An electrochemical approach to fabricate a heterogeneous mixed monolayer on planar polycrystalline Au and its characterization with Lateral Force Microscopy

Scott R. Smith a,1, Sungwon Han a, Andy McDonald b,c, William Zhe c, Jeffrey L. Shepherd a,c

a Department of Chemistry and Biochemistry, Laurentian University, Sudbury, ON, Canada P3E 2C6
b Department of Earth Sciences, Laurentian University, Sudbury, ON, Canada P3E 2C6
c Central Analytical Facility, Laurentian University, Sudbury, ON, Canada P3E 2C6

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A B S T R A C T

A method describing the assembly and characterization of a heterogeneous mixed monolayer composed of 2-aminoethane thiol (AET) and 11-mercaptoundecanoic acid (MUA) on a planar polycrystalline Au electrode is presented. A single component self-assembled monolayer (SAM) of AET was stable on the metal within a narrow range of potentials but at more negative polarizations, cyclic voltammetry (CV) and capacitance measurements confirmed reductive desorption of AET from the Au(111), Au(100) and Au(110) facets of the surface consecutively. By truncating the negative potential limit, desorption of AET occurred selectively from facets with Au(111) character and diffused away from the interface thus limiting oxidative readesorption on the return to positive potentials. The extent of oxidative readesorption was found to be dependent not only on the time spent at the desorption limit but also on electrode geometry and configuration. The largest degree of readesorption occurred on a planar electrode when set in a hanging meniscus configuration. As a result, a modified desorption procedure involving 20 truncated desorption pulses each with a duration of 1 min was utilized to limit readesorption. This produced monolayer voids at the Au(111) facets which were subsequently backfilled with MUA to create the heterogeneous mixed monolayer. Surface characterization was achieved with Electron Backscattered Diffraction (EBSD) which produced a map of a small section of the metal surface crystallography and with Lateral Force Microscopy (LFM) which verified MUA adsorption on the Au(111) facets and AET on all other low index planes.

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1. Introduction

Among the numerous methods to coat surfaces with organic molecules [1] self-assembled monolayers (SAMs) of alkylthiols on noble metals [2] remains a popular choice due to the ease of monolayer formation. There have been many investigations on the characterization and manipulation of alkylthiol SAMs on noble metals and the properties of the interface have been included in a variety of reviews [3–8]. Recently, the interest in Au-thiol chemistry has been renewed due to its relation to nanotechnology as it was discovered that alkylthiols are efficient stabilizing ligands for gold nanoparticles [9]. Since this discovery, different synthesis strategies have been employed to fabricate AuNPs with a variety of alkylthiols [10,11] and monolayer protected AuNPs as (as well as a variety of other nanoparticles) are now being used for analytical applications [12]. AuNPs capped with a mixture of different ligands have also been characterized [13] and have been shown to provide versatility in the amphiphilic [14] drug delivery [15] or biosensing [16] properties of the nanomaterial. For mixed capping ligands, it is particularly important to exert control over the distribution of the mixed thiols on the nanoparticle surface in a repeatable and facile manner and in this regard phase segregated mixed monolayers may play an important role.

It has been the focus of our research group to develop an electrochemical method to control the heterogeneous mixing of two different thiols on bulk Au surfaces [17] with the intent of tuning this procedure for AuNP assemblies. In this case, the AuNPs would need to be assembled in an electric field and this may be achieved using dithiol tethers [18–21] however, care must be taken since these tethers may adsorb as monolayers and bilayers on the surface [22–24].

The development of an electrochemical procedure to control the distribution of two or more domain segregated thiols on the surface of AuNPs may further increase the flexibility and function of the nanomaterial; however, before this can be achieved, the electrochemical procedure should be refined on macroscale surfaces. On bulk electrodes, the fabrication of phase segregated mixed thiol monolayers has been achieved with non-electrochemical methods.
including co-incubation, place exchange reactions, lithography, micro-contact printing and others [25]. In some of these examples, a single component SAM is selectively disrupted to expose voids that may be backfilled with a different molecule. While electrochemical methods have also been used to generate monolayer voids on bulk surfaces [26,27], these have relied on the electrochemical manipulation of a pre-formed mixed monolayer that was already phase segregated on the nanometer scale.

More recently, it has been demonstrated that the surface of a metallic electrode can be exploited in selectively modifying single-component SAMs. For example, some reports [28,29] have demonstrated that single-component SAMs can be selectively desorbed from the metal at a cathodic potential that is dependent on the surface crystallography of the substrate. This selective desorption has been exploited at polycrystalline Au electrodes to remove portions of a single-component SAM from one of the metal surface facets followed by backfilling the voids created with new molecules [30]. Importantly, it is the diffusion of the desorbed thiolate away from the metal surface at negative potentials that limits their ability to oxidatively readsorb on the surface when potential is made more positive. Since this is dependent on a number of parameters including temperature, concentration, solubility, electric potential and electrode geometry, further investigations are necessary to determine the most reproducible conditions of creating monolayer voids. Moreover, once the voids are backfilled with a new molecule, spectroscopic or surface probe analysis of the final mixed monolayer in relation to the electrode surface crystallography is still required.

In our previous investigation [17], 2-aminoethane thiol (AET) was selectively desorbed from the Au(111) facets of a polycrystalline Au bead electrode and the voids backfilled with 11-mercaptoundecanoic acid (MUA). In a 0.250 M KOH electrolyte, it was determined that the most efficient method to produce monolayer voids at Au(111) facets involved the application of a single potential step from 0 to −0.80 V vs. SCE for 15 min. After backfilling with MUA, electrochemical analyses displayed a signature for MUA on the Au(111) facets and AET on Au(110) and Au(100). The desorption event was monitored via differential capacitance, in a manner similar to other reports [32–34] but only crude monolayers of AET (i.e. formed with 10 min incubation) were used.

In this present study, mixed AET/MUA monolayers formed over 10 min and 16 h assembly times are further characterized. More significantly, this present study was primarily conducted on a planar polycrystalline Au electrode whose surface was further characterized with Electron Backscattered Diffraction (EBSD) and Lateral Force Microscopy (LFM).

EBSD is a scanning-electron microscope (SEM)-based technique that uses electrons from a highly focused beam to generate diffraction patterns. With these patterns, information regarding the crystallographic orientation of a material with which the electrons have interacted, can be obtained. In this study, EBSD has been employed to map out the surface facets on planar polycrystalline Au in a manner similar to that reported for different Au samples [35]. In particular, facets with character ranging between Au(111), Au(110) and Au(100) have been quantified and a map of these facets was used in comparison with LFM to determine the presence or absence of a particular thiol on each face. LFM is a form of contact mode imaging in Atomic Force Microscopy (AFM) where the tip is rastered laterally across the surface where horizontal deflections in the cantilever rather than vertical deflections are recorded as the tip passes regions of high and low friction. LFM has been used to validate the distribution of mixed thiol monolayers formed with μ-contact printing [36]; however, to our knowledge, it has not been used in combination with EBSD to map the distribution of a two-component thiol SAM that is formed as a function of substrate surface crystallography.

This study addresses the critical issues related to basic, but essential characterization of these mixed monolayers produced with an electrochemical approach. It also serves to highlight the important role that electrode geometry and configuration plays in the fabrication of the AET/MUA mixed monolayer.

2. Materials and methods

2.1. Electrochemical

All CVs were collected with a VoltaLab® PGP 201 potentiostat/galvanostat at a sweep rate of 25 mV s⁻¹. Differential capacitance was determined following a methodology previously described [37]. Here, a sinusoidal voltage (25 Hz, 5 mV rms) from a dual-phase lock-in-amplifier (Stanford Research Systems SR530) was superimposed onto the linear potential ramp output from the PGP 201. The in-phase and out-of-phase components of current were analyzed with the SR530 and used to calculate capacitance with the interface being modeled as a series RC circuit. All electrochemical data was collected with National Instruments data acquisition cards controlled with in-house software (LabVIEW).

The electrochemical studies were conducted in a three-electrode cell containing a working, counter and reference electrode. The working electrode was either planar polycrystalline Au or a spherical polycrystalline Au bead. The bead electrode was created by melting the end of a Au wire (Alfa Aesar, 99.99%, 0.5 mm diam.) until a sphere with a geometric area of approximately 0.1 cm² was formed. The planar electrode was fashioned by another Au bead that was mounted in an epoxy and polished flat using finer grades of sandpaper in succession (400, 600, 1000 grit) and further polished to a mirror finish using different grades of diamond suspension (6, 3, and 0.25 μm, LECO). Between each polishing cycle, the electrode was sonicated in purified water (Barnstead Easypure Rodi, 18.2 MΩ cm), followed by extensive rinsing. This resulted in a planar working electrode with a polished circular geometric area of approximately 0.04 cm². After the high-quality finish was obtained, the epoxy was dissolved in chloroform and the sample was electropolished in 10% perchloric acid (Fisher Scientific, 70%).

Prior to each electrochemical investigation, the glass components of the cell were cleaned in a heated mixture of sulfuric acid and nitric acid (50:50 by volume; Fisher Scientific) then rinsed with copious amounts of purified water. The supporting electrolyte, 0.250 M KOH (Sigma Aldrich, 99.99%) was added to the cell followed by Ar (Air Liquide, 99.999%) purging to minimize oxygen re-entering the cell. A constant blanket of Ar was maintained above the electrolyte after being passed through purified water for hydration. In an effort to reduce Ar-induced vibrations of the electrolyte surface, the flow rate was maintained at <35 mL min⁻¹. Such a flow rate was suitable for capacitance measurements but was increased during CVs. After the electrolyte was degassed, the working and counter electrodes were introduced to the cell after having been flame annealed. When the planar Au electrode was used, it was arranged in a hanging meniscus configuration [38,39] to ensure that only the polished surface was exposed to the electrolyte. For the bead electrode, only the spherical portion was submerged in the electrolyte so as to minimize the amount of wire exposed to the solution. The counter electrode consisted of a Pt coil and was also flame annealed prior to its introduction to the cell. The reference was a saturated calomel electrode (SCE) connected to the solution through a salt bridge.

For SAM preparation, the Au working electrode was annealed, rinsed with purified water and/or ethanol (95%) and then introduced into a solution containing 1 mM of thiol dissolved in an appropriate solvent. For 11-mercaptoundecanoic acid (MUA, Sigma Aldrich, 95%) and 3-mercaptopropionic acid (MPA, Sigma Aldrich,
99%), ethanol was used as the solvent. Due to the limited solubility of 2-aminoethane thiol (AET, Sigma Aldrich, 98%) in ethanol, the solvent was used a 50:50 mixture (by volume) of ethanol to water. All SAMs were allowed to form on the electrodes for a total time of either 10 min or 16 h followed by extensive rinsing with ethanol and water. Further details of the electrochemical characterization and manipulation of the SAMs using CV and capacitance are described in Section 3.

2.2. Electron Backscattered Diffraction

The EBSD measurement was performed with an HKL EBSD system and a JEOL 6400 scanning electron microscope operated at 20 kV with a 1 nA beam current. The Au sample was prepared by a polishing procedure similar to that described above; however for EBSD analysis, the Au bead was polished flat on both sides to produce a cylindrical puck that could be easily mounted in the EBSD chamber. Prior to EBSD characterization, the sample was annealed at 400 °C for 3 h to expose the grain boundaries and micron-sized facets [35]. The annealed sample was mounted on a pre-tilted specimen holder at 70° to the detector which is required for EBSD analysis. The EBSD system was calibrated using a Si wafer and then the specimen holder at 70°/C176 was calibrated using a Sharp Nitride Lever. The electrochemical characterization of a polycrystalline Au electrode is provided because the properties at the negative potential limit of 2-aminoethane thiol (AET, Sigma Aldrich, 98%) in ethanol, the solvent was used a 50:50 mixture (by volume) of ethanol to water. All SAMs were allowed to form on the electrodes for a total time of either 10 min or 16 h followed by extensive rinsing with ethanol and water. Further details of the electrochemical characterization and manipulation of the SAMs using CV and capacitance are described in Section 3.

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assembly time was used. Characterized in both the absence (dotted line) and presence (solid line) of AET. In (a and c) the AET layers were formed from a 10 min assembly time and in (b and d) a 16 h assembly time was used.

Fig. 1. Reductive desorption of AET from a polycrystalline Au bead electrode revealed in CV (a and b) and differential capacitance (c and d) plots. The Au electrode was characterized in both the absence (dotted line) and presence (solid line) of AET. In (a and c) the AET layers were formed from a 10 min assembly time and in (b and d) a 16 h assembly time was used.

periods of 10 min and 16 h are presented in Fig. 2a and b. The capacitance from the planar electrode set in a hanging meniscus arrangement and modified with equivalent 10 min and 16 h AET layers are given in Fig. 2c and d. Again, the dotted line represents the differential capacitance measured in the absence of AET.

For the bead electrode modified with AET formed over 10 min (Fig. 2a), the desorption curve (solid line) is identical to that presented in Fig. 1c. However, on the positive potential scan, a peak is noted at −1.13 V vs. SCE which may correspond to the oxidative readsorption of the thiolates onto the Au(100) facets. However, readsorption is incomplete because (1) the peak during the positive scan is smaller than that attributed to desorption and (2) the capacitance at the most positive readsorption potential (0 V vs. SCE) is elevated above 50 μF cm⁻² from the initial value of ca. 20 μF cm⁻². These observations confirm that the desorption process disrupts the AET layer in a manner that is irreversible and a third consecutive readsorption curve (dashed-dotted line) shows characteristics of a significantly disrupted AET layer. For example, the readsorption peak at −1.13 V vs. SCE is low and the capacitance at the positive limit is elevated to a value above 80 μF cm⁻² and begins to take the general shape of the capacitance curve of an uncoated metal (dotted line). All of these desorption characteristics for the AET layers formed over 10 min (Fig. 2a) are nearly identical to the results obtained for a bead electrode modified with 16 h AET (Fig. 2b), thus demonstrating that for the two incubation times studied, there is minimal effect on the irreversible desorption/readsorption event.

The irreversible readsorption of thiols is consistent with previous reports on different metal/SAM systems [42,43] and may be related to diffusion of a desorbed thiolate away from the metal surface. It has been suggested that the desorbed thiolates exist as micelles [44] whose solubility in the bulk electrolyte is related to the length of the alkyl chain. Generally, shorter chain thiolates are more soluble resulting in less readsorption because they diffuse away from the electrode surface before the readsorption potential is established.

While the diffusion of desorbed thiolates would also be expected at the planar electrode, the desorption and readsorption scans presented in Fig. 2c and d reveals some fundamental differences between it and the Au bead suggesting that readsorption may be more reversible at the planar surface. These differences are most notably observed in Fig. 2c and d at the negative limit where the capacitance for an AET modified electrode (solid line) remains separated from the capacitance of the unmodified layer by approximately 10 μF cm⁻² for both 10 min and 16 h AET layers. On the return scan (dashed line), there are now two peaks at −1.30 and −1.13 V vs. SCE that are interpreted as being due to readsorption onto the Au(110) and Au(100) facets. These readsorption peaks are more pronounced than that for the bead electrode. Lastly, the capacitance at the positive potential limit on the return scan is only slightly elevated and after the third readsorption cycle (dash-dotted line), and the capacitance is elevated to approximately 50 μF cm⁻² at 0 V vs. SCE in contrast to values above 80 μF cm⁻² for the bead electrode.

If the capacitance of the AET coated electrode (C_AET) is normalized to the bare electrode (C_BARE) at a positive potential (taken here to be 0 V vs. SCE), the relative disruption of the AET layers with each potential scan can be monitored. This analysis is presented in Fig. 2 where the AET disruption at the bead (○) and planar (□) electrodes over the different incubation times are compared. For both the 10 min (Fig. 2e) and 16 h (Fig. 2f) AET modification times, the capacitance ratio at both the bead and planar electrodes show a general increase with scan number. However, the increase is less pronounced for the planar electrode than for the bead electrode. To indicate the reproducibility of this process, triplicate analyses were performed for the AET layers formed over 10 min and the standard deviations are represented by the error bars for the 3rd cycle. Clearly, the disruption of AET with each cycle is consistent for a given electrode and incubation time and it can be concluded that readsorption is more pronounced at the planar electrode.

This limited diffusion of the desorbed AET thiolates away from the interface of the planar electrode could influence the development of the mixed monolayer during the selective desorption and backfilling process. The diffusion of the thiolate from the planar electrode may be enhanced by extending the holding time at the desorption potential limit. This concept was tested using a slightly modified desorption procedure described next.
3.3. Slow re-spreading of AET on planar Au

For this component of the study, only AET layers formed over 10 min were characterized as the desorption and readsorption characteristics of the AET layers formed over 16 h had not yet been found to be distinctly different. To investigate the influence of desorption time on the oxidative readsorption of AET on planar Au, a slow potential scan to \(-1.4\) V vs. SCE was imposed, holding at this potential for 2 min followed by a potential sweep back to 0 V vs. SCE to induce oxidative readsorption.

The results of this analysis are presented in Fig. 3a where the bold line represents the negative scan. At the negative potential limit, the capacitance for the AET coated electrode is again slightly elevated; however, when held at this potential for 2 min followed by a potential sweep back to 0 V vs. SCE to induce oxidative readsorption.

The results of this analysis are presented in Fig. 3a where the bold line represents the negative scan. At the negative potential limit, the capacitance for the AET coated electrode is again slightly elevated; however, when held at this potential for 2 min, the capacitance decays to approximately 25 \(\mu F\) cm\(^{-2}\) indicating complete desorption. On the positive scan (dashed line), only one readsorption peak is observed at \(-1.13\) V vs. SCE and at 0 V vs. SCE, the capacitance reaches a value near 50 \(\mu F\) cm\(^{-2}\) coinciding well with the value obtained after three potential cycles shown in Fig. 2c (dash-dotted line). As such, the extended holding time at the desorption potential appears to limit the oxidative readsorption of AET onto the planar electrode to an appreciable extent. However, a surprising result was noted after the readsorption scan while holding the potential at 0 V vs. SCE for an extended period of time. Here, the capacitance decayed from 50 \(\mu F\) cm\(^{-2}\) to a value close of 20 \(\mu F\) cm\(^{-2}\) within 5 min. This value is close to that obtained for the originally formed layer. This decay is presented in the triplicate analysis of Fig. 3b (AET planar) and the same analysis for the bead electrode is also shown (AET bead) although the decay is not as sharp. These results point to a unique observation related to a geometric influence. On a subsequent desorption scan after the 2 min at desorption and 5 min at adsorption potentials (dash-dotted line in Fig. 3a), the capacitance begins near 20 \(\mu F\) cm\(^{-2}\) and the peaks attributed to the desorption of AET from the Au(100) and Au(110) facets are again pronounced, suggesting that the decay in capacitance resulted from additional adsorption of AET onto the metal. Qu and Morin [34] have engaged in an electrochemical quartz crystal microbalance (EQCM) study to demonstrate that thiols can oxidatively deposit onto Au in a two-step mechanism. The first step is rapid nucleation and growth until the surface is covered by about 80–90% at which point slower Langmuir kinetics dominate. However, in their study, the thiol was added directly to the supporting electrolyte at a concentration of 1 mM which provides excess adsorbate at the interface. In our study, the electrolyte does not contain additional AET in the bulk electrolyte and readsorption can only occur from AET molecules that were originally desorbed from the electrode. Some spectroelectrochemical investigations using water insoluble surfactants have shown that the desorbed molecules may become trapped beneath planar electrodes when set in the hanging meniscus arrangement [45].
Therefore, it is possible that the decay in capacitance observed at positive potentials represents slow respreading of AET that are not in the bulk electrolyte nor in the immediate vicinity of the metal (i.e. a non-specifically adsorbed interfacial species). The hypothesis of a trapped thiolate species being present was tested further in four independent experiments.

Firstly, it is possible that the decay in capacitance is a result of a specific Au–AET interaction because AET has been shown to bind with Ag through either sulfur or nitrogen [41]. In this regard, it is possible that the slow decrease in capacitance at positive potentials corresponds to thiol rearrangement on the surface rather than their occurrence as an interfacial species. MPA was chosen for a comparative study because it has a similar alkyl chain length compared to AET but also has a carboxylic acid moiety. Both the planar and bead surfaces were modified with a layer of MPA and were exposed to the same desorption/readsorption holding procedure as AET. After cycling back to 0 V vs. SCE and holding for 5 min, MPA exhibits a decay in capacitance when on the planar electrode but not on the bead as shown in Fig. 3b. However, the decay in capacitance occurs to a lesser extent than AET, presumably because MPA is negatively charged in 0.250 M KOH and has greater solubility in the electrolyte. These results confirm that the decay in capacitance is not specific to a Au–AET interaction.

Secondly, the decrease in capacitance could be attributed to the manner in which the SAM was formed. In the incubation procedure, the whole electrode was submerged into the thiol solution and the walls of the planar electrode will also be coated with AET. When transferred to the electrochemical cell in the hanging meniscus arrangement, the walls are not in contact with the electrolyte. Because of this, the thiols on the wall should not be desorbed from the electrochemical procedure. When the potential is cycled to 0 V vs. SCE, these thiols that are adsorbed on the walls could potentially diffuse along surface to the planar face. This possibility was eliminated when considering the results presented in Fig. 3c (drop cast). Here, the SAM was formed by drop casting the thiol solution onto the planar face of the electrode without exposing the walls to the surfactant. This layer was then subjected to the same desorption/readsorption holding process and the decay in capacitance at 0 V vs. SCE was again evident.

Thirdly, if the interfacial thioliates are non-specifically adsorbed on the surface, they might be susceptible to rinsing. To test this possibility, the SAM formed from drop casting was exposed to a second desorption/readsorption scan. However, after a few seconds at 0 V vs. SCE, the electrode was removed from the electrochemical cell and rinsed with water for approximately 30 s, the results of which are shown in Fig. 3c (rinse). Clearly, the decay in capacitance occurs initially until the electrode was removed (marked by the gap in the capacitance data). After the electrode was rinsed and replaced in the cell, the capacitance was stable over 4 min. It is important to note that the capacitive decay was initially evident and only became stable after the surface was rinsed. Furthermore, the stable capacitance near 50 μF cm⁻² which is well below that for a bare electrode near 90 μF cm⁻² indicating that the rinsing procedure did not remove the thiols that were chemically bound to the metal.

As a final test, the influence of electrode configuration was studied to evaluate whether the unusual behavior could arise from the planar geometry of the electrode or from its configuration in the hanging meniscus arrangement. For this study, the planar electrode was wrapped in Teflon and modified with AET. In one study, a hanging meniscus was formed and in a separate study, the electrode was submerged into the electrolyte. As the walls of the electrode were insulated from the electrolyte, the effective area of the electrode remains the same for each study. As shown in Fig. 3c (wrap/meriscus and wrap/submerge), the unique decay in capacitance appears to be a function of the hanging meniscus since the sharp decrease is not noted when the electrode is submerged.

From these experiments it can be speculated that the desorption process may result in the production of an interfacial thiolate with limited diffusion at the planar electrode when set in the hanging meniscus arrangement. However, to verify this more completely, a detailed spectroscopic study such as light scattering [46] should be conducted. Regardless of the exact mechanism, the unusual respreading of AET on the planar electrode when set in the hanging meniscus arrangement is worth noting and could affect the ability to form the mixed monolayer with reproducibility. As such, the concept of rinsing away the speculated intermediate species to limit the respreading phenomenon was revisited. The results of this analysis for AET layers formed over 10 min are presented next.

3.4. Full desorption of AET

The most efficient electrochemical method suitable to remove AET from the entire planar Au surface was developed in the next stage of this study. Initially, a 10 min SAM of AET was formed on
the planar electrode and exposed to a potential pulse to $-1.4 \, \text{V vs. SCE}$ for a pre-determined holding time. Afterward, the potential was pulsed back to 0 V vs. SCE and the capacitance measured. This procedure was accomplished in triplicate for each desorption time studied. In this study, the slow respreading process at 0 V vs. SCE was interrupted by removing the electrode and rinsing the surface with water for 30 s. After the electrode was rinsed, it was placed back into the electrochemical cell and the ratio of $C_{\text{AET}}/C_{\text{BASE}}$ determined, the results of which are shown in Fig. 4 (□). When the layer is not exposed to electrochemical desorption, the normalized capacitance remains consistent at approximately 0.25 indicating the presence of AET. For the first desorption holding time of 2 min, the normalized capacitance increases and although the error bars are significant, the values obtained are consistently above 0.25, indicating that the rinsing limits the respreading although not reproducibly. As the desorption holding time is increased, the normalized capacitance trends toward unity with a reduction in the error bars. However, even after 30 min, the value never reaches unity, thus indicating that a portion of the surface still contains thiol. This is a longer desorption time required for the bead electrode as determined in our previous study [17], and suggests that some AET remains trapped. In the case of physically adsorbed surfactants on Au electrodes set in the hanging meniscus arrangement, it was found that the layer can be more significantly disrupted on the application of multiple desorption/readsorption pulses [39]. Presumably, multiple potential steps could modify the interfacial tension and solvent organization at the interface which may in turn disrupt the layer. This concept was applied to AET in a pulse program that provided a 1 min desorption pulse followed by a 10 s readsorption pulse. This was cycled 20 times for AET coated on the planar Au and resulted in a normalized capacitance of near unity as shown in Fig. 4 (△). The multiple potential pulse procedure appears to completely remove AET from the surface, a result further evident by the fact that the electrode did not need to be rinsed and the slow respreading process was not observed. Given that potential pulsing is a procedure suitable to remove AET from the entire planar surface, limiting the desorption limit to $-0.80 \, \text{V vs. SCE}$ should render AET voids only at the Au(111) facets given that this value slightly more negative than the desorption peak attributed to AET from Au(111) surface facets created by the truncated potential scans for three distinct layers on planar Au with each layer initially created with 10 min SAMs. The thin bold line represents the desorption scan of an AET layer that was previously exposed to 20 truncated desorption potential pulses to $-0.80 \, \text{V vs. SCE}$ each with a duration of 1 min. When compared to the desorption scan of undisrupted AET in Fig. 1c, a few differences are noted. Firstly, the capacitance of the disrupted AET layer in Fig. 5a is elevated at 0 V vs. SCE because some of the AET molecules have been removed from the surface. Also, at $-0.75 \, \text{V vs. SCE}$, there is no peak observable in Fig. 5a, demonstrating that AET has been removed from the Au(111) surface facets. This conclusion is further supported by the fact that the desorption peaks of AET from Au(100) and Au(110) facets are maintained at $-1.13$ and $-1.32 \, \text{V vs. SCE}$. The voids were backfilled by exposing the interface to an MUA solution for 10 min to create the heterogeneous mixed monolayer. A single component monolayer of MUA can also undergo reductive desorption by the application of a negative potential. This desorption of a single component MUA layer is represented in the dashed line of Fig. 5a. While the general trend is similar to AET, one distinct difference is the peak at $-1.0 \, \text{V vs. SCE}$.

3.5. Mixed monolayer formation

The capacitance plots shown in Fig. 5a represent the negative potential scans for three distinct layers on planar Au with each

![Fig. 4](image1.png)

**Fig. 4.** Average normalized capacitance for a 10 min AET modified electrode exposed to various holding times at the desorption potential of $-1.4 \, \text{V vs. SCE}$. The capacitance was normalized to the bare electrode at 0 V vs. SCE after the electrode was exposed to a rinsing procedure (□) or 20 desorption pulses to $-1.4 \, \text{V vs. SCE}$ each with a duration of 1 min (△).

![Fig. 5](image2.png)

**Fig. 5.** (a) Differential capacitance and (b) CV desorption curves for of planar polycrystalline Au electrode modified with different SAMs. The thin line represents a SAM of AET with voids at Au(111) surface facets created by the truncated desorption pulse procedure. The dashed line corresponds to a single component SAM of MUA and the bold line represents the desorption scan for the mixed monolayer of MUA on Au(111) and AET on Au(100) and Au(110). (c) A comparison of the differential capacitance desorption scans for mixed monolayers created from 10 min AET layer (solid line) and from a 16 h AET layer (dash-dotted line).
S.R. Smith et al. / Journal of Electroanalytical Chemistry 666 (2012) 76–84

83

SCE which corresponds to the desorption of MUA from the
Au(111) facets of the metal and at more negative potentials, the
desorption from Au(100) and Au(110) are convoluted in one peak.

Then, if the monolayer voids in AET exist only at the Au(111) sites,
backfilling with MUA should result in a peak at −1.0 V vs. SCE cor-
responding to MUA while the two peaks more negative should be
consistent with AET. The bold line of Fig. 5a, represents the desorp-
tion of the mixed monolayer formed by backfilling the voids with
MUA for 10 min. Although this process would result in a crude
backfilled layer, the shorter backfilling time was required in order
to avoid place exchange of AET for MUA at the other facets. As is
evident from this plot, the characteristics of desorption maintain
both MUA and AET features, thus supporting the formation of the
mixed monolayer.

Similar information can also be extracted from the negative
scan of the CVs shown in Fig. 5b. Here, the thin solid line represents
the reductive desorption of the 10 min AET layer previously ex-
posed to the truncated desorption procedure. In comparison with
Fig. 1a, the desorption peak attributed to the Au(111) facet is ab-
sent at −0.75 V vs. SCE, while desorption from the Au(100) and
Au(110) facets are still evident in Fig. 5b. For comparison, the neg-
ative sweep for a single component MUA layer is given by the
dashed line in Fig. 5b, revealing a negative shift in the desorption
potential from the Au(111) facet at a potential approaching −1.0 V vs. SCE and convoluted desorption from the Au(100) and
Au(110) facets at more negative potentials. For the mixed mono-
layer (bold line), although shifted, the desorption from Au(111)
facets of the polycrystalline Au surface delineated by a num-
ber of grain boundaries. On this image, four quadrants are labeled
size facets of the polycrystalline Au surface. Further validation of this is given in the surface probe analysis described next.

3.6. EBSD and LFM characterization of the mixed monolayer

As a final step in the characterization process, the surface of a
planar polycrystalline Au sample was prepared and characterized
with EBSD as described in the experimental section. The purpose
of this was to generate a distribution map of the principal facets
[(100), (110) and (111)] present over the Au surface and in con-
junction with LFM, establish a visual distribution of each thiol on
the surface. Results of this examination are presented in Fig. 6.

Fig. 6a is a AFM-height mode image that reveals the micron
sized facets of the polycrystalline Au surface delineated by a num-
ber of grain boundaries. On this image, four quadrants are labeled
which show unique LFM behavior. Some unique features of this
surface include a polishing line (left) and surface pit (top right)
on the image which were used as a reference for the EBSD analysis.
The EBSD characterization is presented in Fig. 6b (note the polishing
line is faintly visible in the left of the image) and the color key
is provided in Fig. 6c. The color key (also known as a pole figure) shows three extremities which indicate ideal (111), (100), and (110) character. When compared to the EBSD image, it is clear that the surface does not contain pure (111), (100) and (110) domains but rather a variety of crystallographic orientations that range in character. However, all regions of the EBSD image that appear in a shade of blue,² red or green can be considered to have a high degree of (111), (100) and (110) respectively. In the top half of the image, there is a large portion that corresponds closely to Au(111) character (Region I) and another region that corresponds to Au(100) and Au(110) character (Region II). In the lower half of the image, two other regions are noted that are more intermediate (Regions III and IV).

An LFM image of this surface after modification with 10 min AET is presented in Fig. 6d. This shows a relatively uniform distribution friction across the surface, a feature consistent with the properties of a single component SAM that is terminated by one functional group (in this case and amine group). The only deviations in frictional forces are noted at the scratch and pit owing to unusual tip deflection at these surface defects. Fig. 6e shows the LFM image of the interface after exposure to the potential pulse desorption/backfilling procedure. In this image, the heterogeneous distribution of frictional forces are clearly made visible. The bright regions represent high friction from MUA and correlate perfectly with the Au(111) facets represented in blue on the EBSD map. The darker areas on the LFM image correspond to the low frictional AET regions on the Au(100) and Au(110) facets. In particular, the LFM images are most clear in Regions I and II because of their nearly pure Au(111) or non-Au(111) facets. Regions III and IV are slightly less well-defined because of the intermediate character of the surface crystallography within these zones. These same conclusions can be made for a mixed monolayer formed from an initial 16 h AET layer as presented in Fig. 6f. However, Region III less well-defined possibly indicating that the desorption of 16 h AET layers require more than 20 desorption pulses in order to effectively clean all Au(111) sites of AET. It is noteworthy that the general trend of high frictional forces at Au(111) sites is consistent across both surfaces, reflecting the selectivity of the electrochemical desorption/backfilling process.

4. Conclusions

The electrochemical formation of a heterogeneous mixed SAM of AET and MUA on planar polycrystalline Au has been demonstrated and it can be concluded that electrode geometry has an influence on the fabrication process. The electrochemical results support the hypothesis of selective reductive desorption followed by thiolate diffusion into the bulk, thereby limiting the amount of species that can adsorb onto the metal through an oxidative process. While both spherical and bead electrodes exhibit readsorption events, the process is more pronounced at the planar electrode when set in a hanging meniscus arrangement which may stem from interfacial thiolates that do not diffuse away from the interface as readily compared to bead electrodes. In order to efficiently clean the planar electrode of all AET, a potential pulsing procedure has been developed and implemented, resulting in a modification to the general approach used of forming the heterogeneous mixed monolayer of AET/MUA on planar polycrystalline Au. Both electrochemical results and surface characterization with EBSD and LFM confirm the selectivity of this process.

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