles decreases with the

<table>
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<th>Clusters Product</th>
<th>Dnm</th>
<th>N Au%</th>
<th>Dm%</th>
<th>λ522/nm</th>
</tr>
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<tr>
<td>2-MPCs (1)</td>
<td>12.3(2.5)</td>
<td>57680</td>
<td>15</td>
<td>538</td>
</tr>
<tr>
<td>2-MPCs (2)</td>
<td>5.2(1.4)</td>
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<td>35</td>
<td>3.35</td>
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<tr>
<td>2-MPCs (3)</td>
<td>4.7(1.3)</td>
<td>3220</td>
<td>35</td>
<td>3.922</td>
</tr>
<tr>
<td>2-MPCs (4)</td>
<td>4.4(1.2)</td>
<td>2680</td>
<td>40</td>
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<td>5.1520</td>
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<td>2-MPCs (6)</td>
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<td>680</td>
<td>15</td>
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<tr>
<td>1-MPCs (7)</td>
<td>4.7(0.8)</td>
<td>3220</td>
<td>45</td>
<td>4.8158</td>
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</table>

* D: average particle diameter with standard deviation in parentheses (TEM). N_Au: theoretical number of Au atoms in the nanoparticle. F: surface fraction of Au atoms. Dm: weight loss during the desorption. λ522: wavelength at the maximum of the plasmon band.

9512 at 4000–2000 cm−1. Self-assembled monolayers of 2 and 3 on Au-films were measured using specular reflection. These experiments were carried out with an 80° fixed angle using a Nicolet Nexus 670 FTIR spectrometer (1024 scans, 2 cm−1 resolution). Thermo Nicolet Corporation, Madison, USA. The background was the bare gold substrate. The results were confirmed by attenuated total reflection (Smart Performer accessory) IR measurements with ZnSe crystal using the same spectrometer.

### Table 2. Characteristics of 2- and 1-Monolayer Protected Clusters


increasing amount of the dithiol used in the synthesis. The approximate number of Au atoms per one nanoparticle and the corresponding surface fraction is shown in Table 2. These data were calculated with respect to the idealized spherical geometry of the nanoparticles and assuming that the \( \text{Au} - \text{Au} \) bond distance for bulk gold at \( \approx 20 \, ^\circ \text{C} \) is 288 pm, which is in agreement with the calculated distance for the bulk gold based on uniform 12-coordination for the gold atoms. We observed that the studied materials consisted also of some bulky composites which appeared in the desorbed samples (top right inset in Figure 3), partly due to the larger tendency of the “naked” nanoparticles to aggregate. The electron diffraction patterns characteristic of polycrystalline nanoparticles (see top left inset in Figure 3) and, on occasions, for microcrystalline parts of the desorbed samples, were observed. The basic analysis of these diffraction patterns were completely in agreement with data for bulk gold in the database. The phenomenon of aggregation of the naked gold clusters is also observed in XP and UV–vis spectra. This is demonstrated for instance in the XPS spectra of Au (5d 6s) electrons in Figure 7. Besides the size, the disproportionately large size of the bulky composites, it would be misleading to determine the average size of the nanoparticles in the desorbed species and, therefore, we studied these samples from a qualitative point of view only.

**Desorption of the Molecules from the Cluster Surfaces.** We were able to make some qualitative assessments of the desorption process by using an electron ionization mass spectrometric technique. The carborane molecules exhibit extraordinarily high stability toward heating—up to 400 °C unaffected. Therefore, it was reasonable not to consider their decomposition during the desorption experiments. This was confirmed by mass spectra data as discussed further in this paragraph. Using the technique of electron ionization we identified the species escaping from the gold surface as \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S} \) and \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S} \). These results indicate that sulfur atoms remain on the gold surface of the desorbed nanoparticles. This feature was later verified in XPS measurements (see Tables 3 and 4 and Figure 8). The desorbed samples have a high stability and are redissolvable even after several weeks of storage in a dry solid state at room temperature. This high stability can only be rationally explained by the presence of the sulfur atoms that remain on the nanoparticle surface after desorption. Analyses of the time desorption curves for 2-MPCs, made using different concentrations of carbanethiol, revealed either one or two desorption peaks. Figure 5 shows a typical desorption curve with two such peaks (I, II) and respective mass spectra indicating the identity of the molecules escaping from the surface. Fragmentation pathways that are typical of the starting carbanethiol derivatives are observed in both inset spectra. However, the first spectrum, representing molecules escaping from the surface at lower temperature (the first desorption peak), has a dominating isotopic cluster mass-envelope with the most intensive peak at \( m/z \) 174, which corresponds to an isotopic form of the \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S}^+ \) radical cation and indicates that some sulfur atoms may also escape from the surface. The second spectrum, which is characteristic of the molecules that desorb from the surface at higher temperature, exhibits a dominating isotopic cluster mass-envelope with the most intensive peak at \( m/z \) 142, which belongs to an isotopic form of the \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S}^+ \) radical cation. Notably, the higher mass fragment desorbs from the surface at lower temperature. Further investigations revealed that the time desorption curves depend on size of the nanoparticles. In a series of experiments, in which the mole ratio \( \text{HAuCl}_4\cdot3\text{H}_2\text{O} \): 2 was in the range from 1:0.1 to 1:1.1, only the second desorption peak (II) was observed. When the ratio was bigger than 1:1.1 the first peak (I) appeared in the spectra and grew in intensity as the amount of 2 increased. This trend is illustrated in Figure 6 which shows three desorption curves. These results suggest that at a limiting excess of 2 over Au, the carborane dithiol is bound to the gold surface by just one \( \text{B} - \text{S} - \text{Au} \) interaction, the second \( \text{B} - \text{S} - \text{H} \) remaining free. On desorption, this semibonded dithiol escapes as the \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S} \) moiety (the first peak), whereas the second peak corresponds to the doubly bonded 2, which is desorbed as \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S} \) (“carbonyne”). This hypothesis also explains why the heavier \( \text{C}_2\text{B}_{10}\text{H}_{2}\text{S} \) cluster detaches from the gold surface at a lower desorption temperature, and its prevalence at higher ratios of 2: Au. Further evidence supporting this hypothesis is in the fact that the monothiol derivative 1 is desorbed from the 1-MPC material surface just as a \( \text{C}_2\text{B}_{10}\text{H}_{10}\text{S} \) at the same temperature as the first desorption peak for 2-MPCs.

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Table 3. Elemental Concentrations As Determined from XPS Analysis of Colloids and Au Films Modified by Carboranethiols (Atomic Concentrations)\(^a\)

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<th>C(_{15})</th>
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<td>2.0</td>
<td>2.1</td>
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<td>6.7</td>
<td>3.4</td>
<td>1.9</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>AuS ( \delta )</td>
<td>1</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AuS ( \delta_2 )</td>
<td>2.3</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \( D \): average particle diameter (TEM). C\(_{12}\): carbon atoms from hydrocarbons, C\(_{15}\): carbon atoms from carboranes. * These values also contain contribution from C–OH impurities.

molecules on a flat gold surface and the experimental results for packing on a curved gold surface are similar. Indeed, it was found that the larger the nanoparticle was, the closer the number of gold surface atoms occupied by one carboranethiol molecule approximated to seven—the idealized number of atoms for a flat gold surface. It is worthwhile to compare 2-MPCs (3) with 1-MPCs (7) where the average diameter of the nanoparticles is the same for both samples (see Table 2) and we may expect approximately the same surface area. The desorbed mass is bigger for 1-MPCs (7) than for 2-MPCs (3) (see Table 1), which indicates a generally higher packing density of molecules on the gold surface. This difference is caused by the dissimilar steric demands of the mono- and dithiol derivatives; dithiol derivative 2 requires more space, and hence its surface density is lower.

**XPS Measurements.** XPS allowed us to study further the MPCs described above as well as the desorbed samples, and to compare the data with that obtained for SAMs of the carboranethiol derivatives on surface of flat gold films. There were several features observed in the XPS data, which significantly contributed to our understanding of the MPC materials. To avoid confusion, it is best to discuss the XPS data in two parts: first, the MPC materials. To avoid confusion, it is best to discuss the XPS data in two parts: first, the MPCs described above as well as the desorbed samples, and second, the SAMs of 2, 3, and 4 on flat gold films.

The results from the XPS elemental analysis of the nanoparticle samples are summarized in Table 3. A good agreement between the measured chemical composition of the carboranethiol molecules and its nominal stoichiometry was observed. Conversely, the data obtained for Au do not correspond to the actual number of Au atoms. This is due to the attenuation of the Au 4f photoelectrons in the nanoparticle and adsorbed molecules of the thiol derivatives 2 or 1. The spectra of C 1s electrons are composed of two components; the first belonging to carbon from carborane clusters (CCB), and the second belonging to carbon from hydrocarbon species (CHC), the latter most likely being a manifestation of surface contamination from solvents used in synthesis. The measured core level binding energies and corresponding fwhm are displayed in Table 4. The Au 4f core levels are shifted with respect to carbon from hydrocarbon species (CHC), the latter most likely being a manifestation of surface contamination from solvents used in synthesis.
to the bulk value toward higher binding energy by 0.13 eV for the sample with average particle size $d \approx 5$ nm and by 0.19 eV for the sample with $d \approx 2.6$ nm. These shifts can be attributed to modifications of particle electronic structure by size effects and by the bonding of a fraction of Au atoms to sulfur. The observed increase in fwhm of the Au 4f$_{7/2}$ line with decreasing particle size is consistent with this explanation. The measured binding energy of S 2p$_{3/2}$ electrons, 162.7 $\pm$ 0.1 eV, is by 0.7 eV higher than the value reported in the literature for alkane thiols on planar gold surfaces. This indicates lower electron density on S atoms in the thiolate moieties on the gold nanoparticle. A feature located at 167 eV belonging to partially oxidized sulfur was not observed even after a long period of exposure to air. This demonstrates high stability of the prepared MPC materials. In the XPS measurements, we observed a surprisingly high amount of carborane molecules that remained associated with the desorbed samples. A peak representing the binding energy of B 1s electrons typical for carborane clusters was observed in the spectra of these samples. Taking into account the total loss of the dense carboranethiol coverage from the nanoparticle surface known from the desorption experiments, we reasoned that some molecules of 2 are inside the gold cores. Other methods used to study the desorbed MPC, which are discussed in more detail in subsequent pages, also seem to verify our hypothesis of the location of carboranethiol molecules within the gold cluster. In the desorbed samples of 2-MPCs, in which we expect to find just one type of sulfur atoms corresponding to a form of surface gold sulfide, we found instead two different types. Of these two types, one was the thiolate sulfur of the starting nondesorbed 2-MPCs and the second was shifted toward lower binding energy, indicating a higher negative charge on these these (Figure 8-2). We predicted this second type of sulfur to be observed in the XP spectrum of the desorbed sample as a result of the desorption process, and we assigned it to be the sulfur that remains on the surface of the nanoparticles after desorption of the carborane moieties. Comparison of the binding energies, associated with the surface sulfur atoms and sulfur atoms from gold sulfides, did not reveal many similarities. The desorbed samples and gold sulfides differ in electronic structure, which may cause the observed difference in binding energies of S 2p. Nevertheless, it occurred to us that further comparison of gold sulfides and the desorbed samples might be helpful and we later revealed very good agreement between Au$_{1}$S and the desorbed sample in electrochemical behavior (see Figure 11). The spectra in the valence band region, which are dominated by emission from Au 5d electrons, and the spectra of [Au$_{1}$Cl$_{2}$(PPh$_{3}$)$_{3}$]Cl$^{-}$- and Au$_{1}$Cl, included for comparison, are displayed in Figure 7. As expected on the basis of the results obtained with supported gold nanoclusters, an observation was made for the colloidal particles of a decrease in the splitting of the Au 5d band as well as the bandwidth with decreasing of the average size of the nanoparticles. It is known that the splitting of the Au 5d band, which is equal to 1.4 eV for a free Au atom, increases roughly linearly with the number of atoms in the particle up to 2.9 eV for bulk Au. The observation in Figure 7 is that heating of the samples results in an increase of both the 5d splitting and the bandwidth, which is indicative of an aggregation of the nanoparticles after desorption.

The self-assembled monolayers of the thiol derivatives 2, 3, and 4 on Au films were investigated and compared with each other. The data also offer an opportunity to compare the SAMs with the MPCs. Figure 8 shows the XP spectra of S 2p electrons. The thiolate sulfur atoms of the derivative 4 bound to Au film has a lower binding energy by 0.5 eV than that of the derivative 2. An explanation of this shift is obvious when considering the electron densities at different vertexes of the 1,2-C$_{2}$B$_{10}$H$_{12}$ cluster compound. Boron atoms in positions 9 and 12 have considerably higher electron density than carbon vertexes 1 and 2. The XP spectrum of S 2p electrons of the 3-SAM on Au film is composed of two components; one represents the thiolate sulfur atoms that adhere the carborane cluster to the surface, and the second represents the sulfur atoms from free thiol groups. The binding energy of S 2p electrons of the free thiol group is shifted toward higher value by 1.5 eV in comparison to the binding energy of the thiolate sulfur. Comparison of S 2p electron regions of the 2- and 3-SAMs is shown in Figure 8, curves 4 and 5. However, the ratio of the two different types of sulfur atoms in 3-SAM on Au film is not exactly 1:1 as we expected, but we

Figure 9. UV–vis spectra of methanol solution of (A) 2-MPCs, (B) the corresponding desorbed sample, and (C) the thiol derivative 2. Inset: UV–vis spectra of methanol solution of 2-MPCs (2), 2-MPCs (4), and 2-MPCs (6).

Figure 10. Voltammetric curves of 1, 2, and the stabilized gold nanoparticles: 1-MPCs (7) and 2-MPCs (2). The start of scanning is indicated with the cross; the curves are offset for clarity.


reproducibly obtained results with the thiolate sulfur dominant. One possible explanation for observing more of the first (thiolate) sulfur is that they adhere to the surface by both sulfur atoms on step edges still respecting the steric demands of the carborane cluster.

Using the equation derived by Carley and Roberts, we estimated the surface concentration of S atoms from S 2p and Au 4f photoemission peak intensities. In calculations we employed the value of inelastic mean free path of Au and Au 4f photoemission peak intensities. In calculations estimated the surface concentration of S atoms from S 2p spectra.

Elemental analysis of the MPCs and the desorbed species confirmed our hypothesis that some carborane cluster molecules remain inside the nanosize gold clusters of the desorbed samples. Below is an example of the analysis that was characteristic of the studied MPCs and the desorbed species. It unequivocally confirms the results of XPS analysis, demonstrating a relatively high amount of carborane molecules remaining in the desorbed species.

**Figure 11.** Voltammetric curves of Au$_2$S$_3$, Au$_2$S, and desorbed sample.

**UV—Vis Spectroscopy.** Whereas the two previous techniques (desorption and XPS measurements) represented solid phase investigation, electronic spectroscopy allowed us to probe the properties of our nanoparticle samples when dissolved to colloidal solutions. In all spectra, a broad plasmon band (PB) was observed at approximately 500—560 nm, which is consistent with the previous reports on alkanethiol-protected gold nanoparticles. The band is found at about 560 nm for samples with the biggest average size of nanoparticles and shifts to 516 nm as the nanoparticles become smaller. Figure 9 shows the UV—vis spectra of a methanol solution of 2, 2-MPCs (5), and the corresponding desorbed sample. In addition to the PB, the spectrum of 2-MPCs exhibits two peaks (I, II) in ultraviolet region. The first peak (I) overlaps with the absorption band for the pure dithiol derivative 2. The second peak (II), which has the same absorption maximum band energy at 270 nm in all of the studied samples, is independent of core dimensions and surface molecules. We assigned this band to absorption by the carborane clusters incorporated inside the gold cores. In consistence with our model, the electronic spectra of the desorbed samples did not exhibit the first band (I), which is caused by the surface carborane molecules. Considering the dense coverage of the surfaces of the gold nanoparticles before desorption, the UV—vis spectra represent another indirect proof of carboranethiol derivatives inside the gold cores. It corresponds to the B 1s signal observed in the XP spectra of the particles after desorption and distinguishes two different quasi-aromatic carborane cages before desorption.

The UV—vis spectra are also qualitatively indicative of the core dimensions as has been shown previously in the literature. The inset in Figure 9 shows that the intensity of the plasmon band is strongly affected by the nanoparticle size. The intensity decreases as the core size decreases which is in agreement with calculations by Mulvaney. Also the intensity of plasmon band of particles after desorption is effected by the presence of bulky microcrystalline composites that frequently appear in the desorbed samples and cause a more intensive plasmon band.

**Characterization with Infrared Spectroscopy.** The IR spectra of borane and carborane cluster molecules show several characteristic features. Our interest was focused especially on B—H stretching vibrations $\nu_{\text{B—H}}$ that causes a very strong and broad band at approximately 2600 cm$^{-1}$. The spectra of 1-MPCs, 2-MPCs, and the desorbed samples exhibit a band at 2564 cm$^{-1}$. Spectra of the SAMs prepared from 2, 3, and 4 show the characteristic $\nu_{\text{B—H}}$ at 2585, 2617, and 2605 cm$^{-1}$, respectively. The appearance of an obvious band characteristic of B—H stretching vibration in the spectra of the desorbed samples additionally verified the presence of carborane molecules that did not escape during the desorption process. The spectra additionally prove the existence of carborane cluster molecules containing BH bonds and not decomposition of carborane.

**Electrochemical Characterization.** The investigations so far described in this paper have provided basic structural information on both the gold nanoparticles and the flat gold films modified with carboranethiol derivatives. We have deduced that the gold surfaces are densely covered by carboranethiol molecules. The electrochemistry

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The redox properties of the modified gold nanoparticles were investigated using cyclic voltammetry and compared with the starting carboranethiol derivatives. The o-carboranethiol derivatives yield chemically irreversible oxidation peaks (Figure 10), probably due to the oxidative degradation of the molecules initiated by oxidation of the thiol groups. The spectra of 1 (A1, B1) and 2 (A2, B2) are dominated by two main oxidation peaks. Conversely the thiol-capped gold nanoparticles do not exhibit any oxidation peaks except for the oxidation of the gold substrate at potentials overlapping with oxygen evolution reaction at >1 V vs SCE. These results indicate that the thiol groups are strongly bound to the surface of gold nanoparticles.

The cyclic voltammetric curves of the desorbed samples and gold sulfides (Au2S and Au4S) were compared and are shown in Figure 11. A very good qualitative agreement was observed between the desorbed sample and gold(I) sulfide (Au4S). The oxidation peak is bigger in the second scan and shifted toward less positive potential. This unusual feature is typical of both Au2S and the desorbed sample bare gold film on its surface was on the contrary rather hydrophilic because of the free thiol groups that remain on the particle surfaces after desorption.

Gold Films, Bare Electrode vs Modified with 2, 3, or 4. To investigate the properties of the 2, 3-, and 4-covered gold films, Fe3+ ↔ Fe2+ ([Fe(CN)6]3−, [Fe(CN)6]42−) was used as a convenient and reversible redox system. The cyclic voltammetric current—potential (i−E) curves are shown in Figure 12. The voltammograms for the gold film protected with 2, 3, or 4 significantly differ from that for bare gold film; the redox currents are much lower. A reduction current was observed for the 2-modified gold wafer that we assigned to be a ferrocyanide reduction current. However, we did not observe any corresponding oxidation as in the case of the 3-modified gold wafer. One possible explanation for the appearance of only the reduction current might be the dipolar character of the molecules of 2 bound to the surface, which represent a monolayer of organized dipoles directed from the surface upward. The more electronnegative part of the carborane clusters is around the 9 and 12 BH vertexes. These vertexes can be responsible for electrostatic repulsion with the negatively charged redox active species, [Fe(CN)6]4− or 3−. It is obvious that the repulsive forces should be bigger in the case of [Fe(CN)6]3−, and therefore Fe3+ in [Fe(CN)6]3− might be more easily reduced. To investigate this feature more properly we used the dithiol derivative 4, which possesses a dipole moment of approximately the same absolute value as 2 but of an opposite direction; from top to surface. This monolayer has its more electropositive part facing the electrolyte solution and it may rather attracts both ferro—ferricyanide redox species. Therefore, it behaves qualitatively the same as the bare Au electrode. The only difference is that the redox currents are slightly decreased.

Wetting Angles of Water on Bare Gold Film vs Modified with 2, 3, or 4. Measuring of contact angles is a basic method to assess the hydrophobic or hydrophilic character of surfaces. In the case of the present study, it additionally brings confirmative information to the XPS results about the orientation of the molecules in the assembled monolayers on flat surfaces. Table 5 shows the contact angles of water on Au-films: bare and modified with 2, 3, or 4, respectively. Considering the bare Au film to be hydrophobic, the 2-SAM on Au-film caused even bigger hydrophobic character of the surface. This increase is due to the fact, that only B−H nonpolar vertexes are facing the water environment of the drop. The Au film with the 3-SAM on its surface was on the contrary rather hydrophilic because of the free thiol groups that are orientated upward. Finally, we wish to report on the wetting angle of the 4-SAM on Au film. This contact angle was much lower than that on 2-SAM and close to 3-SAM on Au films. The explanation of this observation is closely related to understanding the character of B−H and C−H vertexes. C−H vertexes are significantly more acidic than the B−H vertexes and therefore more readily interact with water molecules. The different wetting angles of water on 2-SAM and 4-SAM underline the difference between the chemical nature of B−H and C−H vertexes in carborane cluster molecules.

Structural Models of the Species. Figure 13 shows an idealized model of the nanoparticle species. It illustrates the proposed modification of the inner space of the nanoparticles and surface coverage before and after desorption. During the synthesis some molecules of the dithiol derivative are immersed by the gold surface atoms and ultimately become incorporated into the gold cores. Modification of flat surfaces is shown schematically in Figure 14. Part A is an illustration of the 2-modified surface.
that fits all evidence gained from the structural characterization experiments. Part B shows the molecules of 3 bound to the flat surface by only a single thiol group. The geometrical reasons of this arrangement were discussed in the Introduction to this article.

Conclusion

In conclusion, we have elucidated important information on the structure, bonding and properties of gold surfaces modified by selected carboranethiol molecules. The carboranethiolate modified gold materials are extraordinarily stable toward oxidation and heating. We did not observe any change in the XP spectra even after several months of exposure to air. The nanoparticle gold surface is densely covered with carboranethiol molecules, and a comparison of the experimental density with the theoretical arrangement of carborane clusters on a flat surface is in a good agreement. The process of desorption indicates that the carborane molecules escape mostly as 1,2-C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} fragments leaving the sulfur atoms on the gold surface. We have observed evidence to suggest a very interesting phenomenon consisting of the incorporation of the carborane clusters into the gold nanoparticles, and we have proposed a structural model for the prepared materials. The prepared monolayers of 1,2-(HS)\textsubscript{2}-1,2-C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} and 9,12-(HS)\textsubscript{2}-1,2-C\textsubscript{2}B\textsubscript{10}H\textsubscript{10} represent organized monolayers of dipoles with approximately the same value but opposite direction.

Acknowledgment. For polishing of the language in this article we are grateful to Dr. Michael G. S. Londesborough from the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic. We acknowledge the Grant Agency of the Academy of Sciences of the Czech Republic for its generous support of this work (Grant Nos. B4032302, K4040110 and T40040413). This article is Contribution No. 105 from the Rež-Leeds Anglo-Czech Polyhedral Collaboration (ACPC) and the authors thank the U.K. EPSRC (Grant Nos. L/49505 and R/61949) for a DTA contribution to M.J.C.

Supporting Information Available: Text giving experimental data for [Au\textsubscript{11}(PPh\textsubscript{3})\textsubscript{8}Cl\textsubscript{2}]\textsuperscript{+}Cl\textsuperscript{-} and crystal data and structure refinement information for the [Au\textsubscript{11}(PPh\textsubscript{3})\textsubscript{8}Cl\textsubscript{2}]\textsuperscript{+}Cl\textsuperscript{-} cluster compound. This material is available free of charge via the Internet at http://pubs.acs.org.

LA051122D