Understanding Reactivity of Self-Assembled Monolayer-Coated Electrodes: SAM-Induced Surface Reconstruction

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TOC

Abstract

Thiolate self-assembled monolayers (SAMs) are often used to modify surface properties, including catalytic activity. These SAMs can also induce reconstruction of some metallic surfaces. Here we show, through formation and subsequent removal of thiolate SAMs from Au polycrystalline electrocatalysts, that irreversible changes to the underlying metal surface can lead to significant changes in catalytic properties, irrespective of specific interactions that might occur between thiolate molecules and various reactants. Using underpotential deposition of Pb as a surface probe, we find that across a range of different thiolates, SAMs tend to increase the proportion of (111)-facets on Au, but they simultaneously increase the defect density upon these and other facets. These changes lead to delayed onset but higher maximum activity toward formic acid oxidation, which is interpreted in terms of both the density of appropriate active site ensembles and changes to the binding isotherm for site-blocking hydroxyl species. The impacts of reconstruction are further illustrated through measured shifts in selectivity for electroreduction of crotonaldehyde, with reconstructed catalysts changing the favored product from butanal to crotyl alcohol. Thus, complex surface reorganization may play a significant role in catalytic behaviors of surfaces where thiol coatings are retained.

Keywords: lead underpotential deposition; formic acid oxidation; α,β-unsaturated carbonyl; surface reconstruction; electrocatalysis; self-assembled monolayer
1. Introduction

Metallic substrates modified by thiolate-based self-assembled monolayers (SAMs) have been used in diverse technological applications including molecular electronics, biotechnology, and for modification of various surface properties.\(^1,2\) They have also been used to modify reactivity and selectivity toward thermo- and electro-chemical catalyzed surface reactions.\(^3\)\(^–\)\(^9\) Thiolate SAMs can be deposited on different metallic surfaces by gas-phase or liquid-phase adsorption of precursors such as thiols, disulfides, or thioalkoxide salt solutions. It has been shown that the final (equilibrium) saturation coverage and corresponding SAM structure do not depend on the preparation method.\(^10\) Thus, on a perfectly flat and defect-free surface, the configuration of a SAM tends toward a dense, organized upright arrangement as the thiol concentration/dose or adsorption time increases. The evolution and geometry of these structures are driven mainly by the stabilization resulting from van der Waals (vdW) interactions between adjacent adsorbed molecules.\(^1,2\) However, in addition to the molecular phenomenon of self-organization, it has also been demonstrated that, on some surfaces, the adsorption of thiol molecules can cause considerable reorganization or reconstruction of the surface itself.

On Au(111), for example, thiol-induced reconstruction is associated with formation of atomic vacancies (V\(_{\text{Au}}\)) and corresponding gold adatom-thiolate complexes ((RS)\(_x\)–Au\(_{\text{ad}}\), \(x = 1 – 4\)), where the Au\(_{\text{ad}}\) species is generally bonded to threefold hollow sites on the underlying Au(111) substrate.\(^11\) Increasing coverage (\(\theta\)) of the thiol promotes increasing degrees of surface reconstruction.\(^12\) For linear alkanethiolate-based SAMs, (RS)\(_2\)–Au\(_{\text{ad}}\) species are mainly formed, with a thiolate saturation surface coverage of 0.33. This requires an Au\(_{\text{ad}}\) coverage of 0.16,\(^13\) which may mainly be provided by removal from step edges,\(^14\) but also by the uptake of Au surface atoms from terraces or uplifted islands/defects,\(^1,2\) depending on the location and mechanism of thiolate adsorption. Atomic vacancies (V\(_{\text{Au}}\), \(\theta_{\text{vac}} \approx 0.12\))\(^13,14\) can later coalesce to form vacancy islands at terraces or diffuse to yield serration-like steps.\(^14,15\) A more complex dynamic is observed for thiols with terminal groups distinct from alkyl. As examples, thiophenol (PhSH)\(^16\) and 4-mercaptopyridine (4MPy)\(^17\) form ordered SAMs with lower surface saturation coverage, \(0.2 < \theta < 0.25\). Whereas alkanethiolate-based SAMs show both V\(_{\text{Au}}\) and Au\(_{\text{ad}}\), V\(_{\text{Au}}\) and vacancy islands
have not been observed on Au(111) reconstructed by PhSH-SAMs, and only isolated V_{Au} have been found for 4MPy-SAMs.\textsuperscript{17,18}

While reconstruction phenomena have been studied on Au (and many other metals)\textsuperscript{1} extensively using high-resolution STM, only flat, nearly defect-free, and generally single-crystalline surfaces have been studied. Little is known about the dynamics and progression of reconstruction on polycrystalline surfaces—for example, whether native defects are etched or modified, and the extent to which edges and kinks are modified relative to terraces, remain open questions. It may nonetheless be expected that reorganization phenomena occur and could influence the chemical reactivity of the surface.

In the context of catalysis, thiols present in the substrate/SAM system can have different functions: (i) they can be the actual catalytic sites by anchoring a catalytic head group—this motif has been successfully employed on a multitude of reactions\textsuperscript{19}—or, (ii) they can tune the interface environment and/or underlying catalyst surface reactivity. For example, steric impediment of specific sites (terraces vs. edges) and interaction between thiols and reactants have been found to influence the adsorption geometry of reactants on catalytic sites, promoting substantial selectivity shifts for various (thermo)catalytic reactions.\textsuperscript{3,20–25} Examples in electrocatalysis have also recently been increasingly reported. Enhancement of formic acid oxidation has been observed on Au(111) electrodes modified with 4-mercaptopyridine SAM.\textsuperscript{4} The improvements were suggested to relate to changes in local hydrophobicity promoted by the presence of thiol, as well as interactions (acid-base and electrostatic) between thiol and reactants/intermediates.\textsuperscript{4} In addition, diverse examples of the catalytic effects promoted by SAMs have been shown for the CO\textsubscript{2} reduction reaction, where the selectivity and activity have been proposed to be affected by CO\textsubscript{2} gas trapping in the hydrophobic thiol layer,\textsuperscript{7} dipole interaction between thiols and adsorbed intermediates on the catalytic surface,\textsuperscript{8} and/or stabilization of a cationic-state of the metallic substrate.\textsuperscript{9} Similar phenomena have also been invoked with respect to electrocatalytic nitrogen reduction.\textsuperscript{5,6}

Despite widespread examples where coating catalysts with thiol-SAMs has promoted interesting catalytic behaviors, a remaining unexplored question involves the degree to which reconstruction may contribute to observed catalytic differences. Even in cases where the sulfur content on the catalyst is unaltered
during the reaction, the SAM structure may be dynamic or the reaction may occur on reconstructed thiol-free regions present on SAM-coated catalysts. Herein, we analyze SAM-induced surface reconstruction on polycrystalline Au surfaces by deposition and subsequent removal of thiol SAMs. The surface facet distribution and defect morphology are probed through underpotential-deposited Pb-stripping experiments, where SAMs are found to increase the population of (111)-surface domains while also increasing the density of defects within those domains. We then explore how the changes in surface structure impact two reactions: oxidation of formic acid (which is known to be sensitive to various surface facets and defects), and the reduction of crotonaldehyde, an α,β unsaturated carbonyl compound for which selectivity in reduction is critical and could be influenced by reconstruction phenomena. Formic acid oxidation is found to have a later onset but higher maximum activity on reconstructed surfaces, while crotonaldehyde reduction exhibits significant shifts in product selectivity due to reconstruction.

2. Experimental

2.1. Materials and Chemicals

All analytical grade chemicals were obtained from Sigma-Aldrich (when not specified) and used directly without further purification. Sodium thiomethoxide (precursor of methanethiol, C1SH, 95%), 1-Propanethiol (C3SH, 99%), 1-Hexanethiol (C6SH, 95%), 1-Adamantanethiol (AdmT, 95%), Thiophenol (PhSH, 97%), 4-Mercaptopyridine (4MPy, 95%), anhydrous ethyl alcohol (≥ 99.5%), NaOH (99.995% trace metals basis), NaClO4 (>99.9%), Pb(ClO4)2 (> 98%), NaHCO3 (> 99.5%), Suprapure HClO4 (> 99.999%), NaH2PO4 (Synth, >95%), Na2HPO4 (Synth, >95%), formic acid (≥ 95%), crotonaldehyde (≥ 99%, predominantly trans, 0.1-0.2% BHT and 1% H2O as stabilizers), crotyl alcohol (≥ 96%, cis and trans mixture), butyraldehyde (≥ 96%), 1-Butanol (anhydrous, ≥ 99.8%), 0.05 wt.% sodium 3-(trimethylsilyl)-2,2,3,3-tetradesuteropropionate (TMSP) in D2O (99.9 at. % D), Argon (UHP, Airgas Inc.). Au plate (Goodfellow, 0.25 mm thickness, 99.99% purity), Au wire (Goodfellow, 0.75 mm diameter, ≥99.95% purity), ultra-pure deionized water (specific resistance >18.2 MΩ cm, Elga Purelab Flex water purification system) was used to prepare all solutions.
2.2. Electrochemical experiments

Electrochemical experiments were carried out using a potentiostat/galvanostat (Gamry Instruments, Reference 3000). Two different three-electrode cells were used for specific experiments: a conventional H-type cell and a home-made µ-cell (more details can be found in Supporting Information, Figure S1). The H-cell had cathodic and anodic compartments of 10 mL each, while the µ-cell had compartments of 450 µL. For both cells, the compartments were separated by a proton- or anion-exchange membrane (Fuel Cell Store Nafion® 117 or Fumapem® FAA-3-50, respectively), depending on pH. A leak-free Ag/AgCl/Cl\textsuperscript{−}\textsuperscript{(sat. KCl)} or Hg/HgO\textsuperscript{0.1M NaOH} (for experiments at pH 13) electrode was used as the reference electrode (RE), and Au plates or wires were used as auxiliary electrodes (AE). A reversible hydrogen electrode (RHE) was used to calibrate the RE, and all potentials in this work are referenced to RHE, unless otherwise noted. Uncompensated resistance (R\textsubscript{u}) was measured by current interrupt and/or electrochemical impedance spectroscopy (EIS), and all measurements were R\textsubscript{u} corrected. The systems were degassed with Ar\textsubscript{(g)} and the H-cell temperature was controlled by a thermostatic bath (Fisher Scientific).

2.2.1. Self-assembled monolayer formation, and electrochemical characterization and removal

Six different thiolate self-assembled films were grown on Au electrodes at room temperature from ethanolic thiol solutions, with concentrations of 1 or 5 mM. Before the deposition process, the Au surface was, sequentially, cleaned in perchloric-piranha solution (PP-cleaning), flame polished, electrochemically polished, and soaked in anhydrous ethanol for 5 min (for surface conditioning and removal of remaining AuO\textsubscript{x})\textsuperscript{26}—additional details can be found for individual cases below. Then, the substrate was transferred to the respective fresh-prepared ethanolic thiol solution and left soaking for 30 min at room temperature. After the self-assembly process, the electrode (Au-SAM) was vigorously rinsed with pure ethanol (for elimination of non-chemically bound thiols) and immediately used for electrochemical experiments. The thiols used in this work were (structures shown in Supporting Information, Figure S2): Methanethiol (C1SH), 1-propanethiol (C3SH), 1-hexanethiol (C6SH), 1-adamantanethiol (AdmT), thiophenol (PhSH), and 4-mercaptopyridine (4MPy). A control sample, referred
to as “unreconstructed-Au (ur-Au)” was also submitted to the same preparation process, minus the deposition in thiol solution.

Electrochemical desorption of thiols (reductive stripping) was characterized by linear sweep voltammetry (LSV) in 0.1 M NaOH (as supporting electrolyte, pH 13) at a scan rate of 20 mV s⁻¹ and potential window from -0.3 to -1.4 V vs. Ag/AgCl_{(sat KCl)}. The voltammograms can be seen in the Supporting Information (Figure S3) and show that all the thiols used in this work can be electrochemically stripped prior to reaching -1.4 V vs. Ag/AgCl_{(sat KCl)}. Thus, the removal of the thiols from the Au surfaces was performed potentiostatically by polarizing the electrode at -1.4 V vs. Ag/AgCl_{(sat KCl)} for 2 min in 0.1 M NaOH under vigorous Ar bubbling and mechanical stirring; this facilitates mass transport of the thiols away from the electrode and eliminates re-adsorption. These electrodes will be called “reconstructed (r-)” from now on in the text. It is worth emphasizing here that “reconstructed electrodes”, in this context, are thiol-free/sulfur-free electrodes with surface reconstruction induced by SAM adsorption and retained after electrochemical removal of the SAM. In addition, we note that it has been extensively demonstrated that Au surfaces remain reconstructed after electrochemical removal of thiols (i.e., Au_{ad} and V_{Au} defects are still present on the surface). This stands in contrast to thermal desorption of SAMs, where defects have higher mobility and can be diminished by annealing processes.

To determine the electrochemical surface area (ECSA), capacitance measurements were calibrated against Au surface oxide reduction. The reason that the oxide reduction peak could not be used directly is that high oxidizing potentials can alter the surface in comparison to what is formed by interactions with the SAMs. For this experiment, electrodes were first cleaned by electropolishing in 0.1 M HClO₄ (pH 1) by cycling 50 times from 0.5 to 1.7 V vs. RHE, at 300 mV s⁻¹. Then, the ECSAs of eight (8) different ur-electrodes were measured by integrating the charge of the AuOₓ reduction peak (where 390 µC is equivalent to 1 cm²) from cyclic voltammograms (CV) collected in 0.1 M HClO₄ (pH 1) from 0.24 to 1.44 V vs. Ag/AgCl_{(sat KCl)} (0.5 to 1.7 V vs. RHE) at 20 mV s⁻¹. The respective specific capacitance of each electrode was also measured in the same supporting electrolyte using CVs collected between 0.3 to 0.7 V vs. Ag/AgCl_{(sat KCl)}— the pure capacitive region— at different scan rates (50, 100, 150, 200, 250, and 300 mV s⁻¹). The voltammograms and plots of capacitance
vs. scan rate for this experiment can be seen in the Supporting Information (Figure S4). The relationship between capacitance at 0.5 V and ECSA obtained from the polycrystalline Au electrodes was $32.4 \pm 2.6 \text{ (n =8) } \mu\text{F cm}^{-2}_{\text{ECSA}}$. From this method, complete thiol removal was confirmed before every experiment—see Figures S5 and S8.

### 2.2.2. Lead underpotential deposition

For lead underpotential deposition (Pb-UPD) experiments, a Au-bead electrode was used. To make this electrode, a gold wire (Goodfellow, 0.75 mm diameter, ≥99.95% purity) was cleaned for ca. 30 minutes in hot perchloric-piranha solution (PP-cleaning, 3 parts concentrated HClO$_4$ to one part 30% H$_2$O$_2$ by volume) followed by rinsing with ultrapure water and ultrasonication for 5 min. After PP-cleaning, the wire was melted into a spherical bead of approximately 2.5 mm in diameter and left to slowly cool in the air (room temperature of 18°C) for 1 minute before being rinsed with ultrapure water. To improve reproducibility and simulate the treatment done on Au plates used in electrolysis experiments (crotonaldehyde reduction further below), the bead electrode was always submitted to PP-cleaning, flame polishing and electropolishing between each experiment with thiols.

Pb-UPD experiments were performed on ur- and r- electrodes (six different thiolate-SAM depositions for reconstruction). An oxygen-free H-cell was used, and a Pb-UPD monolayer was potentiostatically deposited at -0.4 V vs. Ag/AgCl(sat KCl) for 1 minute from a solution containing 0.1 M NaClO$_4$, 0.01 M HClO$_4$, and 0.001 M Pb(ClO$_4$)$_2$, following well-established procedures.$^{31,32}$ Stripping linear sweep voltammograms were collected at a scan rate of 20 mV s$^{-1}$, from -0.4 to 0.4 V vs. Ag/AgCl(sat KCl). Stripping peaks were deconvoluted using Gaussian functions and can be observed in the Supporting Information (Figure S6).

### 2.2.3. Electro-oxidation of formic acid

The formic acid oxidation reaction (FAOR) was performed on ur- and r-Au-bead electrodes, prepared identically to the description for Pb-UPD experiments. Each electrode was studied by cyclic voltammograms collected in 0.1 M HClO$_4$ + 0.1 M HCOOH, from 0 to 1.2 V vs. RHE, at a scan rate of 20 mV
s⁻¹, in an H-cell. Differential electrochemical mass spectroscopy (DIMS) was also used to confirm CO₂ production and probe the possible production of H₂ during FAOR, since several works have demonstrated small amounts of H₂ production from FA on other metals.³³ DIMS experiments were only performed on ur-Au in the µ-cell. For these tests, an Au film was deposited on a gas diffusion layer and, using an MS capillary probe, the µ-cell was coupled to the quadrupole vacuum system of a Hiden HPR40 mass spectrometer during LSV and pulsed-potential experiments (more details can be found in Supporting Information, Figure S7). An electron energy of 70 eV and emission current of 700 μA were used for ionizing all species. A scanning electron multiplier (multiple ion detection mode) with a multiplier voltage of 1.4 kV was applied to simultaneously detect H₂ (m/z = 2) and CO₂ (m/z = 44).

2.2.4. Electro-reduction of crotonaldehyde

The electrochemical reduction of crotonaldehyde (CRAL) was initially performed in a gas-tight H-cell with headspace sampling by gas chromatography. After verifying H₂ and other gases were negligible, a µ-cell (Figure S9 Supporting Information) was utilized for electrolyses, with Au-plates (ur- and r-) used as working electrodes. These plates were mechanically polished with alumina slurry (0.05 μm, Allied High Tech Products Inc.) to a mirror-like finish, followed by ultrasonic cleaning (in ultrapure water and ethanol for 5 min each) to remove residual alumina. Then, similarly to what was done to the Au-bead electrodes, the plates were subjected to flame polishing, electropolishing, and ethanol soaking. The reconstruction induced by thiolate-SAMs was created using the same procedure mentioned in previous sections (i.e., thiol deposition and removal, followed by capacitance check to make sure the surface was thiol-free—see Figure S5).

A quick pH and electrolyte screening was first performed using LSV as an optimization guide. Then, electrolyses were performed at four different potentials (-0.55, -0.70, -0.85, and -1.00 V vs. RHE) and two different charges (1 and 2 F per mol of CRAL), using an initial CRAL concentration of 50 mM. Based on these exploratory experiments (data and discussion are presented in the Supporting Information, Figure S10), electrocatalytic studies were performed with ur- and r-electrodes in 0.1 M NaClO₄ + 0.1 M NaHCO₃ (buffered pH 8) as the supporting
electrolyte, at -0.70 V vs. RHE and room temperature, passing a total charge of 1 F per mol of CRAL (i.e., 2.17 C for 450 µL of 50 mM CRAL). The product analysis was performed by \(^1\)H NMR and liquid chromatography (LC); analytical procedure details are organized in the Supporting Information (and Figures S10 – S12). For NMR analysis, a Bruker AVANCE-III 400 MHz NMR spectrometer was used, and LC analyses were performed on an Advion 2000 HPLC equipped with a 300 mm x 6.5 mm sulfonated polystyrene gel column (Hi-Plex H, Agilent) and a UV diode array detector (DAD).

3. Results and discussion

3.1. Signatures of reconstruction from lead underpotential deposition

Direct measurement of surface reconstruction on Au particles, e.g. via microscopy, is challenging. A more straightforward approach is to use indirect probes of the distribution of surface sites. It has been well-established that the phenomenon of underpotential deposition (UPD) is very sensitive to the crystalline structure of the substrate surface. Lead-UPD and its subsequent monolayer stripping have been extensively studied on Au, Ag, Cu, and Pt single- and poly-crystalline surfaces.\(^{35,36}\) For this reason, Pb-UPD was chosen as a probe for studying the surface reconstruction of polycrystalline Au caused by SAM deposition. Reconstruction was studied with six different thiols: Methanethiol (C1SH), 1-propanethiol (C3SH), 1-hexanethiol (C6SH), 1-adamantanethiol (AdmT), thiophenol (PhSH), and 4-mercaptopypyridine (4MPy). Capacitance measurements performed before and after SAM removal on the reconstructed surfaces showed that the thiols were completely removed by voltammetric stripping prior to UPD, as discussed in the Experimental section and the Supporting Information (Figure S5). Linear sweep voltammograms (LSVs) of Pb-UPD monolayer stripping were collected on each unreconstructed (ur) and reconstructed (r) polycrystalline Au surface and are shown in Figure 1a.
Figure 1. Pb-UPD adlayer desorption experiments on different polycrystalline Au surfaces (unreconstructed, ur-, and reconstructed, r-) by different thiol-SAMs after deposition and removal: a) stripping linear sweep voltammograms after Pb monolayer was grown at -0.4 V for 60 s, and b) relative peak potential shift ($\Delta E_{\text{peak}}$), full width at half maximum (FWHM$_{\text{peak}}$), and peak-charge ($Q_{\text{peak}}$) for major features.
Five main Pb-adlayer stripping peaks are observed and labeled as follows: (a) with peak potential ($E_{\text{peak}}$) ca. -0.32 V, (b) at ca. -0.21 V, (c) at ca. -0.16 V, (d) a small shoulder at ca. -0.12 V (more evident in ur-Au), and (e) between 0 and 0.03 V, all vs. Ag/AgCl(Sat. KCl). Peak-a is known to be partial stripping from very compact adlayers formed with a reorganization of Pb adatoms already deposited at less negative potentials on (110) and (100) terraces.\textsuperscript{31,32} This reorganization, which compresses the adlayers and accommodates extra adatoms, does not happen on wide (111)-terraces (at least 6 atoms wide). Peak-b and peak-c next correspond to the stripping of Pb from the (111)-terraces, which begins with coverage of roughly 0.9. Thermodynamic and kinetic effects make the (111)-adlayer, present before the stripping at peak-b, convert into stable Pb-islands that are next stripped at peak-c.\textsuperscript{31,32,35} The presence of peak-c is thus associated with large, extended (111)-facets.\textsuperscript{37–40} Finally, peak-d is associated with the majority of stripping from (100)-terraces,\textsuperscript{31,32,41} while the broad peak-e is composed of several processes, including removal of some residual Pb on (100)-surfaces, stripping from (110)-facets, and steps and kinks on various faces. Contributions from atomic defects (e.g., vacancies and adatoms) have not been systematically probed in past studies,\textsuperscript{31,32} but we expect that scattered atomic defects most distinctively lead to broadening of the signature peaks for the various faces upon which they form.

To evaluate differences between r- and ur-surfaces, Figure 1b shows relative changes in peak potential ($\Delta E_{\text{peak}}$), full widths at half maximum (FWHM\textsubscript{peak}, right axis), and relative integrated peak charges (Q\textsubscript{peak}). These metrics come from deconvolution of all peaks present in the stripping signatures with Gaussian functions, as shown in the Supporting Information, Figure S6. To also help visualize effects created by reconstruction, Figure 2 schematically shows a variety of structural motifs that will be referenced below.
The combined analysis of UPD data shown in Figure 1b suggest that reconstruction via thiolate deposition and stripping results in an increased prevalence of defect-laden (111) terraces with a broad size distribution. First, observing $\Delta E_{\text{peak}}$ values in the top-frame in Figure 1b, the modest variation ($< 10$ mV) for peak-b and peak-c (Pb$_{\text{ad}}$ on (111)-terraces) suggests that changes in defects on the (111)-terraces (promoted by reconstruction) do not significantly affect the average formation energy of Pb-islands or Pb-full-adlayers on these facets relative to ur-Au. However, as shown in the bottom-frame of Figure 1b, the relative stripping charge (rel. $Q_{\text{peak}}$, defined by fraction of total charge for a peak, normalized to values on ur-Au) for the sum of peak-b and peak-c increases for almost all reconstructed surfaces (all except for C6SH, which forms the most ordered and stable SAM among all). This suggests that (111)-terraces are extended/created by etching large native defects (e.g. uplifted steps or clusters/islands) and/or relocating atoms to add to (111)-domains, as depicted in Figure 2. Despite the increased charge associated with (111)-facets, there is also a general growth in FWHM$_{\text{peak}}$ values for peak-b and peak-c (middle-frame in Figure 1b), for all explored thiols except PhSH (discussed further below). Peak broadening can be considered an indicator of a widening distribution of ensemble sizes (number of atoms composing the continuous domains), and/or the
existence of more atomic defects upon those ensembles. Thus, combining both $Q_{\text{peak}}$ and $\text{FWHM}_{\text{peak}}$ for the (111)-domain features, the data suggest a general increase in the density of large—albeit atomic-defect-laden—(111)-terrace domains. The $\text{FWHM}_{\text{peak}}$ for peak-c is less affected than peak-b since peak-c is associated with stripping of Pb islands (e.g., at the center of (111)-terraces); the initiation events that cause peak-b would be more variable with the creation of more $\text{Au}_{\text{ad}}$ and/or $V_{\text{Au}}$ species by reconstruction. Moving to peak-d and peak-e in Figure 1, $\Delta E_{\text{peak}}$ values are associated with the character and density of surface steps, kinks, and defects present outside of the (111)-terrace domains (peak-d mainly varying due to interference from peak-e). Although it is not possible to deconvolute and specify all types of defects sampled in this feature, it is evident from the $\Delta E_{\text{peak}}$ of peak-e that reconstruction by different thiols causes distinct and complex restructuring dynamics outside of the (111)-terraces (shifting distributions of defect types and relative degrees of facet exposure). C3SH and AdmT promoted these effects to the greatest degree, based on their outsized influence on peak-e.

In summary, SAM-induced reconstruction generally appears to increase the size of (111)-terrace domains but to simultaneously change the nature and distribution of defects within all domains. C3SH, AdmT, and 4MPy promoted the highest degree of restructuring outside of (111)-terraces (order of change compared to ur: AdmT > C3SH > 4MPy > PhSH > C1SH ≈ C6SH, based on $\Delta E_{\text{peak}}$ for peak-e). C3SH promoted the most dispersion in continuous (111)-domains (order: C3SH > C1SH ≈ 4MPy > C6SH ≈ AdmT > ur > PhSH, from $\text{FWHM}_{\text{peak}}$), while AdmT made the total quantity of (111)-terraces increase the most (order: AdmT > 4MPy > C1SH > C3SH ≈ PhSH > ur > C6SH, from $Q_{\text{peak}}$). While deconvoluting the contribution of each existent face or group of defects in finer detail from Pb-UPD is difficult, the changes in the overall stripping profiles themselves are strong evidence for the complex surface reorganization promoted by different thiolate-SAMs. These must, in turn, affect the catalytic properties of the respective surfaces. This is explored in the following two sections.
3.2. Formic acid oxidation

The electrochemical formic acid oxidation reaction (FAOR) is known to be most rapid on (111)-terraces of Au\textsuperscript{42,43}, so it would be expected that SAM-induced restructuring should impact the specific activity of Au for FAOR. Figure 3a shows CVs for FAOR on ur-Au and r-Au surfaces, with a comparison of extracted metrics compiled in Figure 3b: (i) relative peak potential shifts (\(\Delta E_{\text{peak}}\)) vs. ur-Au; (ii) “onset” potential shift, defined as the relative overpotential (\(\Delta E\)) vs. ur-Au to reach current density 10 \(\mu\)A/cm\(^2\); (iii) relative rate at 1.00 V (rel-R\textsubscript{FAOR}, the ratio between current density for r-Au catalysts and ur-Au at its \(E_{\text{peak}}\), 1.00 V); and (iv) hysteresis factor (potential span between forward and backward scan at half maximum current density, \(\text{HE}_{M/2}\)). A quick analysis of the figure makes clear that all r-surfaces show small positive \(\Delta E\) at \(i = 10 \mu\)A/cm\(^2\) ECSA (delayed onset), but generally have much higher rel-R\textsubscript{FAOR} values. We stress that the upper potential limit is well below the gold oxide formation potential, so these effects are solely introduced by structural changes created by the adsorption and removal of SAMs. Plateaus and decreases in the current at high potential are also not caused by mass transfer limitations, but rather by competition between the reactant and surface hydroxyl groups that block active sites\textsuperscript{42}:

\[
\text{H}_2\text{O}^{(l)} + 1^* \rightarrow 1^- + \text{OH}_{\text{ad}} + \text{H}^+_{\text{(sol.)}} \quad (\text{eq. 1})
\]

By comparing UPD features and FAOR profiles, it appears that increasing the quantity of (111)-surface area could contribute to accelerating the reaction, but it cannot fully explain (i) delayed onset potentials, and (ii) that the maximum currents generally grow by larger factors than the gains in (111)-surface area (based on \(Q_{\text{peak}}\) for peaks b and c).
Figure 3. a) Cyclic voltammograms for formic acid oxidation on different polycrystalline Au surfaces at a scan rate of 20 mV s$^{-1}$ in 0.1 M HClO$_4$ + 0.1 M HCOOH solution. b) Shifts for peak potential (Δ$E_{\text{peak}}$) (where applicable), potential at a current density of 10 µA cm$^2$, relative rate at 1.00 V ($E_{\text{peak}}$ for ur-Au), and hysteresis factor (potential span between forward and backward scan at half maximum current density, HE$_{M2}$). Labels signify unreconstructed (ur-), and reconstructed (r-) surfaces exposed to different thiol-SAMs (after complete electrochemical removal of the thiol molecules).
To help interpret the role of reconstruction, we note that FAOR occurs on Au electrodes via a single direct path. The mechanism involves electroadsorption of formic acid dimers, \((\text{HCOOH})_2\), (transferring one electron and one proton per monomer) to yield surface formates \((\text{HCOO}_{\text{ad}})\). This is followed by a purely chemical, rate-determining bimolecular decomposition reaction between adjacent surface formates, producing one \(\text{H}_2\) and two \(\text{CO}_2\) molecules for each dimeric unit. This is notably in contrast to FAOR on Pt-group metals, where indirect paths (via \(\text{CO}_{\text{ad}}\) intermediate) can also be present and require participation of \(\text{OH}_{\text{ad}}\). Two additional electrons are gained from oxidation of \(\text{H}_2\), as the potential is generally high above the threshold for that reaction. We confirmed that \(\text{H}_2\) gas generation was negligible by DEMS experiments (Supporting Information, Figure S7). The aforementioned steps are summarized below:

\[
(\text{HCOOH})_2(\text{sol.}) + 4^* \rightarrow 2e^- + 2\text{HCOO}_{\text{ad}} + 2\text{H}^+(\text{sol.}) \quad \text{(eq. 2)}
\]

\[
2\text{HCOO}_{\text{ad}} \rightarrow 2\text{CO}_2(\text{g, sol.}) + \text{H}_2(\text{g, sol.}) + 4^* \quad \text{(eq. 3)}
\]

\[
\text{H}_2(\text{g, sol.}) \rightarrow 2e^- + 2\text{H}^+(\text{sol.}) \quad \text{(eq. 4)}
\]

Since bimolecular decomposition (eq. 3) requires terrace ensembles with at least four sites that can accommodate two adjacent \(\text{HCOO}_{\text{ad}}\), we suggest that the delayed onset behavior of \(r\)-catalysts is likely a byproduct of the increase in defect density on the expanded (111)-terraces. Although we cannot comment on the precise geometry or distributions of available ensembles, Figure 2 illustrates examples of some possible four-site configurations on (111)-terraces. Defects may disrupt site ensembles with appropriate symmetry for \(\text{HCOO}_{\text{ad}}\) pairs to undergo second-order surface reactions. Increased defect density could also, or alternatively, overstabilize formate species and slow their rate of turnover. This would depend on an unknown interplay with \(\text{OH}_{\text{ad}}\), however, since these species will tend to accumulate at defect sites and could contribute either strengthening (e.g., through H-bonding) or weakening (e.g., through higher overall coverage/Frumkin isotherm) influences on \(\text{HCOO}_{\text{ad}}\).

At higher potentials that permit rapid adsorption, high coverages of \(\text{HCOO}_{\text{ad}}\) will be reached. The associated increase in peak currents for \(r\)-catalysts could partly be attributable to higher overall populations of (111)-domains and the (pure chemical) turnover rate upon those facets. However, we hypothesize that
beneficial adsorbate-adsorbate interactions with OH$_{\text{ad}}$ (populating defect sites), could also play a role, since the gains are disproportionate to the increases in surface area. The adsorption of OH$_{\text{ad}}$ to terraces can be probed from the values of $\Delta E_{\text{peak}}$ (potential where it outcompetes formate) as well as $\text{HE}_{\text{M}/2}$ (since hysteresis is created by reaching high OH$_{\text{ad}}$ coverages and slowing the subsequent desorption on the reverse scan), both given in Figure 3b. These signatures indicate that all r-surfaces have a lower OH$_{\text{ad}}$ coverage on open terraces than ur-Au for any given potential. Given that the growth in defects promotes “early” OH adsorption directly at those sites, the consequence may be a weakening of OH binding strength on nearby terraces (Frumkin isotherm). Defect-OH$_{\text{ad}}$ could thus play either an indirect (e.g., by making terrace sites more available) or direct (e.g., by stabilizing a key transition state), role in enhancing the apparent rate per unit of (111)-surface area at high potential. Regardless of the exact interpretation, rough surfaces are not in general beneficial for FAOR, so it appears that combining (111)-facets with highly dispersed defects is a key characteristic.

Summarizing, FAOR can act as a probe to analyze reconstruction phenomena promoted by different thiolate-SAMs deposited on polycrystalline Au. Complementing insights from Pb-UPD experiments, we observed that most of the thiols promoted an etching of low-coordinated features and large defects, enlarging (111)-surface ensembles, though likely leaving significant residual defects such as adatoms and vacancies. These defects in turn lead to a reduction in site ensembles having ideal symmetry for the FAOR (slowing onset), but the larger quantity of terraces and some synergistic benefit to highly dispersed defects ultimately raises the rel-R$_{\text{FAOR}}$ at high overpotential. This is probed in Figure 4, where the FWHM for (111) Pb-stripping (peaks b+c) is plotted against the maximum rel-R$_{\text{FAOR}}$. The order of maximum FAOR activity (from rel-R$_{\text{FAOR}}$) is C3SH > PhSH > C6SH ≈ AdmT > C1SH > ur > 4MPy; meanwhile, the density of strong OH trapping defects (inferred from $\text{HE}_{\text{M}/2}$) is ur ≈ C1SH ≈ 4MPy > AdmT ≈ C6SH > PhSH = C3SH. Considering these observations with exceptions to the correlation in Figure 4, we suggest that an extreme case and partial exception to the enhancement of maximum rate comes from 4MPy SAM, where the onset potential is shifted to very large positive potentials. Speculatively, this could be due to a very high atomic defect density on (111)-terraces causing the defect
density to reach such a level that bimolecular reaction steps are impeded even at high reactant surface coverage. Meanwhile, PhSH appears to have a relatively low defect density and high rates—this could correlate to more pristine (111) facets, consistent with documented observations that PhSH causes facet reconstruction with less defect formation.

![Figure 4](image.png)

**Figure 4.** Comparison between the FWHM of Pb-UPD peaks b+c for r-surfaces (from Figure 1b) with the relative rate of FAOR at 1.0 V (from Figure 3b).

### 3.3. Electrochemical reduction of crotonaldehyde

Achieving high selectivity, yield, and faradaic efficiency for (electro)reduction of α,β-unsaturated carbonyl compounds such as (E, Z)-2-butenal (crotonaldehyde, CRAL) is a major challenge. It has been found that CRAL can be unselectively reduced not only to crotyl alcohol (CROL), butyraldehyde (BuAL), and 1-Butanol (BuOL), but also to highly hydrogenated C$_4$-hydrocarbons (e.g. 1-butene, $n$-butane, cis,trans-2-butene), as shown in Scheme 1. In addition, the mass balance and faradaic efficiency (FE) can be greatly affected by competing polymerization paths and the hydrogen evolution reaction (HER). Under commonly studied conditions, Ni, Co, Cu, Au, Pd, and Pt are all found to be most selective toward BuAL (selectivity over 50%), while Ag is more selective to CROL, and Fe to BuOL. However, in addition to conditions such as supporting electrolyte composition, potential, and charge passage, catalyst surface morphology can also play an important role in the observed selectivity.
Part of the challenge in selective reduction of CRAL is that the hybridization of multiple molecular orbitals (some more localized on C=O, others on C=C) with $d$-states from metallic catalysts makes adsorption paths through C=O and C=C both favorable in many cases.\textsuperscript{49,50} It has also been discussed that coverage effects (associated with steric and lateral interactions) can make the adsorption mode shift from C=C (lower coverage) to C=O (higher coverage). Because of this complexity and sensitivity toward surface properties, this reaction was chosen for extending our observation of reconstruction effects on electrocatalytic behavior.

\textbf{Scheme 1.} Electrochemical reduction of crotonaldehyde (CRAL). Adsorption configurations will favor formation of crotyl alcohol (CROL) or butanal (BuAL). Intermediate radical anions (or adsorbed anions) can lead to polymerization side reactions. Homogenous hydrolysis reactions are not shown.
Based on an optimization of reaction conditions (shown in Supporting Information Section 3), electrocatalytic studies were performed on the ur- and r-electrodes using 0.1 M NaClO₄ + 0.1 M NaHCO₃ (buffered pH 8) as the supporting electrolyte, applying a constant potential of -0.70 V vs. RHE and passing a total charge of 1F per mol of CRAL. Figure 5 shows the resulting rates (average over reaction), selectivity, mass balance (MB), and faradaic efficiency (FE) for CRAL reduction on ur- and various r-Au electrodes.

Figure 5. Selectivity, mass balance (MB), faradaic efficiency ($F_{E_{CRAL}}$), and product formation rate for CRALR on polycrystalline-Au surfaces, unreconstructed (ur-) and reconstructed (r-) by different thiol-SAM (after complete electrochemical removal of the thiol molecules). Electrolyses were performed from 50 mM CRAL in 0.1 M NaClO₄ + 0.1 M NaHCO₃ (buffered pH 8), at -0.70 V vs. RHE (iR-corrected) and room temperature, passing a total charge of 1F per mol of CRAL.

Analyzing Figure 5, we can clearly see that the reconstruction promoted by thiolate-SAMs impacts CRAL reduction; the selectivity on all r-catalyst shifted 20 – 40% toward CROL compared to the ur-catalyst. Even though very little is known about the reactivity of CRAL on different sites (terraces, edges, kinks, general defects) present on polycrystalline Au, this result suggests that, compared to ur-Au, the r-electrodes have a higher density of sites (per ECSA) that: i) bind CRAL molecules through C=O, promoting reduction of CRAL into
CROL; and/or ii) promote higher CRAL coverage, making the adsorption through C=O favored; or/and even iii) have a higher turnover frequency for CROL production. Aside from the selectivity gains, r-catalysts showed FE’s and MB’s that are somewhat higher than observed for ur-Au; thus, we can speculate that the reaction pathway toward CROL (reduction of C=O instead of C=C) is less susceptible to side polymerization reactions, or that the reconstructed films have a lower density of sites that catalyze side reactions (e.g., these could happen on defects or higher index facets). Reaction rates also had small improvements with reconstruction, with the most substantial rate gains (factor of 2-3) on surfaces reconstructed by C1SH and C3SH. Given that C1SH and C3SH also had the greatest selectivities toward CROL, this may indicate that the turnover frequency on the sites that favor CROL is slightly higher than that on the sites selective to BuAL—in other words, the selectivity comes from accelerating CROL formation more than from suppressing BuAL formation.

4. Conclusions
The catalytic behaviors of thiol-free polycrystalline Au catalysts subjected to SAM-induced reconstruction were studied by different electrochemical probes: Pb underpotential deposition, formic acid oxidation, and reduction of an α,β unsaturated carbonyl compound (crotonaldehyde). Based on Pb-UPD, the reconstruction seems to increase the density of atomic defects on (111)-terraces, as well as the size of these domains. A simultaneous change in the nature and distribution of defects within all domains was also observed. This complex surface reorganization promoted a slower onset but higher activity for FAOR, and a 20 – 40% shift of CRAL selectivity toward CROL, giving collective evidence that this effect may have a significant contribution to the catalytic behaviors of thiol-coated SAM surfaces as well.

Conflicts of interest
There are no conflicts to declare.

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