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Electrochemical Stability of Low-Density Carboxylic Acid Terminated Monolayers

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Using cyclic voltammetry, we studied the reductive desorption of a series of low-density self-assembled monolayers (LD-SAMs) made from mercaptohexadecanoic acid (MHA). Desorption experiments indicate that LD-SAMs are significantly less stable than a full MHA monolayer. All three LD-SAMs investigated presented a broad desorption peak in the region between -1.0 and -0.8 V vs SCE, which is in contrast to the single peak with a narrow distribution at -1.11 V observed for the full MHA monolayer. Upon backfilling the LD-SAM with a shorter-chain thiol (mercaptohexanol), the desorption of the mixed monolayer displayed a single peak, indicative of a well-mixed monolayer. Our results show that LD-SAMs are promising candidates for mixed monolayers and suggest that the broad desorption peak observed for LD-SAMs might arise due to adsorption at different binding sites.

Introduction

Molecular assembly at the solid–liquid interface has had a tremendous impact on micro- and nanoscale technologies, where precise control over interfacial chemistry has become an important approach to dictate device functionality.^{1–3} Thiolated self-assembled monolayers (SAMs) on gold typically produce pseudocrystalline monolayers whose electrochemical stability is well-characterized.⁴ Although often a desired feature, the crystalline nature obtained from thiolated SAMs can limit their use for applications where mixed surface functionality or conformational freedom is needed. Therefore, there is a need to develop methods to control the packing density of SAMs, as a loosely packed monolayer could allow for the fine-tuning of properties, such as wetting and ion transport.^{5–8} In addition, low-density SAMs (LD-SAMs) can be designed to respond to external stimuli, such as change of pH or in applied potential,^{6,9,10} which could lead to innovations in chemical sensing and separation. The electrochemical stability⁷ of LD-SAMs is central to many of their applications; however, the effect of a harsh environment (such as high temperature, departure from neutral pHs, or large applied potentials) has not been investigated.

Reductive desorption using cyclic voltammetry provides a platform to study the electrochemical stability of LD-SAMs. Desorption experiments lead to a direct measure of the stability,⁴ the surface coverage,^{4,11} and the desorption kinetics of the films.^{4,11,12} For example, SAMs formed from thiols with longer chains desorb at more negative potential.⁴ Different chain lengths and terminal groups determine the kinetics of the desorption and readsorption process of the SAMs.^{12,13} Moreover, the presence (or absence) of multiple desorption peaks can be assigned to microscopic SAM domains (as small as 15 nm^2),¹⁴ different binding sites,^{15–17} or variation of the underlying gold crystalline structure.^{18–20} Desorption of well-characterized, ordered, monolayers has been instrumental to interpreting the features of the voltammograms (such as the shape, area, and position of the desorption and readsorption peaks).^{4,19,21} Alternatively, LD-SAMs could provide additional insight into SAMs'

desorption as they allow us to explore the importance of chain–chain interactions on the desorption of the monolayers.

This work details our efforts to characterize the electrochemical stability of LD-SAMs of mercaptohexadecanoic acid (MHA). The LD-SAMs were formed using a method we developed relying on noncovalent ion-pair interactions in solution to control the molecular packing density of SAMs on gold surfaces.²² In this method (illustrated in Scheme 1), the size of an ion complex formed in solution between MHA and various tetraalkyl ammonium cations (TAA^+) dictates the spacing between the MHA chains bound on the surface. The ion-pair SAMs can then be converted into LD-SAMs using an ion-exchange step. Three different TAA^+ cations were employed to reduce the surface coverage: tetrapentylammonium (TPeA^+), tetrapropylammonium (TProA^+), and tetraethylammonium (TEA^+), leading to a packing density that varies from approximately 30% to 60% of a full thiol monolayer.

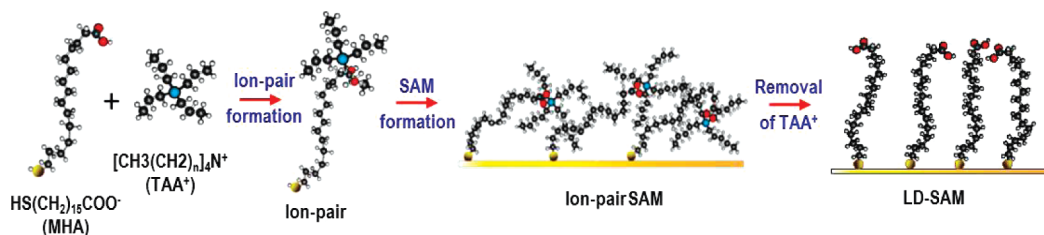
Here, we show that LD-SAMs are less stable than their fully packed MHA counterparts (i.e., MHA monolayers formed without artificially increasing the steric hindrance between chains).²³ The surface coverage obtained by calculating the charge under the desorption peak is consistent with the surface coverage measured using other techniques. In addition, we observe that the desorption potentials for the three LD-SAMs investigated are more positive than the desorption potential of a crystalline MHA monolayer. Surprisingly, we did not observe a significant shift to a more positive desorption potential as the coverage of the LD-SAMs decreased from 60% to 30%. Multiple (or broad) desorption peaks were observed in the cyclic voltammograms and were hypothesized to originate from the thiols binding on different gold sites. Finally, we demonstrate that mixed SAMs without domains can be made by backfilling the LD-SAMs with a shorter thiol.

Experimental Section

Materials. 16-Mercaptohexadecanoic acid (MHA, 99.8%), mercaptohexanol (97%), carbon tetrachloride (99.99%), potassium perchlorate (99%), and tetraalkylammonium hydroxide salts of increasing chain lengths, $[\text{CH}_3(\text{CH}_2)_n\text{N}^+\text{OH}^-]$ (TAAOH , where the TAA^+ cation is hereafter referred to as TEA^+ for n

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SCHEME 1: Illustration of the Steps Involved in the Formation of LD-SAMs



= 1, TProA⁺ for $n = 2$, and TPeA⁺ for $n = 4$), were purchased as 1 M aqueous solutions from Sigma-Aldrich and were used as received. KOH pellets (99.99%), PbO (99.999%), HClO₄, H₂SO₄, H₂O₂, and dimethylsulfoxide (DMSO) were purchased from Fisher Scientific. Mica sheets were obtained from S&J Trading. Gold wire (99.99%) was purchased from Kurt J. Lesker. Chromium (99.99%) was purchased from Alfa Aesar. Ethanol (200 proof) was used as received from Warner-Graham Co. Purified water (18.3 MΩ·cm) was obtained from a Milli-Q Gradient system.

Preparation of Gold Substrates. The Au/mica substrates were prepared by thermal evaporation of a 5 nm layer of Cr at a rate of 0.1 nm/s, followed by 350 nm of gold at a rate of 0.3–0.5 nm/s, inside a turbo-pumped vacuum chamber at less than 2×10^{-6} Torr, using a Nano38 coating system (Kurt J. Lesker). The gold films were cleaned prior to SAM deposition by rinsing with acetone and Milli-Q water, followed by a 10 min immersion in piranha solution (H₂SO₄/H₂O₂ = 4:1. *Caution: piranha is a vigorous oxidant and should be used with extreme caution*). The gold films were annealed at 220 °C for 3 h under light vacuum. Annealing produced gold films with 98% <111> crystalline planes (of which 65% consist of extended terraces), as evidenced from UPD (see Figure S2 and Table S1 in the Supporting Information). The enhanced gold <111> texture after thermal annealing is in agreement with literature reports.^{24–26}

Formation of LD-SAMs. TAA–MHA ion-pair solutions were synthesized by mixing TAAOH solution and MHA in CCl₄ (molar ratio of TAAOH/MHA = 4:1), followed by sonicating for 15 min. The ion-pair solutions were made at either a 1 mM MHA concentration or a 5 mM MHA concentration (the latter were then diluted to 1 mM prior to SAM formation). The ion-pair solutions were then stored in a temperature-controlled oil bath at 40 °C for TProA–MHA and TPeA–MHA and at room temperature for TEA–MHA. Infrared spectra of TAA–MHA in CCl₄ solution confirm the presence of the TAA⁺ cations and the deprotonated MHA molecules (see Figure S1 in the Supporting Information). TAA–MHA ion-pair SAMs were prepared by immersing the gold substrates in the ion-pair solution for at least 24 h. Upon removal from the ion-pair solution, all SAMs were rinsed with copious amounts of ethanol and purified water. Ion exchange was then performed by immersing the SAMs into 0.01 M KClO₄ in dimethyl sulfoxide solution. The resulting LD-SAMs were rinsed with ethanol and dried with a stream of nitrogen and were then ready for further characterization. More details on the synthesis and characterization can be found in our previous studies.^{6,22} In addition, control MHA monolayers were prepared by immersing clean gold substrates in a 1 mM concentration of pure MHA in CCl₄ for 24 h.

Infrared Spectroscopy. A Varian 650-IR spectrometer (Varian, Inc.) with a liquid-nitrogen-cooled mercury cadmium telluride detector was employed for infrared spectroscopy. The formation of TAA–MHA ion pairs and the conversion of ion-pair films into loosely packed MHA monolayers was character-

ized by infrared spectroscopy. Measurements in liquids were performed via reflectance–absorption using an ATR reflectance accessory. Surface films were characterized with a universal reflectance accessory (set to a reflectance angle of 80°) using a deuterated SAM as the background.

Electrochemical Measurements. Underpotential deposition (UPD) and cyclic voltammetry (CV) experiments were performed in a standard three-electrode electrochemical flat cell (Princeton Applied Research) using a CHI 650B electrochemical workstation (CH Instruments). The test samples were mounted to the flat cell, which has a fixed working electrode area of 1 cm². Ag/AgCl/3 M KCl (aq) was used as a reference electrode (CH Instruments) and platinum mesh as a counter electrode. UPD measurements were conducted after deposition of a lead monolayer on the working electrode in an aqueous solution containing 1 mM PbO and 1 M HClO₄. Cyclic voltammograms were acquired in 0.5 M KOH by scanning between −1.4 V and +0.3 V with respect to the standard calomel electrode (SCE) at 100 mV/s. All experiments were performed at room temperature after deaerating the electrolyte with ultrapure nitrogen gas for at least 30 min. After each measurement, the desorption peak areas were calculated by fitting the data with Gaussian peaks after baseline subtraction. The surface coverage was estimated by converting the entire area under the curve into charge and by comparing that value to what is obtained for fully packed MHA. The surface coverage listed in Table 2 is the average from at least eight measurements taken on different samples.

Contact Angle Measurements. Contact angle measurements in the presence of an applied potential were performed at room temperature by the sessile drop method using a FTA125 apparatus (First Ten Angstroms) with a liquid droplet of 0.1 M KOH (droplet volume of approximately 5 μL). The gold substrate acted as the working electrode and a silver (Ag) wire and a platinum wire were inserted into the drop as the reference and counter electrodes, respectively. The potential of the gold substrate, relative to the Ag wire, was controlled using a potentiostat and scanned between 0 and −2.0 V.

Results and Discussions

Surface Characterization. The absence of methyl stretches in the infrared spectra of the three LD-SAMs is indicative of the complete removal of the TAA⁺ cations from the surface (Figure 1). The characteristic peak positions listed in Table 1 show asymmetric and symmetric CH₂ stretches at ~2918 and ~2850 cm^{−1} for an MHA monolayer, consistent with a well-ordered pseudocrystalline structure.^{27–29} Significant shift in the asymmetric and symmetric methylene C–H stretches from ~2918 to ~2928 cm^{−1} and from ~2850 to ~2856 cm^{−1} is observed (Figure 1). Such shift is consistent with an increase in disorder of the MHA molecules with decreasing packing densities^{5,8} and follows the sequence MHA → LD-MHA(TEA⁺) → LD-MHA(TProA⁺) → LD-MHA(TPeA⁺). In this study, all the electrochemical experiments are conducted on LD-SAMs

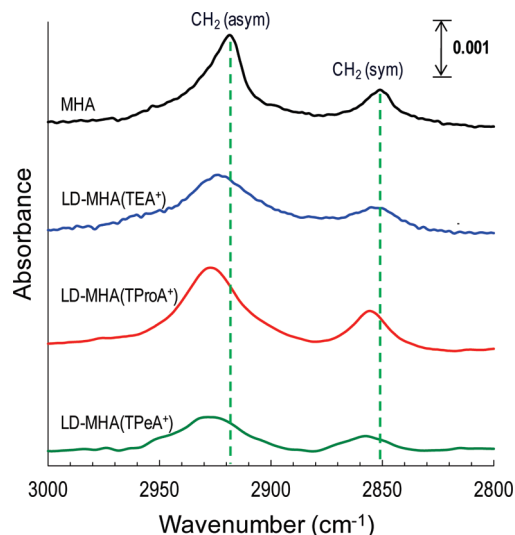


Figure 1. FTIR spectra of MHA and LD-SAMs with different packing densities.

TABLE 1: FT-IR Peak Positions for the Monolayers Investigated

wavenumber (cm ⁻¹)	MHA	LD-MHA (TEA ⁺)	LD-MHA (TProA ⁺)	LD-MHA (TPeA ⁺)
$\nu_{\text{as}}(\text{CH}_2)$	2918 ± 1	2921 ± 2	2926 ± 4	2928 ± 1
$\nu_{\text{s}}(\text{CH}_2)$	2850 ± 1	2851 ± 7	2856 ± 3	2856 ± 1

and fully packed MHA (i.e., the TAA⁺ has been removed via ion exchange).

Reductive Desorption. For the four SAMs investigated, the packing density strongly influences the shape and position of the desorption peaks (Figure 2). The peaks observed from -0.8 to -1.1 V correspond to the reductive desorption of a control MHA monolayer (Figure 2a) and of three LD-SAMs with

decreasing packing densities (Figure 2b–d). The high current density at -1.4 V represents the hydrogen evolution. Upon scanning in the reverse direction, readsorption of the free MHA molecules from the electrolyte takes place (ca. -1.0 V). On the second scan (dashed lines in Figure 2), the decrease of the desorption peak indicates that MHA does not fully readsorb to the gold electrode. This is in line with literature reports pointing out that the amount of readsorption is a strong function of the solubility of the free and associated chains in the electrolyte and the time allowed for diffusion.¹²

The decrease in surface coverage (obtained by increasing the size of the TAA⁺ ion in the ion-pair synthesis of the LD-SAMs) is associated with a decrease in the desorption charge. This effect is readily seen from the reduction of the area under the desorption peak with decreasing coverage (Figure 2). Assuming that desorption is a single-electron process ($\text{Au-RS} + \text{e}^- \rightarrow \text{Au} + \text{RS}^-$) provides us with a means to estimate the surface coverage.^{4,12,19} We note that, even with background subtraction, the contribution of the electrical double layer during the desorption cannot be completely neglected and will contribute to errors in the estimation of the surface coverage (especially for low surface coverage; see ref 19 for more discussion). Although reductive desorption is not an exact method for the measurement of the surface coverage, it does provide us with a basis to look at the role of the ion pairs on the surface coverage and on the role of chain–chain interactions on desorption. The charge associated with reductive desorption of fully packed MHA was found to be $86 \pm 6 \mu\text{C}/\text{cm}^2$, leading to a footprint of $0.19 \text{ nm}^2/\text{molecule}$, which is consistent with published values of $90 \pm 7 \mu\text{C}/\text{cm}^2$.⁴ The surface coverage of the three LD-SAMs investigated was obtained by comparing their desorption charge with that of fully packed MHA. As seen in Table 2, LD-SAMs have lower surface coverage than fully packed MHA monolayers. The footprint of the MHA chains increases with the size of the cations employed in the ion-pair step (i.e., the surface

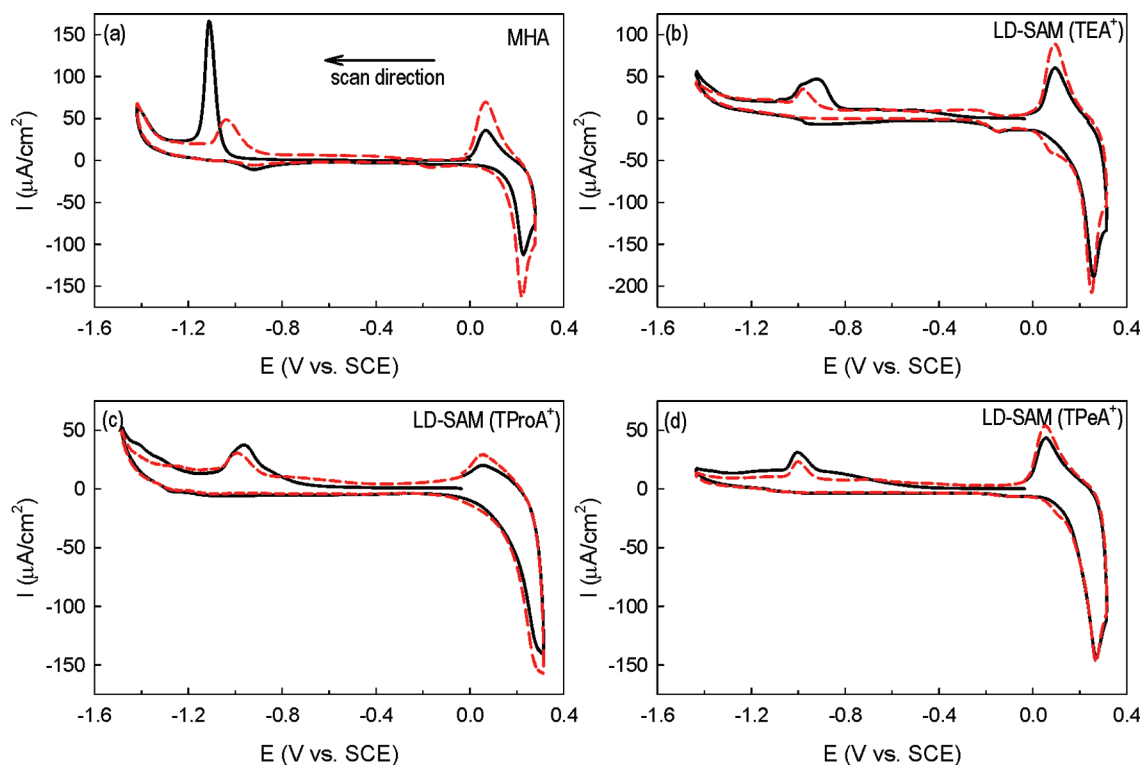


Figure 2. Cyclic voltammograms of MHA and LD-SAMs with different packing densities. Solid and dashed lines represent the first and second cycles. The scan rate was 100 mV/s. Note that the scale for the y axis is not the same for all the panels.

TABLE 2: Surface Coverage and Desorption Peak Analysis from the First Scan Cycle of Cyclic Voltammograms

	surface coverage		E_{p1} (V)	E_{p2} (V)	A_1/A_2	fwhm (mV)
	%	nm ² /molecule				
MHA	100	0.19 ± 0.01	−1.11 ± 0.00		N/A	48 ± 10
LD-MHA(TEA ⁺)	60 ± 11	0.32 ± 0.06	−1.04 ± 0.02	−0.92 ± 0.00	2.1 ± 0.5	110 ± 19
LD-MHA(TProA ⁺)	42 ± 6	0.45 ± 0.06	−0.99 ± 0.03	−0.95 ± 0.01	1.5 ± 0.6	86 ± 5
LD-MHA(TPeA ⁺)	33 ± 6	0.57 ± 0.10	−1.02 ± 0.02	−0.93 ± 0.01	1.9 ± 0.4	104 ± 8

coverage is the lowest for the largest cation, TPeA⁺). This estimate of the surface coverage is in excellent agreement with the prediction made from molecular size calculations and confirms values obtained using other techniques (XPS and contact angle measurements;²² see Table S2 in the Supporting Information).

The desorption of an MHA monolayer (Figure 2a) consists of a strong single peak with a narrow distribution at −1.11 V (consistent with a reported value of −1.06 at a scan rate of 20 mV/s).^{4,23} This is in sharp contrast to the desorption of the three LD-SAMs investigated, which presents a much broader peak in the region between −0.8 and −1.1 V (Figure 2b–d). LD-SAMs desorb at more positive potentials than fully packed MHA monolayers. This shift toward more positive desorption potentials for disordered SAMs is consistent with an increase of permeability, facilitating the ion transport necessary for charge neutrality.⁴ We also observe that LD-SAMs with lower coverage complete desorption at more positive potentials than those with higher coverage (Figure 3). Surprisingly, we did not observe a statistically significant shift in desorption potentials for the three LD-SAMs investigated (even if the order in the film increases with packing density; see Table 1). Electrochemical impedance spectroscopy study has shown that LD-SAM(TEA⁺) has a resistance to ion transport of less than 10⁶ Ω·cm², which is significantly lower than what is observed for full MHA monolayer.⁶ This increase in permeability through the monolayer could allow for unhindered ion transport for the three SAMs investigated, which could explain why the desorption potentials do not vary for the three LD-SAMs, even as the surface coverage

decreases. The analysis for the second scan is available in Table S3 in the Supporting Information.

The broad desorption peak for LD-SAMs is better fitted with doublet peaks (Figure 3), a feature not observed for a full MHA monolayer. Multiple peaks in reductive desorption can be due to domains,^{14,30} phase separation in the case of mixed monolayers,¹⁴ or substrate crystallography.^{18–20} Although we do not have a definite answer as to why doublets (E_{p1} and E_{p2} in Table 2) are observed, our experiments allow us to eliminate many of the possibilities mentioned above. For instance, binding on ⟨110⟩–⟨100⟩ step sites is unlikely because the gold films are thermally annealed prior to SAM deposition, and from UPD, we have determined that the annealed gold film do not contain more than 2% of ⟨110⟩–⟨100⟩ sites (see Figure S2 in the Supporting Information). In fact, in agreement with literature reports,^{15,18,20} an additional desorption peak due to binding on ⟨110⟩–⟨100⟩ step sites is observed on SAMs formed on gold that has not been annealed (Figure S3 in the Supporting Information). Different adsorption states (chemisorption vs physisorption) could also lead to doublet formation. To explore this possibility, we performed contact angle measurements as the potential was scanned in and out of the desorption region (Figure 4). We observe no change in contact angle prior to ca. −0.8 V, which is consistent with no loss of physisorbed chains. Interestingly, features of the contact angle measurements parallel the cyclic voltammograms. Mainly, if we compare the change in contact angle with the one measured for a full hexadecanethiol (HDT), we observe that the LD-SAM desorbs at more positive potential and over a larger potential range (Figure 4). Previous XPS characterization also confirmed covalent attachment of the MHA monolayer to the gold substrate.²²

Domains present within the LD-SAMs are a common cause for multiple desorption peaks. We explored this possibility by verifying that we could create homogeneously mixed SAMs by backfilling the LD-MHA SAMs with a shorter thiol. Domains as small as 15 nm² in mixed SAMs have showed up as a separate peak in cyclic voltammograms.¹⁴ LD-MHA SAMs made from

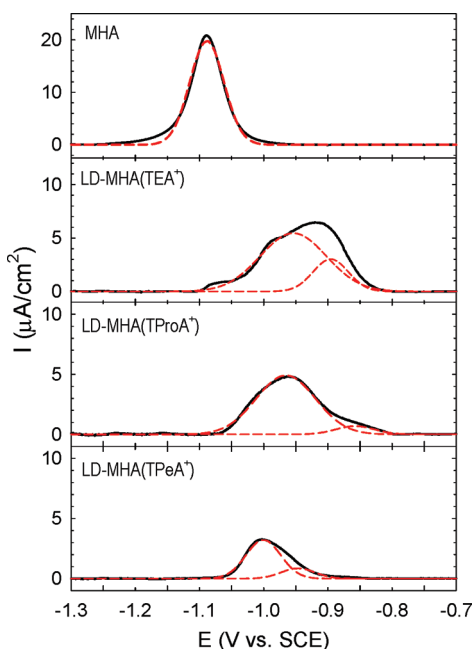


Figure 3. Desorption peaks after baseline subtraction for MHA and three LD-SAMs with different surface coverages. The solid line corresponds to the original desorption peak, and the dashed line corresponds to the Gaussian fitted peaks.

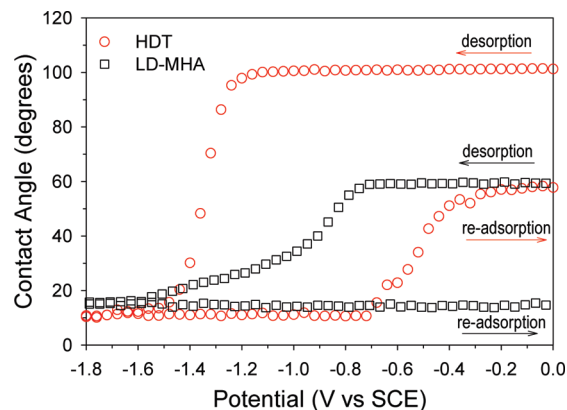


Figure 4. Contact angle measurement during separate cyclic voltammetry (CV) experiments. The squares correspond to the contact angle change for LD-MHA(TPeA⁺), and the circles are for a hexadecanethiol (HDT) control.

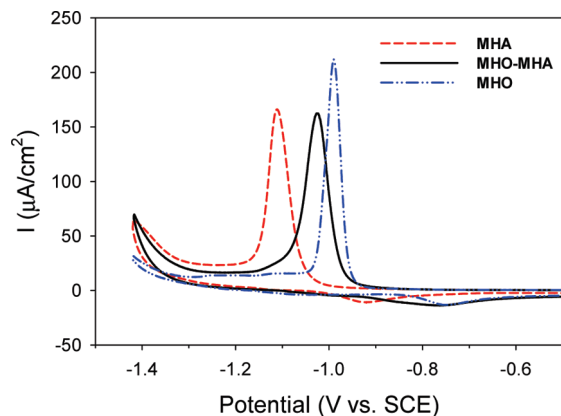


Figure 5. Reductive desorption of a mixed MHA–MHO SAM (solid line) made by backfilling an LD-MHA(TPeA⁺) monolayer. The desorption peaks of pure MHA (dashed) and MHO (dashed-dotted) are also shown.

TPeA–MHA pairs were backfilled with mercaptohexanol (MHO). The LD-SAMs were immersed in 1 mM MHO ethanol solution for 5 h. The resulting mixed SAMs were reductively desorbed in 0.5 M KOH. As seen in Figure 5, the reductive desorption of the mixed MHO–MHA monolayer presents a single sharp desorption peak. Moreover, the desorption potential of the mixed SAM (−1.02 V) falls between the desorption potential of the fully packed MHA (−1.11 V) and the one of the fully packed MHO (−0.99 V). The single sharp desorption peak of the mixed monolayer suggests a well-mixed monolayer, supporting the idea that our LD-SAMs are homogeneous and without domains.^{9,30–32} In addition, the full width at half-maximum (fwhm) of the MHA–MHO monolayer is 54 mV, also indicative of well-mixed SAMs with homogeneous coverage and without domains and phase separation.^{30–32} Our MHA–MHO SAMs present a smaller fwhm than one reported for mixed SAMs made using a different method (desorption peaks at −0.99 V vs SCE with an fwhm of approximately 105 mV).⁹ These preliminary results on mixed monolayers indicate that our LD-SAMs approach could be used as a template to create surfaces with mixed functionality, something that has been shown to be challenging and that we will explore in future work.

A possible hypothesis for the presence of doublets (or broad peaks) could be the competitive adsorption between two different adsorption sites. Such an adsorption mechanism has been discussed in detail in the two-site adsorption model developed by Salvarezza et al.^{33–35} They proposed that adsorption of alkanethiol molecules takes place at both on-top sites and fcc sites, although adsorption at fcc sites is more stable. The large chain–chain interactions of densely packed monolayers hinder their diffusion from on-top sites to the more stable fcc sites and, therefore, form a ($\sqrt{3} \times \sqrt{3}$)-R30° lattice at on-top sites. Conversely, alkanethiol molecules from LD-SAMs could diffuse spontaneously to fcc sites due to the decreased chain–chain interactions. If this is the case for our LD-SAMs, it would imply that the desorption peak at E_{p2} comes from adsorption at on-top sites and the one at E_{p1} from fcc sites. Here, we calculated A_1/A_2 (the ratio of peak area at E_{p1} and E_{p2}). A_1/A_2 is larger than 1 for all three LD-SAMs, indicating that MHA molecules in LD-SAMs prefer to adsorb at fcc sites than at on-top sites (Table 2).

We compared the desorption potentials of LD-SAMs with the ones reported for densely packed *n*-alkanethiol monolayers of different chain lengths.⁴ The electrochemical stability in terms of desorption potential of our LD-SAMs is found to be

equivalent to fully packed SAMs with $n = 8$. In addition, if our hypothesis of a two-site model is true, our results suggest that binding at different adsorption sites can be observed readily with disordered LD-SAMs. This sensitivity to the adsorption sites could be employed to study the binding and diffusion of the thiols on the gold surface.

Conclusions

We have investigated the electrochemical desorption of MHA monolayers with different packing densities from a gold surface. The single narrow desorption peak of backfilled mixed SAMs suggest that LD-SAMs are homogeneous and without domains. The surface coverage measured from cyclic voltammetry is consistent with the one obtained from XPS, contact angle, and calculations. Analysis of the voltammograms indicates that the surface coverage correlates with the size of the supramolecular complex formed in the solutions between the MHA molecule and the quaternary ammonium cation. The lower packing density leads to a significant decrease in the electrochemical stability of the monolayers. Doublet peaks were observed in the desorption of all the LD-SAMs investigated. We hypothesized that the doublet peaks could be due to a two-site adsorption mechanism.

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Supporting Information Available: The following characterization data is available in the Supporting Information: (1) FTIR characterization of ion-pair formation in solution, (2) UPD of lead on gold surfaces, (3) effect of thermal annealing on reductive desorption, (4) comparison of surface coverage obtained from different techniques, and (5) desorption peaks from readsorbed MHA monolayers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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