X-ray Studies of Self-Assembled Monolayers on Coinage Metals. 1. Alignment and Photooxidation in 1,8-Octanedithiol and 1-Octanethiol on Au

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X-ray Studies of Self-Assembled Monolayers on Coinage Metals. 1. Alignment and Photooxidation in 1,8-Octanedithiol and 1-Octanethiol on Au

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X-ray photoelectron spectroscopy (XPS) has been employed in an investigation of the structure and photooxidation of self-assembled monolayers (SAMs) formed by the immersion of evaporated Au films into ethanolic solutions of 1-octanethiol and 1,8-octanedithiol. XPS has been used to confirm unambiguously that individual molecules in SAMs formed from 1,8-octanedithiol and 1-octanethiol are in both cases attached to the surface through a single Au–thiolate bond. In the case of the dithiol this is consistent with an "upright" alignment of the hydrocarbon chains (perpendicular to the surface) rather than a "looped" configuration dictated by the simultaneous binding of both ends of the molecule to the surface. Photooxidation at the SAM/Au interface was not detected after 3 h of exposure of either SAM to laboratory lighting and air, indicating that the monolayers provided an effective barrier against the penetration of atmospheric oxygen to the substrate. In the case of 1,8-octanedithiol, however, photooxidation occurred at the ω-thiol group (RSH), remote from the surface and exposed at the SAM/air interface, to yield a sulfonic acid species (RSO$_3$H). It is proposed that the most likely mechanism for this reaction involves the transfer of "hot" (subvacuum) electrons from the Au surface to the ω-thiol group at the SAM/air interface followed by reaction with proximal atmospheric oxygen. In cases where atmospheric oxygen can penetrate to the Au surface, a similar mechanism is proposed to explain the photooxidation of thiolate (RS–Au) to sulfonate (RSO$_3$–Au), which is commonly observed in alkanethiol SAMs.

1. Introduction

Much of the interest generated by self-assembled monolayers (SAMs) in recent years has arisen due to the vast array of potentially useful applications that have been suggested and, in many cases, explored. Crucial to the success of many of these applications[1,2] is a detailed understanding of the mechanism of photooxidation, since the oxidized SAM is relatively weakly bound to the surface and slowly desorbs.[3] X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and laser desorption Fourier transform mass spectrometry (LID-FTMS), have proved useful techniques for the investigation of SAM photooxidation. Li et al. employed LID-FTMS to characterize SAMs prepared from the thiol compounds $C_nH_{2n+1}SH$ (n = 4, 6, 8, 9, 12, 16, 18) on gold.[4] For SAMs of $n \geq 8$, in addition to the deprotonated parent fragment,

or thiolate species RS$^-$, they recorded the existence of a fragment ion lying 48 u higher. This peak was assigned to the sulfonate species RSO$_3^-$, which it was thought had arisen due to photooxidation under ambient (laboratory) conditions. Spectra of SAMs comprising thiols of $n \leq 6$ contained much stronger sulfonate signals, while the thiolate peaks were barely visible. The RSO$_3^-$ species was also detected by Tarlov and Newman during a static secondary ion mass spectrometry (SIMS) investigation of alkanethiol SAMs on Au.[5] Samples exposed to air for several days exhibited intense sulfonate features in the negative-ion SIMS spectra, which were found to diminish following immersion into fresh thiol solutions for a period of 1 h. In a combined XPS and LID-FTMS study, Huang and Hemminger observed rapid SAM photooxidation upon exposure to radiation from a mercury lamp, in the presence of air.[6] The suggested mechanism for this process involved the transfer of a subvacuum or "hot" electron, from the metal either to the RS species or to coadsorbed O$_2$, followed by oxidation of the thiolate to sulfonate.

Rieley et al.[7] used near-edge X-ray absorption fine structure (NEXAFS) to verify the coexistence of the thiolate and sulfonate oxidation states in octanethiol SAMs which had undergone exposure to ambient laboratory conditions. Furthermore, the presence of both states in the NEXAFS of a SAM prepared from 1,8-octanedithiol on gold suggested that the oxidation not only required light and oxygen but also was mediated by the metal surface.[8] This conclusion was supported by XPS and SIMS

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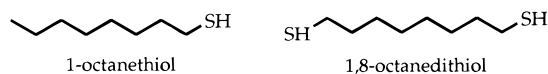
Figure 1. Molecules investigated in this XPS study of alignment and photooxidation in SAMs on Au.

data of chlorooctane disulfide SAMs on Au.[9] Samples exposed to laboratory lighting ($\lambda > 400$ nm) and air promoted not only photooxidation of the thiolate moiety but also photodetachment of Cl$^-$. Since the energy of incident radiation (~ 3 eV) was below the work function of the Au substrate ($\Phi_{Au} \sim 5$ eV[10]), it was argued that hot electron transfer was crucial to the reaction scheme. However, it is not clear whether the presence of chemisorbed oxygen also played a pivotal role in the mechanism.

Recent work by Hutt and Leggett[11] established that atmospheric oxygen can penetrate to the thiolate/Au interface and be incorporated into the sulfonate group following exposure to a mercury arc lamp radiation source. The proposed mechanism involved the formation of an excited (possibly singlet) oxygen precursor, followed by diffusion of this species to the thiolate/substrate interface. The rate of photooxidation followed two distinct kinetic regimes, depending on the length of the adsorbate hydrocarbon chain. For $n \leq 8$, oxidation was fast; the rate increased sharply with decreasing n. Thiols of this length are known to form less well-ordered SAMs, hence it was thought that the rate determining step in this regime was production of the active oxygen species. In the longer chain SAMs, $n \geq 12$, oxidation was slow; the rate decreased slowly with increasing n. In this kinetic region, it was proposed that the rate was limited by transport of O$_2$ through the densely packed hydrocarbon chains.

The successful utility of SAMs in photopatterning applications lies in exploiting the weakly bound nature of the sulfonate species. The irradiated regions of a partially masked SAM may be removed by rinsing with H$_2$O,[12] thus exposing the underlying substrate that may then be etched to a high degree of spatial resolution. A second possibility is displacement of the sulfonate by another thiolate species, perhaps of differing terminal functionality.[13] The advancement of potentially useful applications such as these provides the impetus to acquire a comprehensive understanding of the photochemistry of SAMs. The precise mechanism of photooxidation remains unknown. It is unclear whether the process requires oxygen to first adsorb at the surface, in which case photooxidation may be hindered by blocking surface sites. Also yet to be established is whether oxygen must undergo excitation to the singlet state, as proposed by Hutt and Leggett. If so, then the process by which this excitation occurs needs to be resolved.

In the work presented here the photooxidation of 1-octanethiol and 1,8-octanedithiol (Figure 1) SAMs on gold have been investigated using chiefly XPS and, to a lesser extent, SIMS. A comparison is made between the two systems studied, followed by a discussion of the possible mechanism involved in the photooxidation reac-
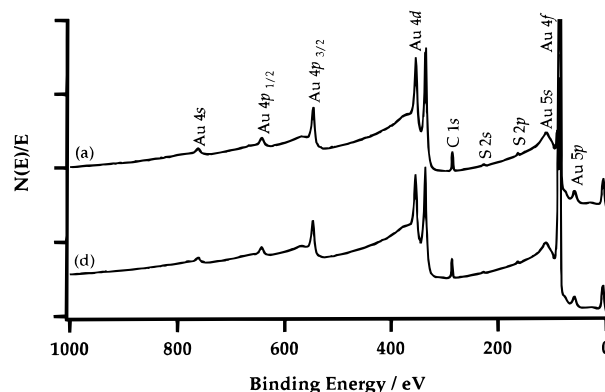
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Figure 2. XPS surveys of 1-octanethiol SAMs on an evaporated Au film: (a) exposed to light and oxygen; (d) stored under nitrogen in the absence of light.

tion. It will be shown that the data are consistent with a scheme in which hot electrons are transferred to the thiolate group prior to reaction with oxygen.

2. Experimental Section

Gold substrates were prepared by vapor deposition of gold onto 10 × 10 mm silica slides, using a commercial evaporator (Edwards High Vacuum Ltd., U.K.). A 2 nm layer of chromium was first deposited to aid adhesion, followed by a 20 nm layer of high purity gold (99.95%, Goodfellow Ltd., U.K.). The slides were stored under an atmosphere of nitrogen until required. Adsorbate solutions of 1-octanethiol and 1,8-octanedithiol (Aldrich) were prepared immediately prior to use, to reduce the opportunity for thiol oxidation in advance of derivatization. Operating within the confines of a nitrogen-filled glovebag, SAMs were formed by immersion of four substrate slides into the relevant solution for a period of 3 h. After being rinsed thoroughly with high-purity ethanol, the samples were allowed to dry under a stream of nitrogen. A different set of conditions were then applied to each of the four sample types. Sample a underwent exposure to light (supplied by laboratory fluorescent lighting, $\lambda > 400$ nm) and oxygen (laboratory air), while sample b was kept in the dark under the same atmosphere. To ensure the four permutations necessary to conduct the antithetical experiment, samples c and d both remained in a nitrogen atmosphere, under which they were subjected to the conditions of light and dark, respectively. After approximately 3 h the samples were transported, under nitrogen and in the absence of light, to a commercial ultrahigh vacuum (UHV) analysis chamber (Perkin-Elmer, PHI Multi-technique system) for immediate characterization. Avoiding exposure to either light or oxygen, the specimens were transferred to the system via a fast-entry load−lock mechanism.

The XPS source employed was monochromated Al Kα radiation, which was incident at an angle of 45° to the surface normal, irradiating a sample area of approximately 2 × 2 mm. Energy distribution curves (EDCs) were recorded for each specimen over the available energy range 1400−0 eV, followed by high-resolution scans over the S 2p (178−158 eV) and O 1s (545−525 eV) photoelectron binding energy regions. Spectra of underivatized gold slides, stored in pure ethanol for 3 h (in accordance with the immersion time employed for SAM formation), were also recorded to act as control samples. SIMS analyses were performed on selected 1 × 1 mm areas of each sample, using Ar$^+$ ions to detach secondary ions from the surface. The ion beam energy used was 3 kV, and the ion current at the sample was 2.3 nA. Spectra were typically acquired over a period of ca. 15 min in the mass to charge range $m/z = 0-300$.

3. Results

3.1. 1-Octanethiol on Au. Figure 2 shows XPS survey scans obtained for SAMs of 1-octanethiol on gold. Since all four samples exhibited similar features in terms of position and intensity, the illustration includes data from samples a and d only. The existence of several intense
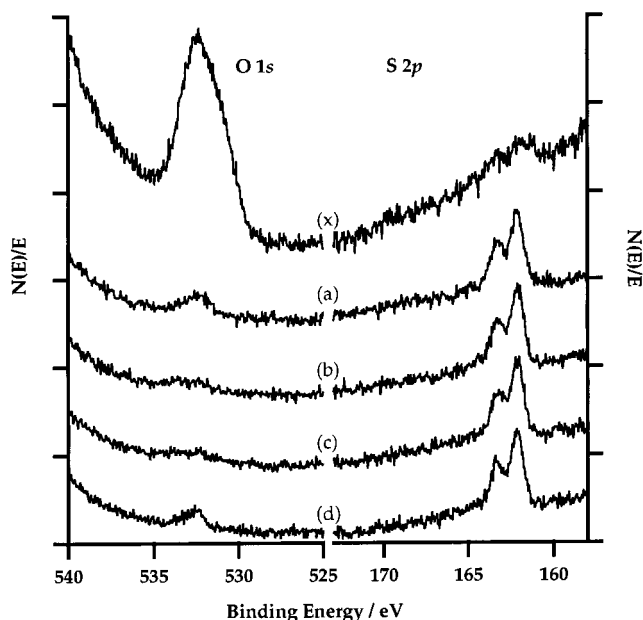
Figure 3. High-resolution XPS scans of O 1s and S 2p regions for 1-octanethiol on Au. Exposure conditions were as follows: (a) O_2/light; (b) O_2/dark; (c) N_2/light; (d) N_2/dark. Trace x represents the underivatized control sample.

Figure 4. XPS surveys of 1,8-octanedithiol SAMs on Au: (a) exposed to light and oxygen; (d) stored under nitrogen in the absence of light.

substrate peaks, coupled with features corresponding to carbon and sulfur species, is consistent with the formation of 1-octanethiol SAMs on Au. The data are lacking in signals corresponding to contaminant species, for example, oxygen or chlorine. High-resolution XPS scans over the O 1s and S 2p binding energy regions for each sample are presented in Figure 3, along with data recorded for the underivatized gold slide. The oxygen and sulfur peaks were normalized to their respective XPS sensitivities, and both sets of data are plotted using a common abscissa. This allows the plotted intensities to be used for direct comparison of the atomic abundances.

There appears to be little difference between the four SAM samples in the O 1s and S 2p binding energy regions. The S 2p doublet, occurring at 162.0/163.1 eV, differs neither in position nor intensity. In each spectrum, the existence of a small amount of oxygen on the surface is manifest in the weak features visible at a binding energy of 533 eV. Inspection of the control spectrum, presented in Figure 3x, reveals a considerable degree of oxygen contamination in the underivatized gold substrate. Evans et al. report the presence of oxygen on evaporated gold films that had been stored in a range of pure solvents, including ethanol.[14] It is therefore assumed that the oxygen contamination observed in the control sample originated from immersion of the freshly prepared gold slide in ethanol. The comparatively small oxygen signals in the four SAM spectra are thus considered to be of minor significance. Indeed, it is possible, given the relative intensities of these peaks, that the self-assembly process may displace surface oxygen to a large extent.

3.2. 1,8-Octanedithiol on Au. XPS survey spectra recorded for 1,8-octanedithiol on Au are presented in Figure 4. Data from samples a and d are illustrated, since the spectra obtained for samples b and c were identical to trace d. Inspection of the survey data reveals the appearance in (a) of oxygen photoelectron and Auger emission features that are absent in (d). The O 1s and S 2p high-resolution XPS scans are illustrated in scans a–d
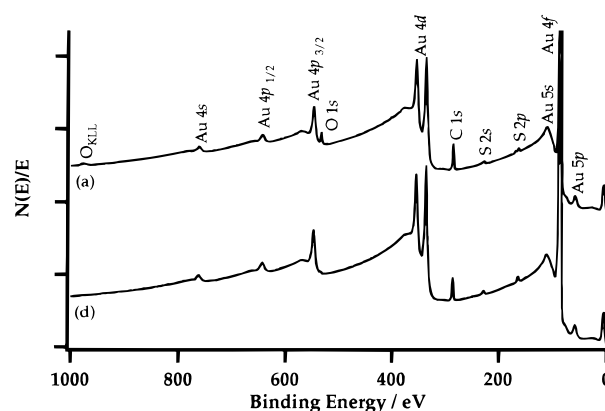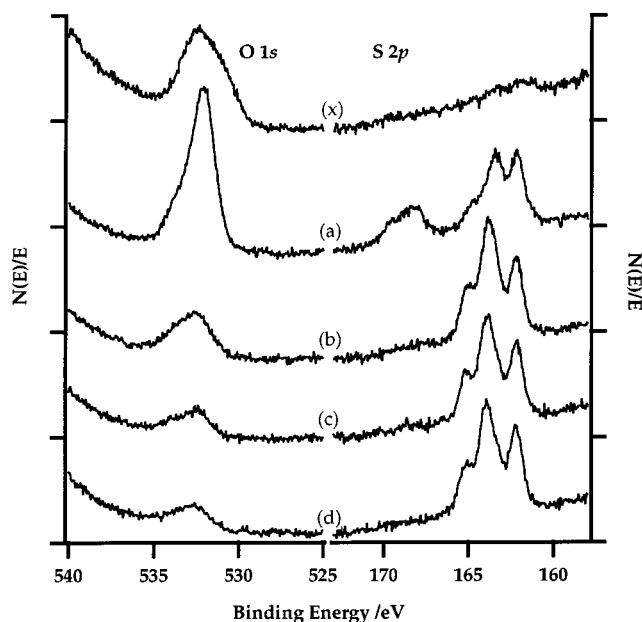

Figure 5. High-resolution XPS scans of O 1s and S 2p regions for 1,8-octanedithiol on Au. Exposure conditions were as follows: (a) O_2/light; (b) O_2/dark; (c) N_2/light; (d) N_2/dark. Trace x represents the underivatized control sample.

in Figure 5, along with corresponding data from the control sample, displayed in Figure 5x. In Figure 5a, it is clear that the exposure conditions have resulted in a change in the adsorbed species, evidenced by differences in both binding energy regions compared with scans b–d in Figure 5. Trace a is distinguished by a large O 1s signal and two discrete features in the S 2p region, while traces b, c, and d all exhibit small oxygen features and only one distinct sulfur signal. As in the case of 1-octanethiol, the data have been normalized by their respective XPS sensitivities, allowing a direct comparison to be made of atomic abundance.

To resolve the fine structure of the S 2p features, a computerized curve-fitting procedure was followed for traces a and d, as presented in Figure 6. The signals corresponding to each sulfur species were fitted using two Gaussian functions, separated by ∼1 eV with an intensity ratio of 2:1, in accordance with literature examples.[15] It was found that trace d was best described by two partially

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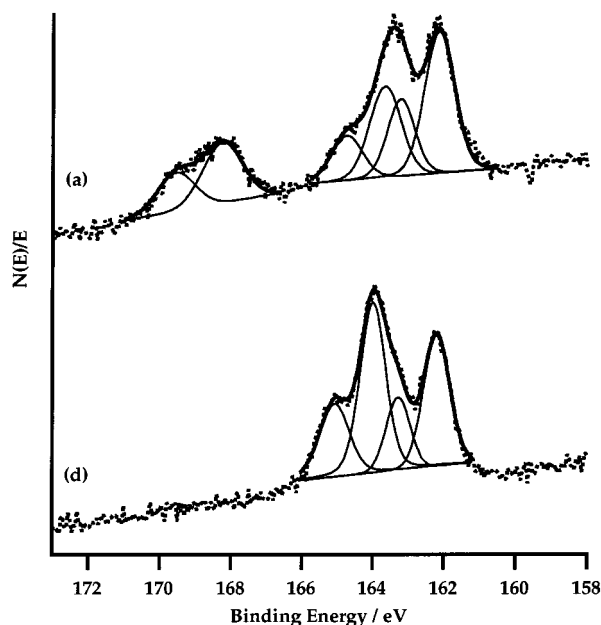
Figure 6. High-resolution XPS data for S 2p binding energy regions, showing curve-fitting components for (a) O_2/light and (d) N_2/dark.
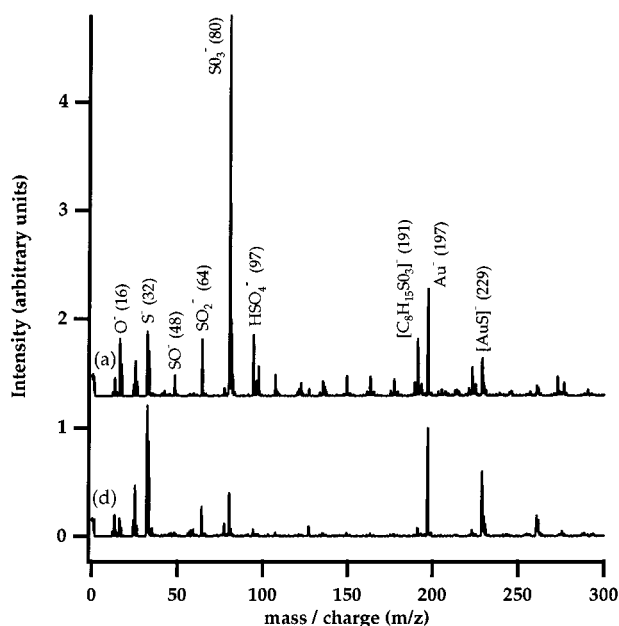

Figure 7. Negative-ion SIMS data recorded for 1,8-octanedithiol SAMs on Au, exposed to (a) O_2/light are (d) N_2/dark.

overlapping doublets, of almost equal intensity, appearing at 162.0/163.1 eV and 163.5/164.8 eV, respectively. Both these species were present in sample a, though with quite different intensities and with the addition of a third doublet centered at ~169 eV.

Negative-ion SIMS data, recorded for samples a and d, are presented in Figure 7, in which spectra are normalized to the Au peak at $m/z = 197$. The strongest features in the mass spectra are readily identified and indicate significant differences between the composition of the two SAMs. The SIMS spectrum of sample d exhibits features characteristic of n-alkanethiols adsorbed on an Au surface, namely, the prominence of S^-, SH^- and AuS^-. Indeed, the spectra of the adsorbed 1,8-octanedithiol in samples b, c, and d were not significantly different from those recorded of all the 1-octanethiol samples studied in this work (their spectra closely resemble that shown in Figure

7d) and those of n-alkanethiols studied elsewhere.[5,6,9] Sample a, having undergone exposure to light and oxygen, exhibits negative-ion features that provide evidence for the existence of oxidation products. Intense peaks visible in trace a, which are greatly enhanced with respect to trace d, include $m/z = 80$, 97, and 191, corresponding to SO_3^-, HSO_4^-, and $[C_8H_{15}SO_3]^-$, respectively. Such negative-ion features and the occurrence of a significant number of fragments in the $m/z = 100-200$ range are clear signatures of the presence of sulfonate (RSO_3^-) species in the SAM of sample a.[5,6,9] In the context of this study, SIMS serves to confirm the chemical nature of the adsorbed species but is unable to discriminate between different adsorption geometries.

4. Discussion

4.1. 1-Octanethiol on Au. From the high-resolution XPS data displayed in Figure 3, it is apparent that none of the four exposure conditions applied to 1-octanethiol SAMs have produced any detectable change in the chemical nature of the adsorbed compound. The well-resolved S 2p doublet feature, appearing at a binding energy of 162.0/163.1 eV, is indicative of a gold—thiolate sulfur species ($R-S-Au$),[15] in accordance with the findings of Laibinis et al.[16] This indicates that exposure to light and oxygen has induced little or no photooxidation within the 3 h time frame of the experiment.

Hutt and Leggett[11] reported rapid photooxidation of 1-octanethiol SAMs on Au, subjected to light from a mercury arc lamp, in the presence of air. They detected the growth of a sulfonate ($R-SO_3-Au$) peak at ~169 eV after just 11 min of exposure, followed by complete monolayer oxidation 31 min later. In their proposed mechanism, the initial formation of an active oxygen species (they suggested singlet oxygen as a possibility) is followed by its diffusion through the SAM to the gold surface, from where oxidation of thiolate to sulfonate proceeds directly. Supporting this scheme was the evidence that the rate of photooxidation was strongly related to the alkyl chain packing efficiency. SAMs comprising short-chain thiols had the highest disorder and thus oxidized most rapidly, with rate of oxidation increasing sharply with decreasing chain length. For the close-packed SAMs consisting of long-chain thiols, the rate of oxidation was reduced and was found to decrease slowly with increasing chain length.

It is possible, therefore, that in the experiments reported here, that the laboratory lighting to which the SAMs were subjected was either insufficient in energy to produce excited-state oxygen or in intensity to produce it in abundance. The wavelength of the laboratory lighting ($\lambda > 400$ nm) was certainly well below the energy threshold for the direct production of singlet oxygen. Indeed, the first optically allowed excitation of ground-state oxygen, which occurs at a wavelength $\lambda \sim 280$ nm,[17] gives rise to the excited triplet rather than singlet electronic state. Supposing an alternative mechanism were in operation, in which the required photon energy fell within the range of the broad-band source employed, then it is reasonable to suggest that the incident light intensity may have been too low to promote measurable photooxidation after 3 h of exposure. Such a mechanism may involve hot (i.e., subvacuum) electron transfer from the Au substrate to an adsorbed species, for example, sulfur or oxygen—such

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as has been postulated in the photooxidation of 1,8-chlorooctandisulfide SAMs under similar conditions.[9]

4.2. 1,8-Octanedithiol on Au. In the dithiol experiments, the appearance of a sulfur peak at ~169 eV, corresponding to a sulfonate species,[15] provides evidence of a chemical change. The fact that this feature appears in the SAM exposed to light and oxygen, while absent in SAMs deprived of one or other or both, is indicative of a photooxidation reaction. This conclusion is supported by the negative-ion SIMS data (Figure 7), in which fragment ions corresponding to oxides of sulfur are prominent in sample a, yet virtually absent in sample d. The SIMS technique cannot, in this case, distinguish which of the sulfur atoms in the 1,8-octanedithiol is oxidized. In conjunction with the high-resolution XPS data, however, this issue is resolved.

Before entering a detailed analysis of trace a in Figure 5, it is first necessary to assign fully the features appearing in traces b, c, and d. Initial inspection of the S 2p region reveals a distorted "triplet" feature, centered at a binding energy of approximately 163 eV. Closer examination and curve-fitting reveals that this signal is in fact a superposition of two doublets, almost equal in intensity, as illustrated in Figure 6d. This suggests the presence of two distinct sulfur environments that, according to the best-fit curves, differ in binding energy by approximately 1.9 eV. The lower energy doublet appears at 162.0/163.1 eV and is similar to the S 2p signal seen in the 1-octanethiol monolayer (Figure 3). Zubrägel et al. presented a very similar finding in their XPS study of n-docosanethiol self-assembled on Au(111) and Ag(111), which they attributed to the existence of two distinct adsorption sites for sulfur at the metal surface.[18]

In the experiments reported here, it is possible to make a direct comparison between the XPS spectra of 1-octanethiol and 1,8-octanedithiol adsorbed under air- and light-free conditions, on freshly evaporated gold films. Since the substrates in both cases are identical, the existence of two distinct S environments at the Au/thiol interface, as proposed by Zubrägel et al., would be evident in both the monothiol and the dithiol spectra. The lone doublet in the XPS spectrum of the 1-octanethiol clearly suggests the existence of only one sulfur species at the surface. The implication is that in the 1,8-octanedithiol, the two S environments detected arise because the molecule is oriented "head-down, tail-up". The head (α-) group, R–**S**–Au, appears at the same binding energy as the single sulfur species witnessed in the monothiol spectrum, at 162.0/163.1 eV. The second species, arising at a binding energy of 163.5/164.8 eV, is therefore assigned to the tail (ω-) group, H–**S**–R, at the air/thiol interface. Intuitively, one would expect the ω-S to appear higher in energy than the α–S, because the latter experiences the electron-rich environment of the Au surface. In addition, the lower energy doublet appears marginally less intense than its neighbor due to the increased attenuation of photoelectrons escaping the thiolate/Au interface.[19]

Supporting this adsorption model is evidence extracted from the O 1s binding energy region. In each spectrum there is a considerable oxygen component present at a binding energy of around 533 eV. The size of this peak varies little between samples c and d, while being slightly more prevalent in sample b. In all three samples, the oxygen abundance is less than that in the control sample,

yet considerably more than that in the corresponding monothiol SAMs. This observation may be rationalized by considering the relative hydrophilicity of interfaces comprising thiol groups and methyl groups. In the preparation of samples c and d, all efforts were made to exclude atmospheric oxygen by operating within the confines of a nitrogen-filled glovebag. However, no further measures were taken to eliminate moisture. The hydrophobic methyl-terminated 1-octanethiol SAMs suffered no oxygen contamination under identical preparation conditions. The considerable oxygen presence in each of the 1,8-octanedithiol samples is therefore attributed to the hydrophilicity of the ω-thiol group, encouraging the association of water molecules from the atmosphere. The appearance of this additional oxygen contribution apparently had no effect on the oxidation mechanism, since only in the case of exposure to atmospheric oxygen and light did the reaction proceed. No oxidation products were detected when the SAM was exposed to light in the absence of air.

Analysis of the monothiol and dithiol data prompts a reconsideration of the conclusions of Zubrägel et al.[18] The detection of a single sulfur species in the case of 1-octanethiol immediately questions the hypothesis that there are two chemically distinct adsorption sites for SAMs on Au. Furthermore, the apparent correlation between the 1,8-octanedithiol data presented here and the results of Zubrägel et al. would suggest that in the latter, physisorbed rather than chemisorbed n-docosanethiol was present, leading to the detection of both R–**S**–Au and R–**S**–H groups. Indeed, in a recent XPS study of thiols and disulfides on Au,[20] it was concluded that use of a poor solvent (e.g., ethanol for long-chain alkanethiols) and/or lack of a rinsing step resulted in unbound thiol molecules present at the surface. It is likely, we believe, that this situation may arise due to "interdigitation" of the pendant alkane chains of the adsorbed thiols with the alkane chains of unbound thiols in solution. A drawing showing how these SAMs might look is presented in Figure 8. It is stressed that this situation did not occur in this work.

It is worth emphasizing that, in the experiments reported here, XPS has proved successful in confirming the nature of 1,8-octanedithiol adsorption at a gold surface. In contrast with the monothiol case, two possibilities exist for dithiol adsorption: the first involves the orientation of the molecule head-down and tail-up, while the second requires the alkyl chain to "loop", so that both sulfur atoms bond with Au. The observation that only one of the terminal thiol groups in the free molecule adsorbs at the surface is consistent with a recent study in which the 1,6-hexanedithiol molecule was effective as a connecting link between colloidal gold particles.[21]

As mentioned above, exposure of 1,8-octanedithiol SAMs to laboratory lighting and air promoted photooxidation that, in accordance with the findings of Hemminger et al.[4,6] and Tarlov and Newman,[5] resulted in production of a sulfonate species. Since the 1-octanethiol SAMs suffered no such reaction to identical exposure conditions, it might be expected that the α-S group (adjacent to the Au surface) would remain unchanged. Further curve-fitting, presented in Figure 6a, reveals that this is indeed the most likely scenario. The appearance of the sulfonate feature centered at ~169 eV correlates with the attenuation of the thiolate doublet assigned to the ω-S atom (remote

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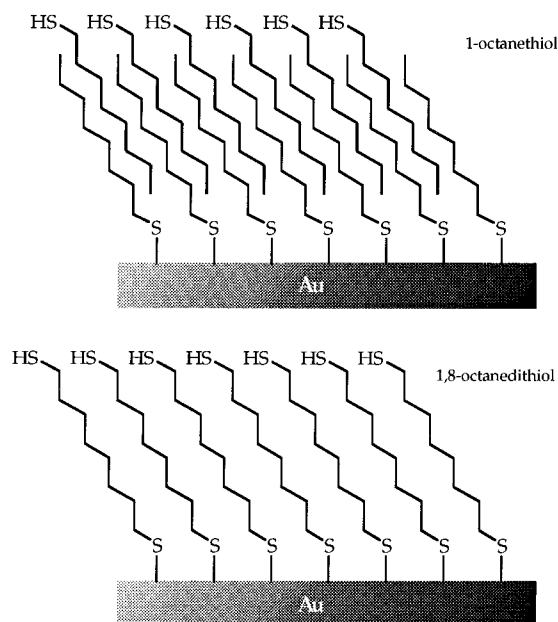
Figure 8. Proposed "interdigitation" of monothiol, illustrating how the resulting SAM would be indistinguishable from the dithiol SAM using XPS. This is not the case in the experiments reported here.

from the Au surface), while the intensity and position of the α-S XPS feature remains constant.

4.3. Mechanism of SAM Photooxidation. The results of the experiments on the 1,8-octandithiol SAMs prove unambiguously that exposure to light and oxygen has promoted photooxidation at the thiol/air interface. No such reaction is detected either at the Au/thiol interface or in the 1-octanethiol SAMs. It has been established both here and elsewhere[4,5,9] that ambient room light is sufficiently energetic for initiating photooxidation in SAMs. Therefore, it is highly unlikely that the mechanism proceeds via direct photoexcitation of molecular oxygen, for which the energy threshold is approximately 280 nm.[17] It is equally improbable that the reaction involves photolytic cleavage of the S—H bond, which has been implicated in the photochemistry of gas- and condensed-phase thiols and has a wavelength threshold of 253 nm.[22] The evidence points to a mechanism that is mediated by the metal surface, most likely via hot electron transfer, since the energy of the light source employed ($\lambda > 400$ nm ≈ 3 eV) lies below the work function of Au ($\Phi_{Au} \sim 5$ eV). This represents a new example of hot electron initiated processes that have long been recognized as being of considerable significance in photochemical reactions at metal surfaces.[23,24]

The observation that no oxidation of the α-S group was observed within the 3 h time frame of the experiments suggests the formation of an effective barrier to oxygen penetration. Hutt and Leggett observed complete photooxidation of 1-octanethiol SAMs on Au after 42 min, implying a very efficient transport of oxygen to the metal surface in their samples. Substrate defects or adsorbate contamination prior to assembly might account for a reduction in the alkyl-chain packing efficiency. Subsequent diffusion of oxygen to the thiolate/Au interface would be facile and thus account for the rapid photooxidation

observed. If the proposed mechanism of hot electron transfer required the initial transport of oxygen to the metal surface, then selective oxidation of the α-S group would be detected. It is unlikely that an electronically excited oxygen molecule at the thiol/Au interface would react preferentially with the ω-S group. The inescapable conclusion is that hot electrons must be transferred from the substrate to the adsorbed thiol molecule itself, rather than to a surface-bound oxygen species. The concentration of oxygen in the proximity of the thiol/Au interface will thus determine the rate of the photooxidation. In the experiments reported here, the formation of high-quality, densely packed SAMs has prevented the penetration of a significant concentration of atmospheric oxygen through to the gold surface.

A further implication of the observed ω-S photooxidation is that transfer of electrons must be possible from the substrate to the tail end of the molecule. This is consistent with the proposal by Rieley et al.[9] that photodetachment of Cl$^-$ ions from 8-chlorooctanedisulfide SAMs on Au explains the loss of ω-Cl upon exposure to light. By use of ambient exposure conditions identical to those employed here, the removal of Cl$^-$ from the tail end of the SAM, confirmed by XPS, was rationalized by electron transfer rather than direct photolysis of the C—Cl bond. Similarly, Huang and Hemminger observed the photodetachment of the same species from chlorothiophenol SAMs on Au, following exposure to radiation from a mercury lamp.[6]

It is noteworthy that in the condensed phase, thiols have a rich and complex oxidation chemistry. The conversion of thiols to disulfides on exposure to air is well-known, as is the sensitivity of the reaction to metal ions, UV light, and other radical initiators.[25] The first and most facile step is the coupling of thiols to form disulfides. The disulfide then leads to a succession of sulfur oxyacids.[26] It is curious, therefore, that of the profusion of oxidized sulfur compounds isolated in condensed phase reactions, only the sulfonate species (RSO$_3^-$) has been identified in the oxidation of SAMs. The only reported instance of differently oxidized sulfur appeared in organosilane SAMs, in which a sulfone ($-SO_2-$) moiety was placed in the middle rather than at the end of the hydrocarbon chain of the surfactant molecule prior to adsorption.[1,27]

We propose that in the immobile, aligned, and densely packed environment of the self-assembled monolayer, the coupling of two thiolate sulfurs either at the Au surface, in the case of monothiols, or at the SAM/air interface, in the case of the dithiols oriented predominantly perpendicular to the surface, is prohibited on energetic and steric grounds. Absorption of radiation by the Au substrate initiates electron transfer to an affinity (unfilled) level in the adsorbed thiol or dithiol localized in the vicinity of an S atom. The radical anion so formed reacts with proximal ground-state dioxygen (O$_2$), which originates from the atmosphere. Given the short lifetimes of negative ion resonances at surfaces[28] it is likely that the reaction with proximal O$_2$ is effectively concerted. The resulting series of events then presumably follows that of the condensed phase species, through to the sulfonate. Since the observed photooxidation product in the dithiol is a sulfonate species at the tail end of the molecule, this most likely exists in the sulfonic acid (RSO$_3$H) form. Scheme 1 shows the

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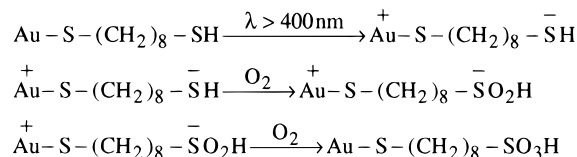
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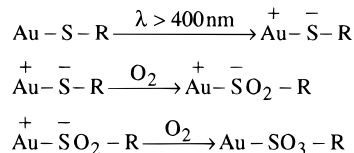(26) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

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Scheme 1.   Proposed Reaction Scheme for Photooxidation of the ω-S Group in 1,8-Octanedithiol SAM on Au

$$Au-S-(CH_2)_8-SH \xrightarrow{\lambda > 400\,nm} \overset{+}{Au}-S-(CH_2)_8-\overset{-}{S}H$$

$$\overset{+}{Au}-S-(CH_2)_8-\overset{-}{S}H \xrightarrow{O_2} \overset{+}{Au}-S-(CH_2)_8-\overset{-}{S}O_2H$$

$$\overset{+}{Au}-S-(CH_2)_8-\overset{-}{S}O_2H \xrightarrow{O_2} Au-S-(CH_2)_8-SO_3H$$

Scheme 2.   Proposed Reaction Scheme for Photooxidation of the α-S Group (at the Au Surface) in Alkanethiol SAMs (R = alkane chain)

$$Au-S-R \xrightarrow{\lambda > 400\,nm} \overset{+}{Au}-\overset{-}{S}-R$$

$$\overset{+}{Au}-\overset{-}{S}-R \xrightarrow{O_2} \overset{+}{Au}-\overset{-}{S}O_2-R$$

$$\overset{+}{Au}-\overset{-}{S}O_2-R \xrightarrow{O_2} Au-SO_3-R$$

proposed photooxidation sequence of a dithiol at the SAM/air interface.

The more commonly observed photooxidation observed in SAMs is the oxidation of thiolate sulfur adsorbed at the gold surface (Au−S−R) to produce the rather less stable sulfonate (Au−SO$_3$−R).[29,30]   Indeed, this is the basis of photopatterning in SAMs.[12,13]   In this case, we propose a similar mechanism for photooxidation, presented as Scheme 2, which occurs when atmospheric oxygen is able to penetrate the SAM to reach the Au/thiolate interface. As in the case of the dithiol, absorption of radiation by the gold substrate initiates electron transfer to an affinity level in the vicinity of the thiolate moiety which reacts with proximal O$_2$ to produce the observed sulfonate. The fact that no species intermediate in oxidation state between the thiolate, S(−II), and the sulfonate, S(IV), have been observed in photooxidized SAMs must reflect an inherent instability of the partially oxidized RSO$_2^-$ species.

5. Summary

SAMs of 1-octanethiol and 1,8-octanedithiol, formed by the immersion of Au slides into ethanolic solutions, have been studied in detail using high-resolution XPS and, to a lesser extent, SIMS. XPS has proved successful in determining the adsorption alignment of 1,8-octanedithiol for the first time. Two chemically inequivalent sulfur atoms exist, consistent with a structure in which one atom is bonded directly to the substrate at the Au/SAM interface, while the other is located remotely from the surface at the SAM/air interface. SIMS was able to confirm the chemical nature of the adsorbed species but could not discriminate between different adsorption geometries.

The photooxidation of these SAMs has been investigated using the antithetical exposure conditions of O$_2$/light, O$_2$/dark, N$_2$/light, and N$_2$/dark. It has been shown that ambient room light ($\lambda > 400$ nm) in the presence of oxygen (air) will promote the photooxidation of S(−II) to S(VI). Within the 3 h time frame of the experiments, no oxidation was observed at the Au/SAM interface, which is consistent with the model in which SAMs can effectively block the access of oxygen to the metal surface, postulated by Laibinis and Whitesides.[31]

It is unlikely that direct excitation of atmospheric dioxygen to singlet oxygen is necessary, since the energy of light required to promote photooxidation is below the threshold for this process. The proposed mechanism for photooxidation in 1,8-octanedithiol SAM involves the transfer of hot electrons from the metal to the thiol moiety remote from the surface followed by reaction with proximal oxygen. Selective oxidation of the tail (ω-) S atom indicates the ability of SAMs to act as a medium for electron transfer. We propose a similar scheme for the more commonly observed photooxidation of thiolate sulfur adsorbed at the gold surface in alkanethiol SAMs, but this relies on atmospheric oxygen penetrating through the pendant hydrocarbon chains to this interface.

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