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To cite this version:
Avni Berisha, Catherine Combellas, Frederic Kanoufi, Jérôme Médard, Philippe Decorse, et al.. Alkyl-Modified Gold Surfaces: Characterization of the Au–C Bond. Langmuir, American Chemical Society, 2018, 10.1021/acs.langmuir.8b01584. hal-02359178

HAL Id: hal-02359178
https://hal.archives-ouvertes.fr/hal-02359178
Submitted on 12 Nov 2019

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Alkyl-Modified Gold Surfaces: Characterization of the Au–C Bond

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Supporting Information

ABSTRACT: The surface of gold can be modified with alkyl groups through a radical crossover reaction involving alkylhalides or bromides in the presence of a sterically hindered diazonium salt. In this paper, we characterize the Au–C(alkyl) bond by surface-enhanced Raman spectroscopy (SERS); the corresponding peak appears at 387 cm⁻¹ close to the value obtained by theoretical modeling. The Au–C(alkyl) bond energy is also calculated, it reaches -36.9 kcal mol⁻¹ similar to that of an Au–S(alkyl) bond but also of an Au–C(aryl) bond. In agreement with the similar energies of Au–C(alkyl) and Au–S(alkyl), we demonstrate experimentally that these groups can be exchanged on the surface of gold.

1. INTRODUCTION

Surface modification by organic films is commonly encountered in our daily life from a painted house gate to the sophisticated processes that prevent cars from rusting and provide the aesthetic finish. Among the many routes that have been developed, some provide a chemical bond between the surface and the organic film. For example, self-assembled monolayers (SAMs) of silanes, phosphonates, and carboxylic acids are formed on surface oxides, while alkenes and alkynes are bonded to hydrogenated silicon or carbon. Long alkyl chain thiols SAMs are attached to gold and some other metals (Ag and Cu). Electrografting strategies have also been investigated such as the electrografting of diazonium salts, which provides aryl films covalently bonded to a variety of surfaces (carbon, metals, oxides, polymers). These different methods provide a number of surface–(organic film) bonds; for example, silanes are bonded through (surface oxygen)–silicon: O–Si bonds, carboxylates through O–C bonds, thiols through Au–S bonds, and diazonium salts through metal–C(aryl) or oxide O–C(aryl).

Alkyl films bonded to various surfaces have been prepared by (i) electrochemical oxidation of carboxylates on carbon anodes and Grignard reagents on hydrogenated silicon and (ii) by electrochemical reduction of iodoalkanes (RI = C₆F₁₃–(CH₂)ₓ–I) on glassy carbon, Au, Fe, and Cu cathodes. However, for the latter process, the reduction takes place at quite negative potentials, which results in the reduction of any reducible group in the film. More recently, it was found that the reaction can be accomplished indirectly at much lower driving force following Scheme 1.

The 2,6-dimethylbenzenediazonium (DMBD) salt is reduced electrochemically at quite low potential [E_p = -0.20 V] saturated calomel electrode (SCE) to its radical [R1]; however, because of steric hindrance this radical cannot react with surfaces [R2], instead it abstracts a iodine atom from RI present in the solution to give the alkyl radical R’ [R3] that reacts with the surface (R4). In the case of RI = C₆F₁₃–(CH₂)ₓ–I, the direct reduction takes place at E_p = -1.9 V/ SCE and the electrografting reaction can be achieved at the reduction potential of 2,6-DMBD with a potential gain of ΔV ≈ 1.7 V. This indirect grafting of alkyl groups has been extended to alkyl bromides to the formation of mixed layers, and to the surface modification of polymers.

The bond between the surface and an aryl group grafted by reduction of diazonium salts has been well characterized by

Scheme 1. Indirect Grafting of Alkylhalides

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2. MATERIALS AND METHODS

2.1. Chemicals. 5-Bromovaleric acid (97%), valeric acid (99%), 2,6-dimethylphenol (99%), tetrabutylammonium tetrafluoroborate (99%), 1-octadecanethiol (99%), 6-mercaptohexanoic acid (90%), acetonitrile (ACN), and diethyl ether were purchased from Sigma-Aldrich. They were used without further purification. Milli-Q water (>18 MΩ cm) and absolute ethanol were used for rinsing the samples. 2,6-DMBD was prepared by the standard procedure in aqueous solution. The product was purified by dissolution in ACN and precipitation in ether. IR-ATR: 1585, 1478 cm⁻¹, BF₂: 1036 cm⁻¹, C–H out of plane: 806 cm⁻¹, 1H NMR (DMSO-d₆, Bruker 400 MHz) δ ppm: 8.02 (t, 1H), 7.65 (d, 2H), 2.95 (s, 6H). 2.2. Substrates. Gold-coated silicon wafers (100 nm) were obtained from Sigma-Aldrich and cut into 1 × 1 cm² plates, immersed in concentrated sulfuric acid and thoroughly rinsed in ultrapure water and then absolue alcohol. Nanostructured indium tin oxide (ITO)/Au surfaces were obtained by depositing gold onto ITO-coated glass slides, using the vacuum sputtering method (dc Ar plasma, gas purity—99.999%, gas pressure 4 Pa, discharge power 7.5 W, sputtering time 120 s, resulting thickness 5–6 nm). Targets for metal deposition were purchased from Saffina. 2.3. Functionalization of Au Plates and ITO/Au (Nanostructured) Electrodes by Alkyl Groups. Electrografting was performed by chronoamperometry (E = −0.5 V/SCE for 300 s) in ACN + 0.1 M NBu₄PF₆ solutions containing 20 mM of 2,6-DMBD and 100 mM of bromovaleric acid. The “thin” and “thick” films used to discuss the growth of the film were prepared as follows in ACN + 0.1 M NBu₄PF₆: “thin” film: 30 mM bromovaleric acid, 7 mM 2,6-DMBD, and six voltammetric cycles between +0.3 and −0.5 V/SCE at 0.1 V s⁻¹; “thick” film: 100 mM bromovaleric acid, 20 mM 2,6-DMBD, and 50 voltammetric cycles between +0.3 and −0.5 V/SCE at 0.1 V s⁻¹. 2.4. Electrochemical Measurements. Electrochemical experiments were performed with an Ametek, Princeton Applied Research VersaSTAT 4 potentiostat/galvanostat and a VersaStudio electrochemistry software 2.4.4.4 version software. All experiments were carried out in ACN solutions deoxygenated with argon. All potentials are referred to the SCE electrode, the counter electrode was a large platinum mesh. After grafting, the modified gold surfaces were rinsed in acetone under sonication for 8 min and then in absolute ethanol. 2.5. IR Spectra. The infrared reflection–absorption spectroscopy (IRRAS) and attenuated total reflection (ATR) spectra of modified plates were recorded using a purged (low CO₂, dry air) Jasco FT/IR-6100 Fourier transform infrared spectrometer equipped with a mercury–cadmium–telluride detector. For each spectrum, 1000 scans were accumulated with a spectral resolution of 4 cm⁻¹. The background recorded before each spectrum was that of a clean substrate. ATR spectra were recorded with a germanium ATR accessory (Jasco ATR PR0470-H). 2.6. Raman Spectra. The SERS spectra were recorded with a Jobin Yvon LabRam HR 800 microspectrometer in backscattering configuration, using an excitation line of 785 nm with a power of 0.6 mW. All spectra were recorded in air within the 150–2700 cm⁻¹ spectral range. The scattered light was collected with a long working distance objective of 100-fold magnification (0.9 NA). The spectral resolution was less than 3 cm⁻¹. The accumulation time for the SERS measurements was set to 10 s with five repetitions. 2.7. XPS Spectra. XPS measurements were performed using a K-Alpha system (Thermo Fisher Scientific, East-Gринstead, UK) fitted with a microfocused and monochromatic Al Kα X-ray source (1486.6 eV, spot size: 400 μm). The pass energy was set to 150 and 40 eV for the survey and the high resolution spectra, respectively. The spectra were calibrated against the C 1s/C–C–H C 1s component set at 285 eV. The chemical composition was determined with version 5.977 Avantage software, by using the manufacturer sensitivity factors. The spectra were calibrated against C 1s set at 285 eV. 2.8. Ellipsometry. Thicknesses of the films on gold plates were measured with a mono wavelength ellipsometer Sentech SE400 with an SE400 advanced 2.20 version software. The following values were taken for gold: ns = 0.207 and ks = 3.41; they were measured on clean surfaces before using the plates for grafting. The film thicknesses were determined from the same plates after modification, taking ns = 1.46 and ks = 0. For the layer, the hydrogen bond, (ii) the growth of the film by atomic force microscopy (AFM), (iii) the bonding energy of alkyl groups (Au–C bond) on gold by theoretical methods and we compare this energy to that of the previously investigated Au–S–alkyl bond, and (iv) based on the results of the simulations, we show that alkyl and thioalkyl groups can be exchanged on the surface of gold [the valeric groups of a Au–(CH₃)₅–COOH film, prepared from bromovaleric acid (Scheme 1), are exchanged by the HS–(CH₃)₅–COOH and HS–(CH₃)₅CH₂ thiols].
3. RESULTS AND DISCUSSION

3.1. Raman Evidence of the Au–Alkyl Bond. To evidence the existence of the bond between the Au surface and the valeric acid group, the Raman SERS spectrum of Au–(CH₂)₄–COOH was recorded on a SERS active surface, and the Au–C bond was assigned by comparison with a calculated spectrum. The experimental spectrum shows a peak at 387 cm⁻¹ assigned to the Au–C bond (Figure 1b); it is neither observed in a blank spectrum of the surface nor in the Au surface (Table 1). Comparison of the experimental and simulated spectra permits the resolution (see overall Raman spectrum in Supporting Information, Figure SI1B). In the calculated spectrum of Au₂₀−S(CH₂)₅−COOH, the Au–S stretching vibrations are observed at 269 and 241 cm⁻¹, in full agreement with those previously calculated for an Au₂₅−thiol cluster.⁴⁰ The comparison of the experimental and simulated spectra permits to demonstrate the existence of an Au–S bond in the modified gold surface (Table 1).

3.2. Growth of the Film. The film grows by attack of the first grafted group by the R⁺ radicals (Scheme 1, reaction [4]) as observed for other radical reactions.⁴⁺,¹¹ The growth of the film was followed by recording the AFM images of a bare gold sample grafted with a “thin” film (th < 1 nm) and a “thick” one (th = 5.7 ± 1.5 nm) (see Experimental Section). The length of the growth of the film increases with the concentration and the dipping time of the sample grafted with the radical, reaching 4 nm. On the “thin” film the structures of gold are less pronounced (~2 nm), which indicates that the valleys are filled before the summits of the structure. With the “thick” film, clumps of organic matter are observed with a height that reaches 6 nm (Figure 2).

Table 1. Calculated and Experimental Raman Spectra

<table>
<thead>
<tr>
<th></th>
<th>wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calculated</td>
<td></td>
</tr>
<tr>
<td>Au₂₀</td>
<td>155, 119</td>
</tr>
<tr>
<td>Au₂₀−(CH₂)₅−COOH</td>
<td>387</td>
</tr>
<tr>
<td>Au₂₀−S(CH₂)₅−COOH</td>
<td>165, 118</td>
</tr>
<tr>
<td>Au₂₀−S(CH₂)₅−COOH</td>
<td>269, 241</td>
</tr>
</tbody>
</table>

“Calculated vibrational wavenumbers as assigned from PED analysis."

Figures 1 and 2.

The bonding energies between the gold surface and the organic group were evaluated by VASP calculations for Au₁₁₁−(CH₂)₅−COOH and Au₁₁₁−S(CH₂)₅−COOH for different binding sites of the slab (Table 2, Figures 3, and SI2 in Supporting Information for the different binding sites). For Au₁₁₁−(CH₂)₅−COOH, the Au–C bond is the strongest for the TOP site: −36.9 kcal/mol, while for the Au₁₁₁−S(CH₂)₅−COOH this occurs at the FCC site: −45.5 kcal/mol. In the literature, the bonding energy of alkylthiols varies from −25 kcal/mol for conjugated molecules to −44 kcal/mol depending on the length and the chemical structure.⁴⁺,⁴² The above values can also be compared...
with that calculated (with two different methods) for Au−C(aryl) bonds obtained by grafting diazonium salts on gold: −34.4 kcal/mol (Au19−C6H4) and −24.0 kcal/mol [Au(111), TOP site]−C6H4. These calculations indicate that the energy of Au(111)−C(aryl) bond is equivalent to that of an Au−C(aryl) bond; the Au(111)−S−alkyl bond is more stable than the Au(111)−C(aryl) one by 8.6 kcal/mol. The lengths for Au−C(aryl) (TOP site) and Au−S (FCC site) bonds are, respectively, 2.30 and 2.03 Å (deduced from Figure 4). The geometries of the bonded molecules (periodic calculations) are almost identical for Au(111)−(CH2)4−COOH (TOP) and Au(111)−S−(CH2)3−COOH (BRD), and there is no apparent pulling of gold atoms from the surface. Considering the above computed bond energies that indicate a significant difference of ~8.6 kcal/mol between the two grafted molecules, one should, in principle, be able to replace reversibly the bonded moiety. This idea of replacement of the grafted moiety is further elaborated experimentally.

### 3.4. Comparison with the Au20 Gold Cluster

The results of the above periodic calculations can be compared with that of nonperiodic DFT calculations on an Au20 cluster. As already observed in the grafting of aryl groups, binding an alkyl group (valeric group) to the surface of Au20 changes its geometry (Figure 5). The bond distances between neighboring gold atoms change after the grafting: in the bare cluster

\[ \text{Au}^{17} \rightarrow \text{Au}^{15} \]

Figure 5. Optimized structures for (A) Au20 cluster, (B) Au20−(CH2)4−COOH, and (C) Au20−S−(CH2)3−COOH grafted clusters.

\[ \text{d(Au15−Au17)} = \text{d(Au15−Au14)} \]

\[ = 2.90 \text{ Å} \]

while after grafting to Au15 the gold atom distance changes: \[ \text{d(Au15−Au17)}/\text{d(Au15−Au14)} \] = 3.03, indicating an effect similar to that observed in the case of thiols and aryl radicals. The dihedral angles are also modified: \[ \text{Au17−Au15−Au11−Au14} \] is 3.6° for Au20 but 20.0° in Au20−(CH2)3−COOH. After grafting, the gold atom is pulled out from the mean surface plane of the Au20 cluster by about 0.86 Å (Figure 5). This demonstrates that a strong interaction takes place. Such an interaction is known for thiols through DFT calculations and STM and also from the X-ray structure of a p-mercaptobenzoic acid (p-MBA)-protected gold nanoparticle (102 gold atoms and 44 p-MBA groups).

Similar effects have been observed for Au20−S−(CH2)3−COOH, where \[ \text{d(Au15−Au17)} = 2.90 \text{ Å} \], whereas \[ \text{d(Au15−Au14)} \] = 3.51 Å; the dihedral angle for \[ \text{Au17−Au15−Au11−Au14} \] is 19.5°, and the gold atom is pulled by 1.11 Å from the surface.

### 3.5. Comparison of Au−C and Au−S Stabilities

Because the above calculations indicate that Au−alkyl and Au−S−alkyl have similar energies, the possible exchange of the valeric group of Au−(CH2)4−COOH by an octadecylthiol group to give Au−S−(CH2)17−CH3 was tested (note that reactions \([\text{RS}]\) and \([\text{RS}b]\) below are not equilibrated; they are not chemical equations, they are only used as a basis of discussion). McDermott previously showed that it is possible to partially replace the grafted aryl groups derived from diazonium (Au−C6H4−NO2) by arylthiol groups (Au−S−C6H4−NO2).

\[
\text{Au−(CH2)4−COOH } + \text{CH3−(CH2)17−SH} \\
\text{RS} \\
\text{RSb}
\]

(RS)

To test this hypothesis, a gold plate was first modified as indicated in the experimental section (film thickness: \(h = 2.5 \pm 1.0 \text{ nm}\), water contact angle \(\theta = 61 \pm 4^\circ\), immersed for 24 h
in a deoxygenated solution of octadecanethiol (CH$_3$−(CH$_2$)$_{17}$−SH) (long-chain thiols are adsorbed preferentially over shorter chains$^{46}$) and finally rinsed in ethanol under ultrasonication. The IRRAS spectrum was recorded before and after the exchange (Figure 6).

The spectrum of Au−(CH$_2$)$_{17}$−COOH is characterized by the bands of the four CH$_2$ groups: 2958, 2930, 2858 cm$^{-1}$ (2963, 2937, 2877 cm$^{-1}$ for valeric acid$^{47}$, CH$_3$−(CH$_2$)$_3$−COOH) and the broad C=O band of the carboxylic group at 1695 cm$^{-1}$ (1712 cm$^{-1}$ for valeric acid) (note also the broad shoulder at >1650 cm$^{-1}$ that could correspond to some esterification of the carboxylic group during ultrasonic rinsing in ethanol). After the exchange reaction [R5f], the CH stretching vibrations increase and the C=O band becomes very small. In the CH stretching region, the spectrum is similar to that of Au−S−(CH$_2$)$_3$−CH$_3$ prepared by reacting a gold surface with C$_{18}$H$_{37}$SH (Figure S13 in Supporting Information); it exhibits the vibrations of the alkyl group at 2964, 2918, 2876, and 2850 cm$^{-1}$ and a very small C=O signal corresponding to unexchanged valeric groups. Note that after [R5f] exchange the CH stretching bands are much narrower$^{48}$ and located at positions characteristic of a crystalline structure (the symmetric and asymmetric CH$_2$ vibrations of C$_{18}$H$_{37}$SH are located at 2855 and 2924 cm$^{-1}$ for the liquid and 2851 and 2918 cm$^{-1}$ for the crystal)$^{48}$. The crystallinity of the Au−S−(CH$_2$)$_{17}$−CH$_3$ film obtained by exchange is not perturbed by the small remaining amounts of valeric acid indicating a segregated structure of the film.

Ultrasonication of a film allows testing qualitatively its stability. All the Au−(CH$_2$)$_{17}$−COOH samples examined herein were rinsed in acetone and ethanol under ultrasonication. The same test was applied to Au−S−(CH$_2$)$_{17}$−CH$_3$. The spectra before and after sonication are similar (Figure S13B in Supporting Information), in good agreement with the binding energies calculated above.

The water contact angle of the film after [R5f] exchange, $\theta = 100 \pm 1^\circ$, indicates that the Au−S−(CH$_2$)$_{17}$−CH$_3$ film prepared through [R5f] presents some defects because for the same film prepared directly from C$_{18}$H$_{37}$SH in alcohol$^{49} \theta = 109 \pm 1^\circ$.

In the XPS spectrum of Au−(CH$_2$)$_{17}$−COOH, the C 1s peak (Figure 7A) presents three contributions at 284.8, 286.5, and 288.8 eV assigned, respectively, to C−C/H, CH$_3$−C=O, and O−C=O; the last two confirm the presence of the carboxylic group on the surface. The survey spectrum of Au−S−(CH$_2$)$_{17}$−CH$_3$ obtained through [R5f] (Figure 7B) shows the presence of Au 4f (24.1%), C 1s (67.3%), N 1s (1.2%), O 1s (5.5%), and S 2p (1.9%; S/Au = 0.08); it is similar to that of Au−S−(CH$_2$)$_{17}$−CH$_3$ (Figure S14 in Supporting Information) obtained directly by dipping a gold plate in the thiol: Au 4f (34.1%), C 1s (60.5%), N 1s (0.6%), O 1s (1.9%), and S 2p (3.0%, S/Au = 0.09). However, the S/Au ratio is ~10% lower for the exchanged surface and two small contributions are observed at 286.5 and 288.8 eV that correspond to some remaining valeric groups on the surface. The presence of sulfur on the surface and the strong decrease of the carboxylic signal indicate that ~90% of the valeric groups have been displaced from the surface by the C$_{18}$ alkyl chain thiol.

The reverse reaction [R5b] was performed on an Au−S−(CH$_2$)$_{17}$−CH$_3$ plate that was submitted to indirect electrografting by bromovaleric acid as in Scheme 1 along the procedure described in the Experimental Section. The IRRAS spectra (Figure 8) show that starting from Au−S−(CH$_2$)$_{17}$−CH$_3$ that does not present any band in the 1800−1600 cm$^{-1}$ range (Figure 8c), after [R5b], a C≡O band is observed at 1695 cm$^{-1}$ (Figure 8b) at the same position as for Au−(CH$_2$)$_{17}$−COOH (Figure 8a) albeit with an absorbance that is 63% lower. In the XPS spectrum, starting from Au−S−
(CH2)17−CH3 with S/Au = 0.09, after [R5b], S/Au = 0.07 and the C 1s peak presents two very small contributions (at 286.5 and 288.8 eV) corresponding to the carboxylic group of Au−(CH2)4−COOH. The water contact angle changes from θ = 107 ± 0.8 to 96.8 ± 1.0°, indicating that thiol groups are still present on the surface in agreement with the IR spectrum. This experiment demonstrates that reaction [R5] is possible in the two directions but the direct reaction ([R5f]) is much more efficient than the reverse one ([R5b]). In addition, it is possible that part of the C=O groups observed after [R5b] correspond to valeric groups attached to the C18 alkyl chain of the thiol owing to a H-atom abstraction from the C18 alkyl chain of the thiol by the valeric radical (R* in reaction [R3]) followed by the coupling of another R* with the CH* radical formed on the C18 alkyl chain.

The exchange between Au−(CH2)4−COOH and SH−(CH2)3−COOH ([R6f]), the structures of which are closely related, was also tested. The comparison of the IR spectrum and water contact angles of Au−(CH2)4−COOH and Au−S−(CH2)3−COOH (θ = 58 ± 0.8°) is not informative because the two grafted surfaces are too similar. However, the XPS spectrum of Au−(CH2)4−COOH and that of Au−S−(CH2)3−COOH obtained directly and by exchange of Au−(CH2)4−COOH via IRRAS and XPS spectra (PDF)

**4. CONCLUSIONS**

Both theoretical and experimental results indicate that during the electrografting of bromovaleric acid onto Au to give Au−(CH2)4−COOH: (i) a covalent bond is formed between the gold surface and the organic group (observed by Raman SERS spectroscopy at 387 cm−1 and identical to the calculated value), (ii) the radical character of this reaction leads to multilayered films as previously observed with diazonium salts and amines,10−12 (iii) the energy of the Au−C(alkyl) bond is ~37 kcal/mol (less stable than that of the Au−S bond of a thiol SAM by 8.6 kcal), and (iv) based on these similar bonding energies, we have shown experimentally that Au−(CH2)4−COOH can be transformed reversibly into Au−S−(CH2)3−CH3 or Au−S−(CH2)4−COOH in the presence of the corresponding thiol.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.8b01584.

Simulated Raman spectrum of Au and Au−CH2−(CH2)3−COOH; different binding sites onto Au(111) surface; and comparison of Au−S−(CH2)3−CH3 obtained directly and by exchange of Au−(CH2)4−COOH via IRRAS and XPS spectra (PDF)

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Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

CNRS, Paris Diderot University, and ANR (Agence Nationale de la Recherche) and CGI (Commissariat à l’Investissement d’Avenir) are gratefully acknowledged for their financial support of this work through Labex SEAM (Science and Engineering for Advanced Materials and devices) ANR 11 LABX 086, ANR 11 IDEX 05 02.

**REFERENCES**

(42) Lassoued, K.; Seydou, M.; Raouafi, F.; Larbi, F.; Lang, P.; Diawara, B. DFT study of the adsorption and dissociation of 5-hydroxy-3-butanedithiol-1,4-naphthaquinone (Jug-C4-thiol) on Au(111) surface. Adsorption 2018, 24, 191−201.