Self-Assembled Monolayers on Oxidized Metals. 3. Alkylthiol and Dialkyl Disulfide Assembly on Gold under Electrochemical Conditions

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Abstract: Alkylthiol monolayers were assembled in ethanol solutions onto gold surfaces held at positive potentials. The developing monolayer introduces a barrier to electron transfer; hence, measurement of the current corresponding to ethanol oxidation at the applied potential provides a convenient means for real-time monitoring of the self-assembly (SA) process and its completion. Monolayers produced by the new method are formed considerably faster than similar monolayers prepared by the common procedure (no applied voltage). Two other processes which occur under the same applied potential include gold surface oxidation and oxidative desorption of the monolayer, both related to the presence of small amounts of water in the ethanol solution. It is shown that the interplay between the combined processes allows considerable control over the SA process before, during, and after monolayer formation, such as the possibility to perform multiple adsorption−desorption cycles for wettability and surface control. An important consequence of understanding the mechanism of alkylthiol SA onto oxidized gold concerns alkylthiol vs dialkyl disulfide adsorption. While the two types of molecules produce similar monolayers on reduced gold surfaces, a totally different result is obtained with oxidized gold, namely, alkylthiols form compact monolayers whereas dialkyl disulfides do not. This, together with the possibility to determine the extent of gold surface preoxidation, opens the way to rational design of mixed monolayers.

Introduction

The past decade has seen unusual interest in systems based on organized organic thin films, as part of a prominent trend in science and technology toward miniaturization and improved organization. Self-assembled monolayers on solid supports have played a major role in this field, providing a combination of molecular dimensions, superior organization, stability, and versatility.[1,2] Monolayers comprising long-chain hydrocarbons bound to a gold surface via a sulfur-containing headgroup are perhaps the most widely studied systems of this kind, where the properties of the gold substrate (electrical conductivity, chemical inertness) may play an important role in determining the overall properties and performance of the monolayer systems.

It is rather self-evident that the nature of the Au-monolayer interface is a major factor in the SA process and the properties of the resulting monolayers, hence effective control of various interfacial properties at all stages of the SA process is highly desirable. To this end, factors such as the Au surface topography and roughness, as well as surface pretreatment, have been studied.[3] However, a rational approach to controlling the SA process is still missing, which affects the reproducibility of monolayer systems obtained by the common procedure (spontaneous adsorption). Moreover, the common procedure offers limited means for manipulating the system at various stages of SA while monitoring the process in real-time.

In our attempt to control the interface and the SA process we have concentrated on oxidative pretreatments of Au, primarily using oxygen plasma or UV/ozone treatment prior to monolayer SA. We have shown that such Au preoxidation, followed by oxide removal in ethanol (i.e., oxide reduction by ethanol), provides highly reproducible Au surfaces for monolayer SA.[4] In an earlier study we have shown that, if the preoxidation step is not followed by Au oxide reduction, alkylthiol SA on the oxidized Au results in densely packed monolayers where a layer of Au oxide is encapsulated under the monolayer.[5]

An issue nearly untouched, but of substantial importance, is the electric field at the interface before, during, or after SA, either at open circuit (OC, i.e., with no externally applied voltage) or under a certain applied potential.[6] The interfacial electric field may influence such elements as molecular orientation, binding of headgroups, and adsorption properties. Moreover, one may envision electrode reactions which serve to influence or monitor SA processes. Hence, the gold substrate may be used as an electrode during the SA process, allowing rational manipulation of basic interfacial variables. Note that the common SA procedure implies self-assembly at OC, namely,

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[1] Finklea, H. O. in *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19.

[2] Ulman, A. *Ultrathin Organic Films*; Academic Press: New York, 1991.

[3] Guo, L. H.; Facci, J. S.; McLendon, G.; Mosher, R. *Langmuir* **1994**, *10*, 4588.

[4] Ron, H.; Matlis, S.; Rubinstein, I., *Langmuir* **1998**, *14*, 1116.

[5] Ron, H.; Rubinstein, I. *Langmuir* **1994**, *10*, 4566.

[6] Porter and co-workers demonstrated alkylthiol adsorption in ethanol/KOH under an applied potential (positive of the alkylthiol reductive desorption). See: Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860.

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under rather arbitrary conditions insofar as the interfacial electric potential is concerned. For example, we have shown that various surface pretreatment protocols reported for SA of monolayers on Au result in exceedingly different OC potentials upon immersion in the adsorption solution; hence, the OC potential of oxidized Au surfaces (in pH = 7.0 phosphate buffer as well as in ethanol) was found to be ~0.6 V (vs KCl-saturated calomel reference electrode, SCE), whereas the reduced Au shows a substantially more negative OC potential.[5]

The stability of *n*-alkylthiol monolayers on Au electrodes subjected to various applied potentials was addressed in several studies. Porter and co-workers[7] demonstrated cathodic desorption of alkylthiol monolayers in KOH solution. Groat and Creager[8] reported that dodecylthiol (C12SH) monolayers are stable in aqueous solutions between −0.5 and 0.3 V (vs Ag/AgCl) and in propylene carbonate between −0.7 and 0.5 V. The monolayers were damaged upon applying potentials between 0.5 and 0.8 V but were reconstructed upon adding C12SH to the solution (propylene carbonate) while performing a continuous scan between 0.0 V to 0.8 V. Everett and Fritsch-Faules[9] showed that C12SH monolayers are stable between −1.0 and 0.5 V (vs Ag/AgCl) both in methylene chloride and in acetonitrile. They also demonstrated that in the presence of increasing amounts of water the stability of alkylthiol monolayers at positive potentials is decreased. On the basis of the work of Wagner and Gerischer[10] it was suggested that under positive potentials of 0.5 V the thiol is exchanged with Au oxide.

When a sufficiently positive potential is applied to a gold electrode immersed in ethanol containing supporting electrolyte (e.g., $LiClO_4$) and a certain amount of water, the following processes take place:
Electrochemical Au oxidation upon reaction with traces of water in the ethanol

$$2Au + 3H_2O - 6e^- \rightarrow Au_2O_3 + 6H^+ \qquad (1)$$

Direct electrochemical oxidation of ethanol

$$CH_3CH_2OH - 2e^- \rightarrow CH_3CHO + 2H^+ \qquad (2)$$

Chemical oxidation of ethanol by gold oxide

$$Au_2O_3 + 3CH_3CH_2OH \rightarrow 2Au(0) + 3CH_3CHO + 3H_2O \qquad (3)$$

The net result of these reactions is a sustained electrical current corresponding to anodic oxidation of the solvent (ethanol), either direct or mediated by Au oxide. These conditions form the basis for the present work, which concerns the following issues:

1. SA of *n*-alkylthiols is demonstrated under potentials where ethanol is electrochemically oxidized, providing convenient real-time monitoring of the SA process and its completion by measurement of the current, assumed to follow the change in monolayer coverage. Highly oriented alkylthiol monolayers prepared under these conditions are formed considerably faster than similar monolayers prepared by the common procedure (i.e., no applied potential).

2. Under these conditions a competition exists between alkylthiol SA and Au oxide formation (due to residual water), the latter effecting monolayer desorption.[9] This allows considerable control of the system, namely monolayer adsorption, desorption, partial adsorption, mixed adsorption, repeated adsorption−desorption, etc. Dynamic control over the wettability of a gold surface can be achieved by alternating adsorption/desorption cycles.

3. While alkylthiols and dialkyl disulfides produce similar monolayers on reduced Au surfaces,[11] entirely different results are realized with oxidized Au. This furnishes a new route for the preparation, on a single substrate, of mixed monolayers with controlled distributions of the two components, by using controlled surface oxidation.

Experimental Section

Gold Substrates. {111} textured gold substrates were prepared by resistive evaporation of 100 nm gold (99.99%) onto cleaned glass microscope cover slides, followed by 3 h annealing at 250 °C in air. Immediately before use the gold substrates were subjected to UV−ozone treatment followed by 20 min immersion in pure ethanol, a procedure shown previously to provide clean, reproducible gold surfaces.[4]

Materials. Octadecylthiol (C18SH) (Sigma, AR) was purified by crystallization from ethanol. Chloroform (Biolab, AR), bicyclohexyl (BCH) (Aldrich, AR), and hexadecane (HD) (Sigma, AR) were passed through a column of activated basic alumina (Alumina B, Akt. 1, ICN). Ethanol (Merck, AR) and $LiClO_4$ (Merck, AR) were used as received. Water was triply distilled.

Dioctadecyl Disulfide $(C18S)_2$ Synthesis. $(C18S)_2$ was synthesized by oxidation of C18SH with iodine[12] as follows: 2.0 g octadecylthiol (C18SH) were dissolved in 150 mL *n*-hexane. 0.5 g I_2 was dissolved in 5 mL methanol. The two solutions were gradually added to a flask with stirring. After 24 h stirring the liquid was left in the flask for another hour without stirring for efficient phase separation. The hexane phase was transferred to a separating funnel where it was washed several times with copious amounts of methanol to remove remaining C18SH. The product was recrystallyzed from methanol. Melting point: 61−62 °C.

Monolayer Self-Assembly. Monolayer preparation was carried out as detailed in the text. After adsorption the samples were rinsed three times with ethanol and chloroform and dried under a stream of purified air.

Electrochemical Instrumentation. The electrochemical system comprised a potentiostat (model 303C, Department of Chemistry, Technion, Haifa, Israel) controlled by a Zenith 486 computer through a A/D-D/A converter. The program that provided waveform generation, potentiostatic control and data acquisition was written by the Laboratory Computers Unit, The Weizmann Institute of Science.

Fast Liquid Exchange ElectroChemical (FLEEC) Cell. A special cell was designed that allows fast solution exchange under applied electrical potential, without interruption of the potential or the current measurement (Figure 1). The FLEEC cell is a three-electrode electrochemical cell, constructed as a vertically positioned, two-part cylindrical tube. The two parts are connected through a Teflon valve, with another Teflon valve at the bottom end of the tube. The lower cylindrical compartment is the electrochemical cell, whereas the upper cylindrical compartment serves as a solution reservoir. In a typical experiment a gold electrode is placed as a working electrode in the electrochemical cell containing a counter electrode (Pt wire) and a KCl-saturated calomel (SCE) reference electrode (in a separate compartment, filled with ethanol + 0.1 M $LiClO_4$). The electrochemical cell is filled with a solution to the top valve level, which is then closed, and the reservoir tube is filled with a different solution. A potential is then applied to the working electrode to initiate the experiment. At a certain instance the solution in the electrochemical cell is rapidly replaced (within a

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[7] (a) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335. (b) Weisshaar, D. E.; Walczak, M. M.; Porter, M. D. *Langmuir* **1993**, *9*, 323.

[8] Groat, K. A.; Creager, S. E. *Langmuir* **1993**, *9*, 3668.

[9] Everett, W. R.; Fritsch-Fauls, I. *Anal. Chim. Acta* **1995**, *307*, 253.

[10] Wagner, D.; Gerischer, H. *J. Electroanal. Chem.* **1989**, *258*, 127.

[11] (a) Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *109*, 2358. (b) Bain, C. D.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1989**, *5*, 723.

[12] Capozzi, G.; Modena, G. in *The Chemistry of the Thiol Group*; Patai, S., Ed.; Wiley: New York, 1974; pp 794−795.

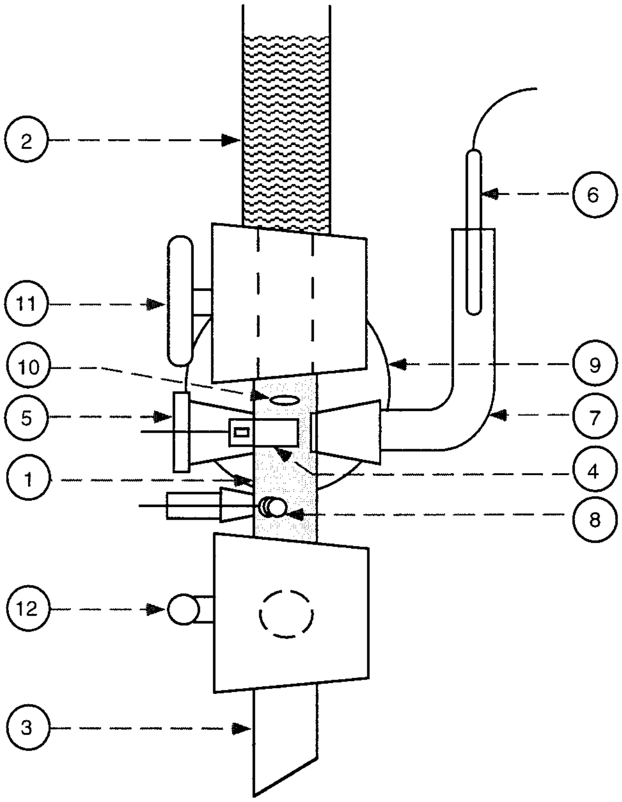

Figure 1. Schematic drawing of the Fast Liquid Exchange Electro-Chemical (FLEEC) cell. (1) Electrochemical cell, (2) solution reservoir, (3) outlet tube, (4) working electrode, (5) working electrode holder, (6) reference electrode, (7) salt bridge, (8) counter electrode, (9) magnetic stirrer, (10) stirring bar, (11) and (12) Teflon valves.

fraction of a second) with the solution in the reservoir tube by opening and closing of the two valves for a short period of time. This allows fast and efficient solution exchange while applying a desired potential to the working electrode and stirring the liquids in the cell, without interrupting the voltage or the current.

The efficiency of solution exchange in the FLEEC cell was tested as follows: The concentration of toluene in ethanol was calibrated using toluene absorbance between 230 and 280 nm.[13] Pure ethanol in the electrochemical cell was exchanged as described above with 8.3 mM toluene in ethanol from the reservoir tube. After solution exchange the concentration of toluene in the electrochemical cell was compared with its concentration in the mother solution. The procedure was repeated six times, and the results showed an average decrease of 2.4% in the toluene concentration compared to the mother solution, which can be taken as the approximate error in the solution-exchange procedure.

Ellipsometry. Ellipsometric measurements were carried out using a Rudolph Research Auto EL-IV ellipsometer with a monochromated tungsten−halogen light source, at an angle of incidence $\Phi = 70°$ and a wavelength $\lambda = 632.8$ nm. The same three points were measured on the bare (cleaned) and the monolayer-covered slide. Monolayer thicknesses were calculated from the change in the ellipsometric Δ and Ψ measured before and after monolayer adsorption, using a film refractive index of $n_f = 1.5$, $k_f = 0$.

Contact-Angle (CA) Measurements. Contact angles (advancing and receding) of H_2O, BCH, and HD were measured shortly (<10 min) after removal of the slides from the adsorption solution. Three measurements at different spots were carried out with each solvent, using a Rame-Hart NRL model 100 contact angle goniometer.

Reflection−Absorption Fourier Transform Infrared (RA-FTIR) Spectroscopy. Grazing incidence FTIR measurements were carried out using a Bruker IFS 66 spectrometer at an angle of incidence of 80° and a resolution of 2 cm^{-1}.

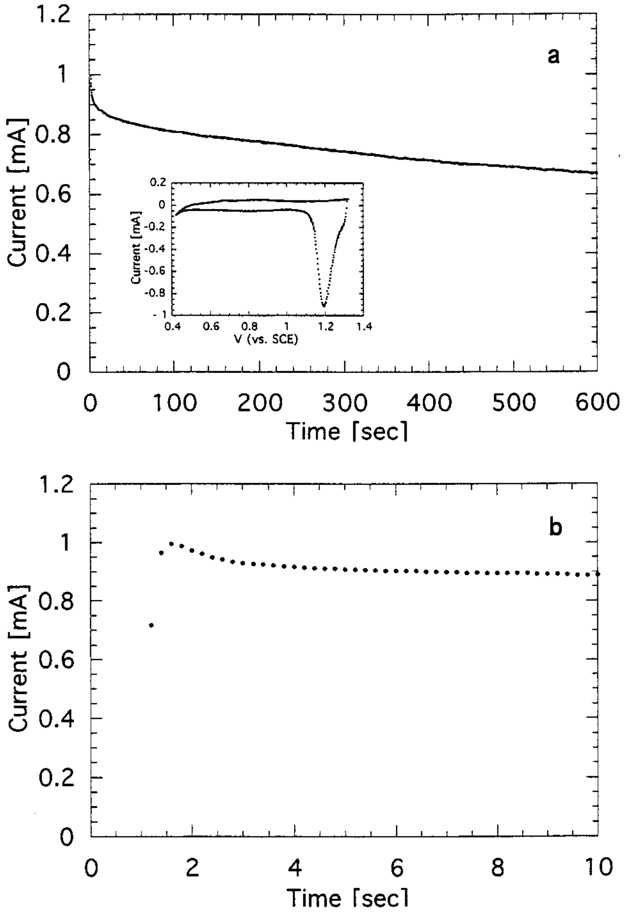

Figure 2. Current vs time curves during anodization of a Au electrode (area: 1.7 cm^2) in 99.8% ethanol containing 10 mM $LiClO_4$ at an applied potential of 1.45 V. (a) The first 10 min, (b) the first 10 s. Inset in (a): Linear potential scan in 0.1 M H_2SO_4 for the stripping of Au oxide produced by applying 1.45 V (vs SCE) in 99.8% ethanol + 10 mM $LiClO_4$ (see text), followed by solution exchange to 0.1 M H_2SO_4 (scan rate: 0.1 V/sec).

Results and Discussion

Anodization of Gold in Ethanol. Figure 2 shows a typical current−time curve (at two time scales) for a gold electrode in 99.8% ethanol + 10 mM $LiClO_4$ solution, following a potential step to 1.45 V.[14] The three processes which take place under these conditions are given in eqs 1−3 above. The applied potential effects net oxidation of ethanol (eqs 2 and 3), which results in a sustained current. The slow current decay is due to eq 1, resulting from the relatively high concentration of water in the ethanol (0.2% water in ethanol, ca. 0.1 M). Oxidation of the Au blocks the surface toward direct ethanol oxidation; the blocking is slowed due to chemical reduction of Au oxide by ethanol (eq 3). Still, after prolonged anodization at 1.45 V (ca. 4 h) it is possible to block almost all ethanol oxidation with Au oxide.

To relate the slow blocking of the electrode (Figure 2a) with Au oxide coverage, the following experiment was carried out: We have previously shown that Au oxide is not reduced when immersed in aqueous H_2SO_4.[5] If after prolonged anodization the electrical circuit is opened and the ethanolic solution in the

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[13] Perkampus, H. H. *UV-Vis Atlas of Organic Compounds*; VCH: New York, 1985.

[14] The electrochemical measurements reported here were carried out without *iR* compensation in order to demonstrate the simplest mode of operation. This implies, however, that the "true" applied potential is initially lower than 1.45 V and it increases and approaches the set value as the current decreases. We verified (by using a range of potentials) that this has no effect on the system behavior or the conclusions drawn.

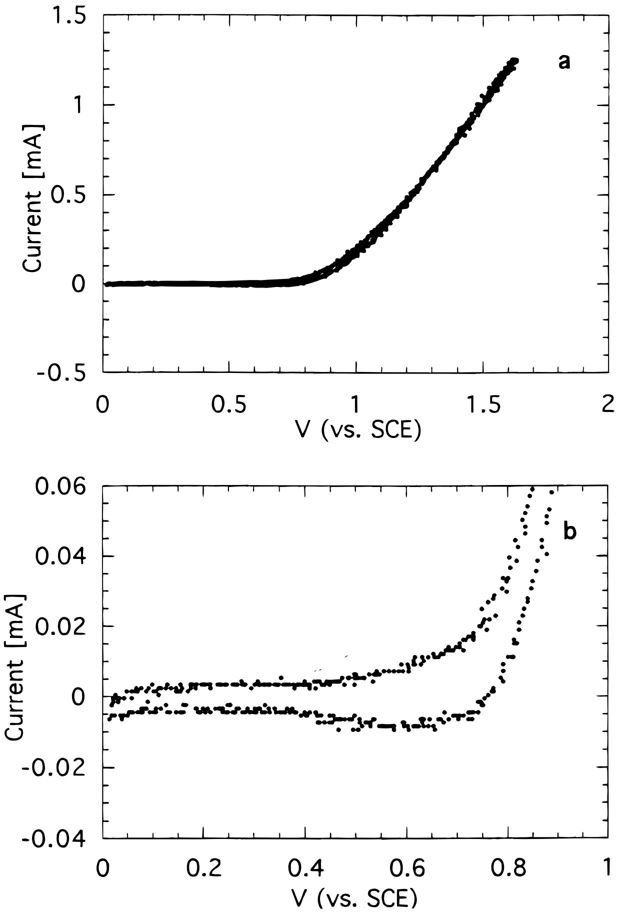

Figure 3. (a) Cyclic voltammogram for the electrochemical oxidation−reduction of a Au electrode in 99.8% ethanol + 10 mM $LiClO_4$ (scan rate: 0.1 V/sec, electrode area: 1.7 cm^2). (b) Same as (a), at more sensitive current and voltage scales.

FLEEC cell is exchanged with aqueous 0.1 M H_2SO_4, then the Au oxide formed can be stripped electrochemically by negatively scanning the potential from 1.3 V[5] (Figure 2a, inset), showing the typical reduction of an almost complete monolayer of Au oxide.[15] If at that point the circuit is disconnected, the solution exchanged back to 99.8% ethanol + 10 mM $LiClO_4$, and a voltage of 1.45 V applied to the Au electrode, then the original initial current is restored. This strongly supports the assumption that the slow current decay is caused by gradual coverage of the surface by Au oxide.

Further understanding of the anodization of Au in ethanolic solution containing traces of water is provided by following the voltammetry of an Au electrode in this solution (Figure 3a). Unlike the voltammogram obtained in aqueous 0.1 M H_2SO_4,[5] the positive scan in ethanol shows a continuous current increase rather than an oxidation wave. Furthermore, the reduction peak in the negative scan, typical of Au cycling in aqueous solutions, is barely observed in Figure 3a. Nearly all of the current in the positive scan is attributed to ethanol oxidation at the Au electrode. Still, when carefully examined using a more sensitive current scale (Figure 3b), a small reduction peak is observed when scanning the potential in the negative direction, attributed to Au oxide reduction. In Figure 3a the potential was scanned at 0.1 V/sec, meaning that the Au surface is under oxidative potential for ca. 10 s; Figure 3b shows that under these conditions a small amount of Au oxide is already formed. Thus, it may be assumed that, on the time scale of seconds, Au surfaces treated as in Figure 2 would be covered with a certain amount of oxide.

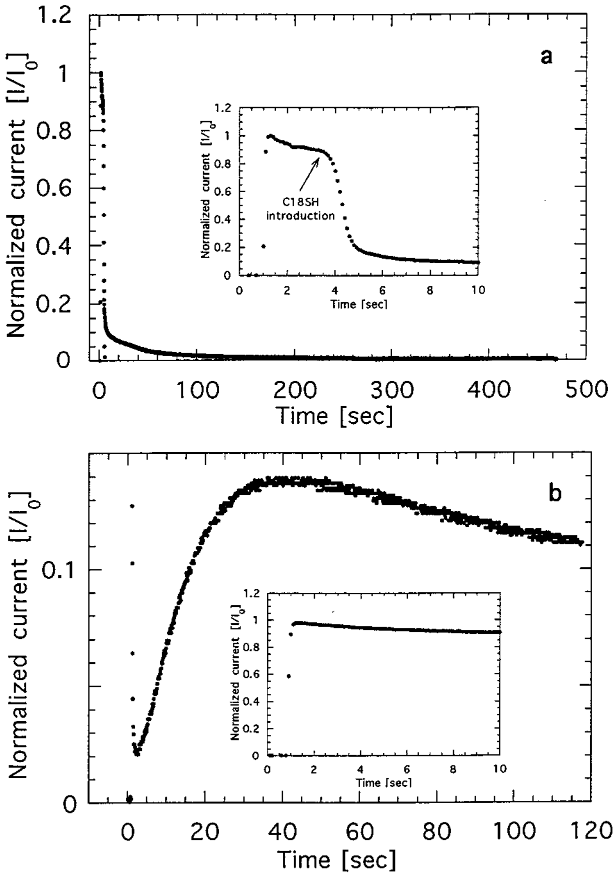

Figure 4. Current vs time curves for Au electrodes polarized at 1.45 V applied potential: (a) SA in 3 mM C18SH in 99.8% ethanol + 10 mM $LiClO_4$. Inset: The initial stages, shown in more detail; the initial current increase indicates application of the potential, and the solution exchange (C18SH introduction) is marked. (b) An electrode treated as in (a), polarized in 10 mM $LiClO_4$ in 95% ethanol (5% water added). Inset: After Au oxide reduction at 0.0 V; polarized in 99.8% ethanol + 10 mM $LiClO_4$. I_0 is the absolute value of the initial current in 4a (or 4b, inset).

Figure 3b shows, in addition, that Au oxide is completely reduced in ethanol under these conditions when potentials negative of 0.3 V are applied. It may therefore be assumed that an OC potential negative of 0.3 V indicates an oxide-free Au surface (for monolayer-covered Au, this applies to the Au fraction in contact with the solution).

SA of Alkylthiols under an Applied Positive Potential. Figure 4a presents a current−time curve for an Au electrode immersed in 99.8% ethanol + 10 mM $LiClO_4$ (in the FLEEC cell), where at $t = 0$ the potential is stepped from 0.0 to 1.45 V followed by solution exchange (without voltage or current interruption) with an identical solution containing 3 mM octadecylthiol (C18SH). Unlike the slow current decrease in Figure 2, resulting from Au surface oxidation, a sharp decrease in the current is immediately observed when the solution is exchanged, as shown in Figure 4a. This fast current decay is the result of alkylthiol adsorption, causing effective blocking of the Au surface by the compact monolayer formed. It is evident from Figure 4a (inset) that *almost all of the Au surface is covered within 1−2 s.* Since blocking of the surface by Au oxide formation in the first 10 s is marginal (Figure 2b), the fast current decay in Figure 4a can essentially be entirely attributed to C18SH monolayer formation. Hence, SA in ethanol

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(15) Vitus, C. M.; Davenport, A. J. *J. Electrochem. Soc.* **1994**, *141*, 1291.

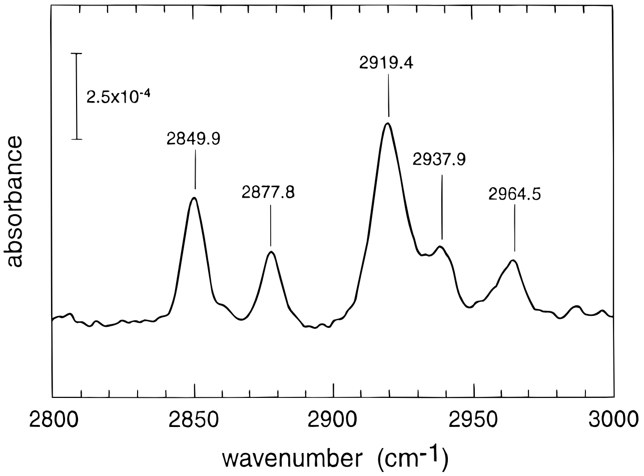

Figure 5. Grazing incidence reflection−absorption FTIR spectrum of a C18SH monolayer adsorbed at 1.45 V applied potential as in Figure 4a.

under positive applied potentials provides a straightforward means for real-time monitoring of the process.

Monolayers prepared by the new procedure were characterized by ellipsometry, CA measurements, and reflection−absorption FTIR spectroscopy. They were compared with C18SH monolayers obtained by the common procedure, i.e., adsorption from ethanol (with or without 10 mM $LiClO_4$; the results are similar) with no applied potential. The FTIR spectra of monolayers obtained by SA at 1.45 V (as exemplified in Figure 5) are characteristic of high-quality C18SH monolayers on {111} Au.[16] As shown in Table 1, rows 1, 2, 3, and 4, the monolayer obtained by 18.5 min adsorption at 1.45 V is indistinguishable (within experimental error) in thickness and CAs from the one obtained by 24 h regular adsorption, but distinctly superior to the monolayer obtained by 20 min regular adsorption. It is therefore clear that *alkylthiol adsorption at positive potentials produces high-quality monolayers much faster (by ca. 2 orders of magnitude) than regular adsorption (i.e., no applied potential).*

Several factors may be responsible for the substantial improvement in the rate of formation of high-quality alkylthiol monolayer on Au under oxidative electrochemical conditions:

1. Lowering of the activation energy for the binding process. It was previously suggested that alkylthiol SA involves formation of a Au−S bond,[11b,17] which in the present case would be strongly favored by the electrochemical oxidation of the gold[6]

$$\mathrm{Au} \rightarrow \mathrm{Au}^+ + \mathrm{e}^- \tag{4}$$

$$\mathrm{Au}^+ + \mathrm{R{-}S{-}H} \rightarrow \mathrm{Au{-}S{-}R} + \mathrm{H}^+ \tag{5}$$

2. During regular adsorption a certain fraction of the alkylthiol molecules is expected to be in a planar orientation, induced by the interaction of the alkyl chains with the high-energy gold surface.[18] This would create a kinetic barrier for the formation of a perpendicularly oriented structure and may introduce defects. SA at positive potentials minimizes the interaction of the alkyl chains with the gold surface due to the electrode charge and the local electric field.[19]

3. The electric field at the interface may have an additional role, i.e., promoting a perpendicular orientation of the S−C dipole in the desired orientation for binding to the Au. This element may be particularly significant at advanced stages of monolayer formation, where the rate may be controlled by penetration of alkylthiol molecules to fill small pinholes in a largely covered surface.[20]

4. Another factor which may improve the monolayer SA is the continuous “pretreatment” of the Au surface (oxidation/reduction) during the SA process.[15] Moreover, as shown below, anodization in ethanolic solution containing water induces removal of the alkylthiol monolayer from the Au surface. It is therefore reasonable to assume that the SA process under these conditions is accompanied by removal of less ordered monolayer fractions, allowing only tightly packed monolayer fractions to remain on the surface.

The relative contribution of each of these factors is yet to be determined.

The Effect of Alkylthiol Concentration. Figure 6 demonstrates the effect of C18SH concentration on the adsorption characteristics (current−time behavior) at 1.45 V applied potential in 99.8% ethanol + 10 mM $LiClO_4$. The overall process is presented in Figure 6a, and the initial stages of adsorption are emphasized in Figure 6b. The current−time behavior is qualitatively similar for all thiol concentrations except 0.01 mM, indicating formation of blocking monolayers. The very slow current decay at long times (Figure 6a) may be due to the blocking of the remaining pinholes by Au oxide; this is supported by the OC potential of ca. 0.6 V measured after long adsorption at 1.45 V, indicating the existence of a minute fraction of oxidized Au surface not covered with the monolayer and in contact with the solution.[5] The current−time curve for 0.01 mM C18SH shows that, at the low thiol concentration, oxide formation overcomes monolayer SA; the bump around 60−70 s indicates that monolayer removal (see below) becomes faster than monolayer SA and further current decrease is dominated by Au oxide formation, as in Figure 2.

As seen in Table 1, rows 4, 5, and 6, similar high-quality C18SH monolayers are obtained at 1.45 V in the concentration range between 1 mM and 5 mM, whereas a certain decrease in quality is seen at 0.2 mM (Table 2, row 2). As shown in Table 1, row 7, at low C18SH concentrations the interference arising from Au oxidation, effected by residual water, inhibits monolayer formation; the ellipsometry and CA results suggest marginal monolayer coverage with largely scattered results at different points on the surface.

Monolayer Desorption. Figure 4b shows a current−time curve obtained for an electrode covered with a compact C18SH monolayer, prepared as in Figure 4a, after exchanging the adsorption solution to 95% ethanol + 10 mM $LiClO_4$ (5% water, no alkylthiol) and then applying 1.45 V to the electrode. The current reaches a maximum of ca. 15% of the initial value observed with bare Au, followed by a relatively slow current decay. The solution in the cell was then replaced with 99.8% ethanol + 10 mM $LiClO_4$ and a potential of 0.0 V applied to the electrode until the OC potential was negative of 0.3 V (i.e., complete removal of any Au oxide). The potential was then stepped to 1.45 V and the current−time curve in Figure

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[16] Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152.

[17] (a) Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87. (b) Reference 2, p 288.

[18] (a) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321. (b) Sun, L.; Crooks, R. M. *J. Electrochem. Soc.* **1991**, *138*, L23.

[19] Neutral organic molecules adsorb on metal electrodes in a limited potential range around the potential of zero charge (PZC); see: Gileadi, E. *Electrode kinetics for Chemists, Chemical Engineers and Materials Scientists*; VCH: New York, 1993; pp 257−259, 309−318.

[20] Sabatani, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, *91*, 6663.

Table 1. Characterization of C18SH Monolayers on Au Prepared by the Common Procedure or at 1.45 V Applied Potential

				contact angle (deg)					
				H_2O		BCH		HD	
	sample description	ads. time (min)	ellips. thickness (Å)	adv.	rec.	adv.	rec.	adv.	rec.
1	1 mM C18SH	1440 (24h)	18.9	107	105	52	51	46	45
2	1 mM C18SH + salt	1440 (24h)	18.1	107	105	52	51	47	45
3	1 mM C18SH	20	15.1	102	90	49	47	44	41
4	1 mM C18SH + salt + pot.	18.5	21.5	107	104	52	50	45	44
5	3 mM C18SH + salt + pot.	7	19.6	107	104	52	50	45	43
6	5 mM C18SH + salt + pot.	6	19.5	106	103	52	51	45	43
7	0.01 mM C18SH + salt + pot.	18.5	5−13	90−104	60−90	30−32	∼0−29	30−35	∼0−18
8	no. 5 after desorption		2.7	90	60	20	<10	12	<10
9	1 mM C18SH + salt + pot., 3rd adsorption after 2 adsorption−desorption cycles	18.5	26.1	109	97	50	47	44	41

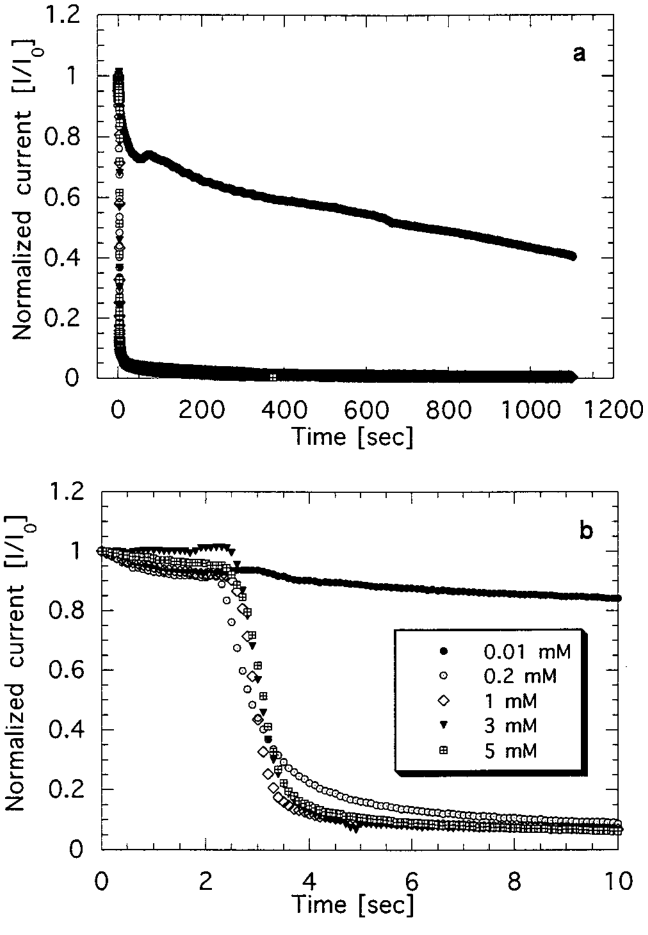

Figure 6. Current vs time curves for the SA of C18SH in 99.8% ethanol + 10 mM $LiClO_4$ at 1.45 V applied potential, carried out with various C18SH concentrations as indicated in the figure. (a) and (b) show different time scales of the process. Zero time indicates application of the potential, while the onset of current decrease indicates solution exchange (C18SH introduction). I_0 is the absolute value of the initial current in 6a (or 6b).

4b (inset) recorded. It is clear from the initial current in Figure 4b (inset) that *short anodization at 1.45 V in ethanolic solution containing water causes complete removal of the C18SH monolayer from the Au surface*. The ellipsometric and CA results shown in Table 1, row 8, substantiate this conclusion. Note that these results are in general agreement with those of Everett and Fritsch-Faules,[9] who demonstrated removal of alkylthiol monolayers at positive potentials in organic solutions containing traces of water.

The current−time curves in Figure 4b are instructive in understanding the process of alkylthiol desorption at positive potentials in ethanolic solution containing water. The initial current increase can be attributed to alkylthiol desorption leaving exposed Au surface, where ethanol can be oxidized. Simultaneous (but slower) Au surface oxidation, which inhibits ethanol oxidation, is responsible for the current maximum and subsequent decrease. This suggestion is supported by (i) the observation that the same qualitative behavior as in Figure 4b is observed in 99.8% ethanol + 10 mM $LiClO_4$, but on a longer time scale; and (ii) the initial current in Figure 4b (inset) following oxide reduction at 0.0 V, which corresponds to bare Au obtained by complete monolayer desorption and oxide removal.

The above explanation suggests that the alkylthiol monolayer desorption occurs in two manners: (i) oxidative thiol desorption, where the thiol is removed and bare Au surface is exposed, allowing ethanol oxidation (relatively fast); and (ii) thiol exchange by Au oxide, induced by dissolved water (relatively slow). The rather low current maximum in Figure 4b suggests that most of the monolayer desorption occurs by direct exchange of the alkylthiol with Au oxide. The latter is also supported by the rate of current decrease (following the current maximum) in Figure 4b, which is much faster than the blocking of bare Au by oxide formation (Figure 2).

It is therefore concluded that the SA of alkylthiols on anodized Au in "wet" ethanol includes the following three concomitant processes: (i) Adsorption of the thiol on bare Au, (ii) desorption of bound thiol molecules upon replacement with Au oxide, and (iii) adsorption of the thiol at oxidized Au,[5] formed on bare Au or upon thiol removal. The overall process, in terms of monolayer formation rate and properties, depends on the relative concentrations of alkylthiol and water in the adsorption solution.

Repeated Adsorption−Desorption of Alkylthiols on Gold. An issue of substantial basic as well as practical interest is that

Table 2. Characterization of $(C18S)_2$ and C18SH Monolayers Assembled at 1.45 V Applied Potential onto Reduced or Preoxidized Au

					contact angle (deg)					
					H_2O		BCH		HD	
	sample description	oxide cover. before SA	ads. time (min)	ellips. thickness (Å)	adv.	rec.	adv.	rec.	adv.	rec.
1	0.1 mM $(C18S)_2$ +salt + pot.	low	10	17.6	108	106	52	50	46	44
2	0.2 mM C18SH + salt + pot.	low	13	18.7	108	104	49	45	45	40
3	3 mM C18SH + salt + pot.	low	18.5	19.6	107	104	52	50	45	43
4	0.1 mM $(C18S)_2$ + salt + pot.	high	9.5	12	90	60	37	20	25	<10
5	0.2 mM C18SH + salt + pot.	high	9.5	20.4	109	102	49	43	44	41
6	3 mM C18SH + salt + pot.	high	6.2	45.6	112	104	49	35	39	33

of control over the wettability of surfaces using self-assembled monolayers. Dynamic electrochemical control of the wettability of monolayer-covered surfaces was shown previously, either by changing the oxidation state of a ferrocene-derivatized monolayer[21] or by monolayer desorption−readsorption[22,23] based on cathodic alkylthiol desorption.[7] In the former case, where actual cycling was shown,[21] the wettability difference deteriorates within several cycles.

The convenient adsorption and desorption of alkylthiol monolayers at positive potentials in the FLEEC cell, together with the ability to rapidly exchange solutions at any desired stage and under potential control, introduce the possibility of performing multiple C18SH monolayer adsorption−desorption cycles for wettability and surface control. The CAs and ellipsometric thickness of a C18SH monolayer adsorbed on a Au electrode after two successive adsorption−desorption cycles is presented in Table 1, row 9. Although a certain decrease in monolayer quality is observed, probably due to surface roughening, it is clear that a reasonable C18SH monolayer is obtained, demonstrating the possibility to turn the surface hydrophobic/hydrophilic upon monolayer adsorption−desorption.

The present approach is different from those of Whitesides and co-workers.[21−23] Whereas the latter authors demonstrated wettability control in a solution of a fixed composition by changing the applied potential, our approach is based on adsorption and desorption at a fixed (possibly uninterrupted) applied potential but requires solution exchange. This introduces an obvious limitation, but also an advantage, in that it allows the use of different molecules in subsequent adsorptions, thereby effectively alternating not just the wettability but possibly also the surface composition.

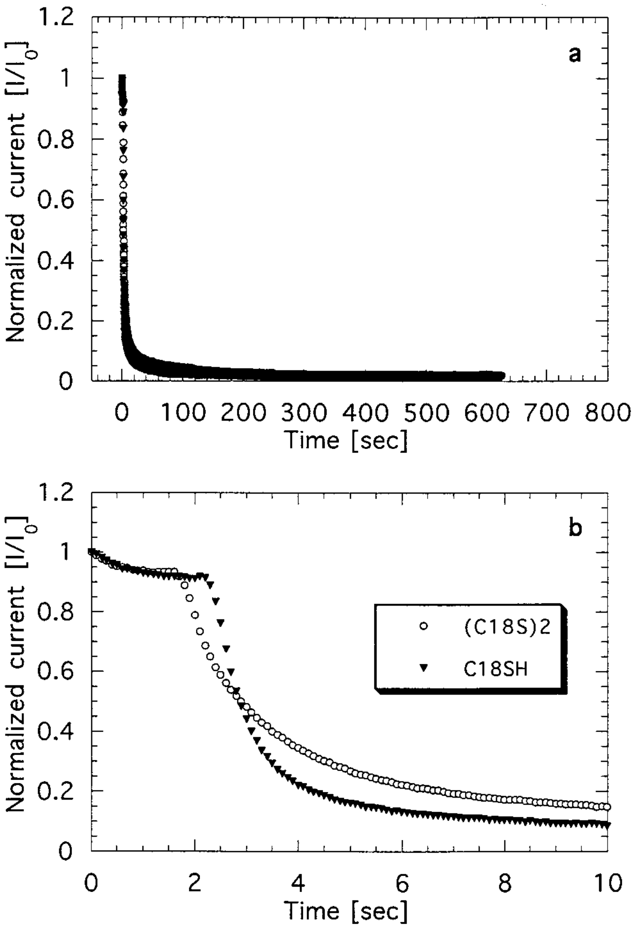

Figure 7. Current vs time curves for the SA of C18SH (0.2 mM) and $(C18S)_2$ (0.1 mM) onto an Au electrode in 99.8% ethanol + 10 mM $LiClO_4$ at 1.45 V applied potential. (a) and (b) show different time scales of the process. Zero time indicates application of the potential, while the onset of current decrease indicates solution exchange. I_0 is the absolute value of the initial current in 7a (or 7b).

SA of Alkylthiols and Dialkyl Disulfides on Oxidized Gold. Figure 7a presents overall current−time curves for SA of C18SH and $(C18S)_2$ (dioctadecyl disulfide) onto slightly oxidized Au; the marginal preoxidation occurs in the short period of time between application of 1.45 V and introduction (by solution exchange) of the adsorption solution into the FLEEC cell. Figure 7b emphasizes the initial stages of SA. The CAs and ellipsometric thickness of the two monolayers are shown in Table 2, rows 1 (0.1 mM $(C18S)_2$) and 2 (0.2 mM C18SH). The concentrations were chosen such that the number of sulfur atoms (or alkyl chains) is the same in both cases. The results are rather similar, although the initial stage of SA of $(C18S)_2$ is somewhat more sluggish. The ellipsometric thickness for the two monolayers is similar, whereas a minor difference is observed in the CAs. The latter is attributed to some encapsulated Au oxide under the C18SH monolayer,[5] absent in the case of $(C18S)_2$ (as discussed below). Note that the thickness and CAs of the $(C18S)_2$ monolayer prepared at 1.45 V (Table 2, row 1) are very close to those observed for a monolayer adsorbed at 1.45 V from a 3 mM C18SH solution (Table 2, row 3) and for a

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[21] Abbott, N. L.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1493.

[22] Gorman, C. B.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1995**, *11*, 2342.

[23] Abbott, N. L.; Gorman, C. B.; Whitesides, G. M. *Langmuir* **1995**, *11*, 16.

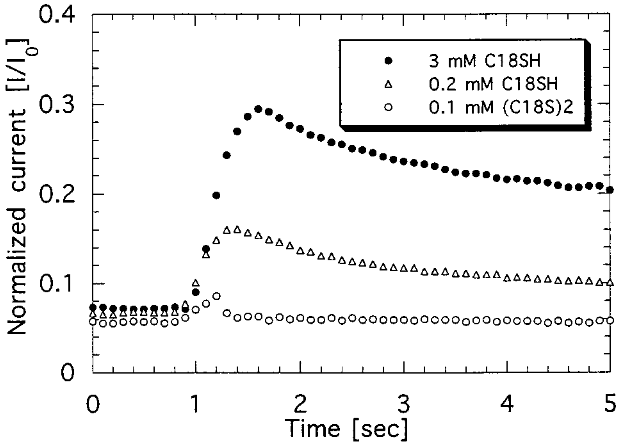

Figure 8. Current vs time curves showing the initial stages of SA of 0.1 mM $(C18S)_2$, 0.2 mM C18SH, and 3 mM C18SH in 99.8% ethanol + 10 mM $LiClO_4$ at 1.45 V applied potential onto electrochemically preoxidized Au. Zero time indicates application of the potential, while the onset of current increase indicates solution exchange. I_0 is the same as in Figure 4.

C18SH monolayer prepared by regular 24 h SA in 1 mM solution (Table 1, row 1).

When comparing monolayers of C18SH and $(C18S)_2$, it is important to examine what are the right adsorption conditions (i.e., concentrations) for a valid comparison. One may compare results for, for example, 0.2 mM C18SH and 0.1 mM $(C18S)_2$, that is, the same number of available alkyl chains. However, 0.1 mM $(C18S)_2$ in ethanol is a supersaturated solution, whereas 0.2 mM C18SH is about an order of magnitude below saturation. Therefore, another valuable comparison would be between, for example, 0.1 mM $(C18S)_2$ and 3 mM C18SH, both slightly supersaturated in ethanol. To give a complete picture we chose in this work to present both.

The SA of C18SH and $(C18S)_2$ monolayers on highly oxidized Au is shown in Figure 8, emphasizing the initial stages of the process by displaying the first 10 s. The Au surface was effectively preoxidized upon applying 1.45 V in ethanol + 10 mM $LiClO_4$ for ca. 4 h (with continuous slow exchange of the solution to avoid accumulation of acetaldehyde) before introduction of the adsorbing molecules into the cell by solution exchange. The CAs and ellipsometric characterization of monolayers SA at 1.45 V on oxidized Au from 0.1 mM $(C18S)_2$, 0.2 mM C18SH and 3 mM C18SH solutions are shown in Table 2, rows 4, 5, and 6, respectively.

The thickness and CAs for $(C18S)_2$ adsorbed at 1.45 V on oxidized Au (Table 2, row 4) indicate very poor monolayer formation. *Clearly, Au oxide prevents adsorption of $(C18S)_2$.* On the other hand, the results for C18SH (Table 2, rows 5 and 6) indicate formation of densely packed monolayers, with a small amount (row 5) and a large amount (row 6) of encapsulated Au oxide.[5] Evidently, this notable difference in the amount of encapsulated Au oxide results from the faster initial monolayer formation in the presence of the much higher C18SH concentration (as shown in Figure 6b for slightly oxidized Au).

Interestingly, the observation that disulfides do not self-assemble onto preoxidized Au was mentioned by Nuzzo and Allara,[24] who noted that “plasma oxidation to form gold oxide surfaces results in no detectable adsorption” (ref 20 in their paper). However, this remark has gone unnoticed since that pioneering paper was published.[25]

The above results can be understood by considering the mechanism of SA of alkylthiols on oxidized Au surface. Wallace[26] demonstrated that thiols react with oxides of Mn, Co, Cu, and Fe; the reaction involves reduction of the metal oxide and oxidation of the thiol to disulfide. Similarly, one can write for Au oxide

$$Au_2O_3 + 6RSH \rightarrow 2Au(0) + 3RSSR + 3H_2O \quad (6)$$

resulting in bare Au surface. Thiol may then adsorb onto the exposed Au, probably proceeding according to (at an applied positive potential)

$$Au(0) + RSH \rightarrow AuSR + H^+ + e^- \quad (7)$$

Alternatively, the oxide reduction may lead directly to adsorbed thiol, as previously suggested by us[5]

$$Au_2O_3 + 6RSH \rightarrow 2AuSR + 2RSSR + 3H_2O \quad (8)$$

In both cases the reaction involves thiol oxidation to disulfide. Therefore, *$(C18S)_2$, which is the reaction product and is not a reducing agent, cannot form a monolayer on oxidized Au.* Note that the reaction in eq 6 is expected to be faster than the one in eq 8, since the mechanism of the former requires simultaneous participation of two thiol molecules, whereas that of the latter requires simultaneous participation of three thiol molecules.

It should be realized that blocking of the Au surface by oxide at 1.45 V is a dynamic process where Au oxide is continuously reduced by ethanol (equation 3) and regenerated by reaction with water (equation 1). The little $(C18S)_2$ adsorption observed when the oxidized Au is exposed to the disulfide (Table 2, row 4) is likely to represent those events when the disulfide reacts with reduced Au faster than water during this dynamic process.

As discussed above, C18SH adsorption at 1.45 V onto oxidized Au may proceed by (i) SA onto bare Au, generated by reaction with the thiol (eq 6) or with ethanol (eq 3) or (ii) SA upon reaction with Au oxide (eq 8). The process depicted in eq 6 is evident in Figure 8, where a current increase is observed upon introduction of C18SH. Bare Au surface is assumed to be initially generated (equation 6), providing additional available surface for ethanol oxidation and thus a current increase. As expected, this is more pronounced with 3 mM C18SH than with 0.2 mM C18SH and is absent in the case of $(C18S)_2$.[27] The current variations following thiol introduction reflect a combination of enhanced ethanol oxidation (current increase) and thiol SA (current decrease). The former is responsible for the initial current rise; the current maximum and subsequent decrease seem to indicate that the remaining (slower) process manifests primarily C18SH adsorption according to eqs 7 or 8.

As noted above, the difference in ellipsometric and CA results between C18SH monolayers adsorbed onto highly oxidized Au from 0.2 mM solution vs 3 mM solution (Table 2, rows 5 and 6) are indicative of a substantial amount of encapsulated Au oxide in the latter case and little, if any, encapsulated oxide in

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[24] Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481.

[25] The work of Hickman et al. (*Langmuir* **1992**, *8*, 357) gives the impression that disulfide molecules adsorb onto oxidized gold. This, however, is not the case. The authors note that no oxidized gold could be detected (by XPS) after adsorption; clearly, the oxidized gold is reduced by the solvent (ethanol), followed by disulfide adsorption onto the reduced gold.

[26] Wallace, T. J. *J. Org. Chem.* **1966**, *31*, 1217.

[27] The very small current increase upon introduction of $(C18S)_2$ (Figure 8) seems to be related to the solution exchange itself; this is evidenced by the fact that a similar small current increase is observed when the ethanolic solution in the cell is exchanged with an identical background solution after prolonged oxidation of the Au electrode.

the former.[5] On the other hand, the results in Figure 8 show that introduction of 3 mM C18SH causes a larger current increase (i.e., more oxide removed) than 0.2 mM C18SH. The two observations combined suggest that the higher C18SH concentration promotes more efficient initial oxide removal but the remaining oxide is better preserved than in the case of the lower C18SH concentration. We suggest that removal of Au oxide upon exposure to the thiol solution may involve not only chemical reduction (eq 6) but also detachment of some Au oxide from the surface upon thiol adsorption. In situ AFM and STM studies on the anodic formation of Au oxide[28] showed an island growth process, with oxide islands comprising more than a monolayer of oxide. AFM studies conducted by us[4] show that thin Au oxide layers coated with a thiol monolayer appear brittle, with loosely bound material that can be removed by the AFM tip. Detachment of Au oxide upon massive adsorption of thiol molecules is feasible only at the beginning of the SA process; as the SA proceeds, the remaining oxide is protected by the thiol coverage.[5] Both processes, namely, initial detachment of Au oxide islands and subsequent blocking of the remaining oxide, are more effective at higher C18SH concentrations. The slower adsorption in 0.2 mM C18SH would allow more thiol molecules to contact the oxidized surface and reduce the oxide before a blocking monolayer is obtained.

Conclusions

Self-assembly of alkylthiol and dialkyl disulfide monolayers in ethanol solutions onto Au surfaces held at positive applied potentials where ethanol is oxidized was demonstrated. The new procedure presents several distinct advantages over the common procedure.[29]

1. Changes in the current corresponding to ethanol oxidation can be used for convenient real-time monitoring of the SA process and its completion. This new method complements others such as surface plasmon resonance or quartz crystal microbalance, while being more sensitive and easier to implement. It presents the possibility to study monolayer adsorption kinetics, an aspect currently under further investigation.

2. Alkylthiol monolayers are formed by the new technique considerably faster (by about 2 orders of magnitude) than by the usual procedure, while monolayers thereby obtained show exceptional properties in terms of monolayer thickness, wettability and FTIR results.

3. Effective removal of alkylthiol monolayers is achieved upon application of the same potentials in wet ethanol solutions (no thiol), while, as noted above, under the exact same conditions high-quality monolayers are obtained in the presence of the thiol in solution. These observations provide the basis for rational manipulation of self-assembled monolayers before, during, and after adsorption. Hence, effective control over the wetting properties of a gold surface was demonstrated upon repeated adsorption−desorption cycles of a C18SH monolayer. This procedure may, in principle, be applied using different molecules in subsequent adsorptions, thereby expanding the possibilities of controlling interfacial properties.

4. Both alkylthiols and dialkyl disulfides form densely packed monolayers (with or without the applied potential) on oxide-free Au surface. However, only alkylthiols (but not dialkyl disulfides) adsorb onto preoxidized Au surface. This appears to be due to the mechanism of alkylthiol SA onto oxidized Au, requiring oxide reduction upon thiol oxidation to disulfide. This may provide a novel way to form mixed monolayers of controlled compositions, by subsequent SA of disulfides and thiols onto partially oxidized gold. The ability to determine the extent of preoxidation, also related to the oxide distribution on the surface,[4] introduces the possibility to design systems with desired relative amounts and distribution of two monolayer components. This is currently under further investigation.

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[28] Nichols, R. J.; Magnussen, O. M.; Hotlos, J.; Twomey, T.; Behm, R. J.; Kolb, D. M. *J. Electroanal. Chem.* **1990**, *290*, 21.

[29] A limitation of the new electrochemical self-assembly procedure is its inapplicability to monolayers containing functional groups that can be oxidized under the applied potential.