

Photo-oxidation and photo-reduction in alkylthiol monolayers self-assembled on gold

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Photo-oxidation and photo-reduction have been observed in self-assembled monolayers (SAMs) of 8-chlorooctylthiol disulfide adsorbed on gold. Using the techniques of X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) we were able to distinguish oxidation at the gold/sulfur interface and reduction at the chlorine/air interface, in an SAM of 8-chlorooctylthiol disulfide pre-exposed to an ambient environment of light and air; but no such evidence was seen in an identical sample kept in the dark with the exclusion of air. A second study, in which the near-edge X-ray absorption fine structure (NEXAFS) of octane-1,8-dithiol self-assembled on gold foil was compared with that of 8-bromooctylthiol disulfide and octane-1-thiol, gave compelling evidence that photo-oxidation is mediated by the gold surface. Since much of the interest in self-assembled monolayers centres on the many potential applications of such ordered layers of tailored functionality, it is important to note that their usage may be restricted to applications in which the monolayer is kept either in the dark or under anaerobic conditions.

The spontaneous self-assembly of alkanethiol derivatives on gold provides a simple means of producing ordered layers with a prescribed chemical functionality. Such films harbour exciting fundamental and technological possibilities in research fields ranging from biochemistry to electrical engineering, *e.g.* mimicry of cell membranes and the fabrication of microelectronic devices.¹ There has been a considerable effort in establishing the characteristics of the interaction of thiols and disulfides with noble metal surfaces and with that of gold, in particular.² FTIR and Raman spectroscopy of SAMs formed by alkylthiols and alkyldisulfides on gold substrates testify to the existence of extended alkane chains bonded to the surface, which are oriented (S-end down) and aligned (predominantly normal to the surface).^{3,4} The high degree of long-range order in the adsorbate has been confirmed by He diffraction⁵ and more recently by scanning tunnelling (electron) microscopy (STM).⁶ Details of the interaction between sulfur and gold single-crystal substrates have been probed using electron⁷ and low energy electron⁸ diffraction. Such studies suggest that the adsorbate sulfur atoms adopt an overlayer lattice of the type $(\sqrt{3} \times \sqrt{3})R30^\circ$. Grazing incidence X-ray diffraction of *n*-dodecanethiol, however, gave evidence for the existence of disulfide linkages resulting from the dimerisation of thiolate S atoms.⁹

Progress has been made in characterising the electronic properties at the metal/sulfur interface. The nature of the gold-thiolate sulfur bond has been examined theoretically by Sellers *et al.*¹⁰ and was predicted to comprise both π - and σ -type interactions. Recent UV photoelectron data highlight the particular contribution of Au 5d orbitals in the bonding.^{11,12} X-Ray photoelectron spectroscopy (XPS) has been used to identify the chemical nature of the S in SAMs prepared by adsorption from solution and in ultra-high vacuum.⁸ XPS¹³ and secondary ion mass spectrometry

(SIMS)¹⁴ or laser desorption Fourier transform mass spectrometry (LID-FTMS)¹⁵ have proved useful techniques for the investigation of photo-oxidation of SAMs. Huang and Hemminger¹⁵ have shown that photo-oxidation of SAMs results from the conversion of a thiolate species, RS^- , to a sulfonate species, RSO_3^- . The sulfonate species is easily removed by washing or may be displaced by another thiolate species. A suggested mechanism for photo-oxidation was UV excitation of 'hot' electrons from the metal to the adsorbate (RS^-), or to coadsorbed oxygen on the surface to form O_2^- . Lewis *et al.*⁴ have recently proposed that photo-oxidation of SAMs on silver proceeds *via* a two-step mechanism: scission of the S—C bond at the thiolate/silver interface followed by oxidation of chemisorbed S to form sulfate. The potential utility of photo-oxidation in SAMs in photopatterning applications^{16,17} highlights the need to study in more detail the photochemistry of SAMs.

In this paper we present results from a surface scientific analysis of SAMs of octanethiol derivatives on gold which were subjected to one of two opposing conditions: exposure to O_2 in the presence of light or exclusion from O_2 in the dark. The preparation procedures followed were those most readily carried out in a typical academic or industrial laboratory. We provide evidence for the occurrence of photo-oxidation at the thiol/gold interface and photo-reduction at the air/thiol interface, both of which have important consequences for the integrity, stability and utility of SAMs.

Experimental

SAMs formed on evaporated gold films were analysed by XPS and SIMS. These samples were prepared by the evaporation of *ca.* 50 Å of Cr followed by 2000 Å of gold onto a glass microscope slide (cleaned first in *aqua regia*) using a commercial evaporator (Edwards High Vacuum Ltd.). Samples of size 10 mm × 15 mm were cut by scoring the reverse side of the slide with a diamond file and snapped by hand. Each was immersed for 5 min in concentrated H_2SO_4 (97%) at 120 °C in

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order to remove hydrocarbon impurities from the surface thoroughly. Immersion for longer periods or in more oxidative acid solutions resulted in peeling and dissolution of the film. In the NEXAFS study, pure gold film (Johnson Matthey, 99.95%) was used and cleaned by a short immersion in *aqua regia*. With the exception of 8-chlorooctyldisulfide, $[\text{Cl}(\text{CH}_2)_8\text{S}]_2$, and the analogous bromo derivative, which were synthesised in-house,¹⁸ the other sulfur compounds used (octane-1-thiol and octane-1,8-dithiol) were obtained commercially (Aldrich Chemical Co. Ltd.). Previous work has shown that SAMs prepared from thiol or the analogous disulfide are indistinguishable.¹⁹ Solutions of thiol and disulfide were prepared in *ca.* 2 mM concentration in ethanol (99.9%). The solutions were not de-aerated or kept under nitrogen. The gold substrates were typically immersed overnight to ensure the formation of well ordered layers. On removal from solution, the gold substrates were rinsed thoroughly with ethanol and dried under a stream of dry nitrogen. One of the 8-chlorooctyldisulfide samples and samples prepared from octane-1,8-dithiol and 8-bromooctyldisulfide were exposed to the ambient room temperature laboratory atmosphere and lighting for several hours before their respective analyses took place (preparation procedure B: SAM exposed to O_2 and light). Conversely, a second 8-chlorooctyldisulfide sample and a sample prepared from octane-1-thiol were removed from solution, washed and dried immediately prior to analysis, avoiding prolonged exposure to air and light (preparation procedure A: SAM excluded from O_2 and light). The laboratory fluorescent lighting was a broad-band source with a short wavelength cut-off of *ca.* 400 nm, determined by a glass envelope. We present elsewhere the findings of a study on octane-1-thiol SAMs prepared on evaporated gold slides in which identical results were obtained for samples subjected to procedure A, those exposed to air but kept in the dark, and those kept under nitrogen in the light.²⁰ As such, for the purposes of this work we treat procedures A and B as being antithetical.

XPS and SIMS were performed in a commercial ultra-high vacuum (UHV) analysis chamber (Perkin-Elmer, PHI Multi-technique system). Samples of evaporated gold films derivatised with 8-chlorooctyldisulfide were introduced into the system *via* a fast-entry load lock and subsequently analysed under UHV conditions. The XPS source employed was monochromated $\text{Al-K}\alpha$ radiation which was incident at an angle of 45° to the surface normal, irradiating an area of *ca.* 2 mm \times 2 mm. The secondary electron distribution curves were recorded with a fixed analyser transmission pass energy of 93 eV for survey spectra over the available energy range (1–1400 eV) and 23.5 eV for high resolution spectra centred on specific atomic features. Survey spectra were collected over a period of *ca.* 8 min, while detailed spectra over specific binding energy regions were collected in multiplex mode over a period of 8 h: the photoelectron energy resolution was 0.8 eV. Tests conducted on the Cl 2p XPS signal showed that, under the X-ray conditions employed (150 W source), there was no detectable degradation of the SAMs over the period of data collection.

SIMS of selected 1 mm \times 1 mm areas of samples was conducted by quadrupole mass filtering secondary negative ions which became detached from the sample surface upon bombardment with Ar^+ ions. The ion beam energy used was 3 kV and the ion current at the sample was 2.3 nA. Spectra were typically recorded over a period of *ca.* 15 min over the mass to charge range $m/z = 0$ –250.

Near edge X-ray absorption fine structure (NEXAFS) measurements were made on Beamline 4.2 at the Synchrotron Radiation Source, Daresbury Laboratories, Warrington, UK. Samples of SAMs prepared on gold foil were mounted normal to the monochromated synchrotron beam in an evacuated (*ca.* 10^{-8} mbar) chamber. Absorption around the sulfur K-edge (2470–2495 eV) was monitored by recording the total electron

yield as a function of beam energy. The spectra were normalised with respect to the incident beam intensity, but were otherwise uncorrected.

Results

The techniques of XPS and SIMS were employed to analyse the chemical nature and composition of SAMs prepared by derivatising an evaporated gold film with 8-chlorooctyldisulfide. Specifically, a direct comparison was made between the two preparation procedures, A and B. Fig. 1 shows XPS survey spectra for two such samples. Fig. 1(a) is the XPS spectrum obtained for a sample prepared following procedure A, in which exposure of the SAM to the ambient atmosphere and lighting was kept to a minimum. Fig. 1(b) is the corresponding spectrum for a similar sample prepared following procedure B, in which the SAM was purposely exposed to laboratory air and light. At the coarse resolution displayed in Fig. 1 the two spectra are very similar in appearance. Many of the strongest features, as indicated by their adjacent labels, are due to photoelectron emission from the gold substrate. Both spectra exhibit features which indicate the presence of significant amounts of oxygen and carbon at the surface, and the relative intensities of the O 1s and C 1s emission features are increased and decreased, respectively, in the O_2 /light exposed film. The presence of residual oxygen could be detected in a clean gold sample, which had been exposed to the ambient environment, and is, we believe, due to the presence of gold oxide, as postulated by King.²¹ Weak features attributable to emission from Cl 2p and S 2p are also apparent with binding energies centred at 201 and 165 eV, respectively. There are clear differences in these weak features between the two spectra and we have concentrated on these weak features with higher resolution and higher sensitivity. The results of this analysis are presented in Fig. 2 in which both components of the Cl 2p and S 2p photoemission features are resolved: these are labelled '1/2' and '3/2' on the figure. There is an obvious reduction in the integrated intensity of both these emission signals in the sample which was exposed to O_2 and light (preparation B). Furthermore, the reduction in the case of the Cl 2p feature is more pronounced than that observed for the S 2p feature. We interpret these intensity changes as a loss of S and of (greater amounts of) Cl from the SAM due to exposure to O_2 and light.

The precise binding energy positions of XPS features are indicative of the chemical nature, or oxidation state, of the atoms being probed. Through comparison with tabulated XPS data of a range of compounds²² we are able to identify the oxidation states of Cl and S present in samples prepared *via* procedures A and B. The Cl 2p_(1/2) and Cl 2p_(3/2) features are characteristic of Cl^- or Cl^{-1} and this is the only Cl species present in either sample. The S 2p doublet in Fig. 2(a) is centred around 162 eV and is characteristic of S in a sulfide or S^{2-} . In Fig. 2(b), however, this S^{2-} signal diminishes in intensity while a new feature, centred at 168 eV, emerges which is characteristic of highly oxidised sulfur, S^{VI} .

Negative ion SIMS was performed on the same samples of 8-chlorooctyldisulfide SAMs previously analysed with XPS, in order to probe their chemical composition. Survey spectra over $m/z = 0$ –250 for the two samples are presented in Fig. 3. The strongest features in the mass spectra are readily identified and point to significant differences in the composition and stability of the two SAMs as a result of their preparation procedure. Peaks due to the underlying gold (Au ; $m/z = 197$) and glass (SiO_2 ; $m/z = 60$) are common to both spectra and are independent of the SAM preparation procedure which confirms that the gold substrates are rather similar in each case and are themselves, apparently unaffected by exposure to O_2 and light. Perhaps the clearest difference between the spectra

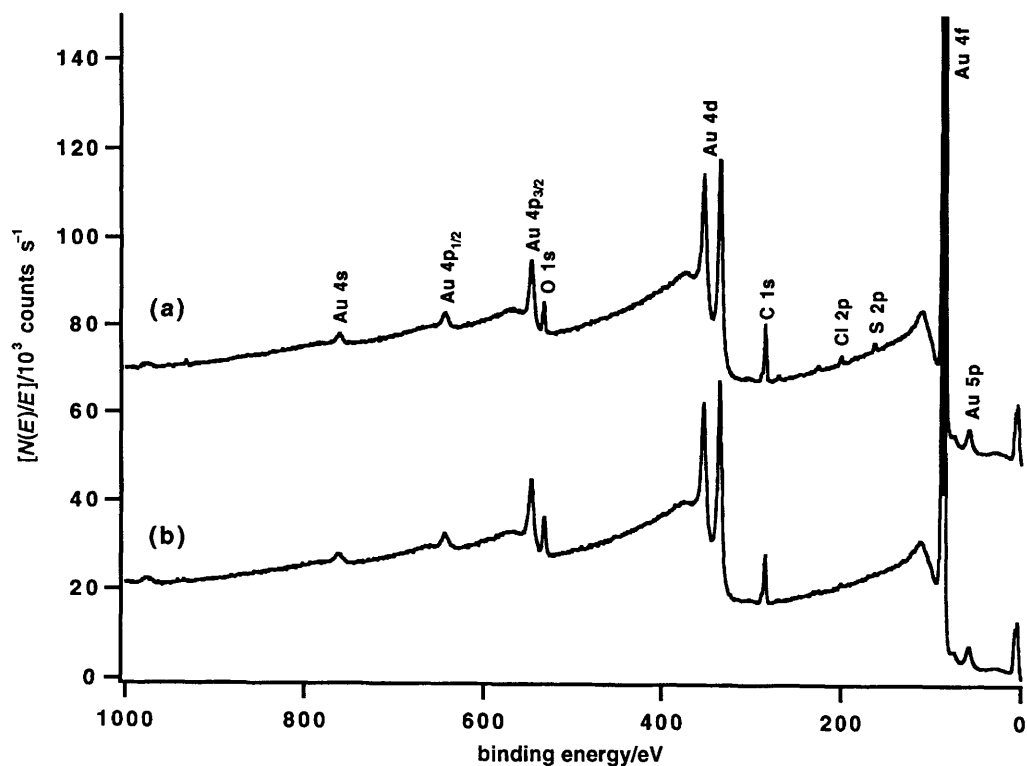


Fig. 1 XPS survey spectra of 8-chlorooctylsulfide SAMs prepared on evaporated gold films using (a) procedure A (excluded from light and O_2) and (b) procedure B (exposed to light and O_2). The major features have the assignment indicated.

in Fig. 3(a) and (b) is in the dominance of the Cl^- signal in 3(a) and that of sulfur oxide anions in 3(b). In addition, Fig. 3(b) shows a more extensive fragmentation pattern at higher m/z . This difference is made clear in Fig. 4, which shows, in higher resolution, the range $m/z = 145$ –250. Fig. 4(a) is distinguished by an almost total absence of fragment masses in the spectrum: the only evidence of the sputtered SAM is the peak at $m/z = 229$ which can be assigned to an AuS^- species.

Higher mass fragments at $m/z = 232$ and 234 are consistent with $Au^{35}Cl^-$ and $Au^{37}Cl^-$, respectively. Conversely, the spectrum in Fig. 4(b) displays an extensive fragmentation pattern which is consistent with the Ar^+ induced desorption and cracking of an 8-chlorooctylsulfonate parent species, $^{35}Cl(CH_2)_8SO_3^-$, at $m/z = 227$. The highest mass, singly charged species, of significant intensity appears at $m/z = 229$ and corresponds to the ^{37}Cl isotope of 8-chlorooctylsulfonate

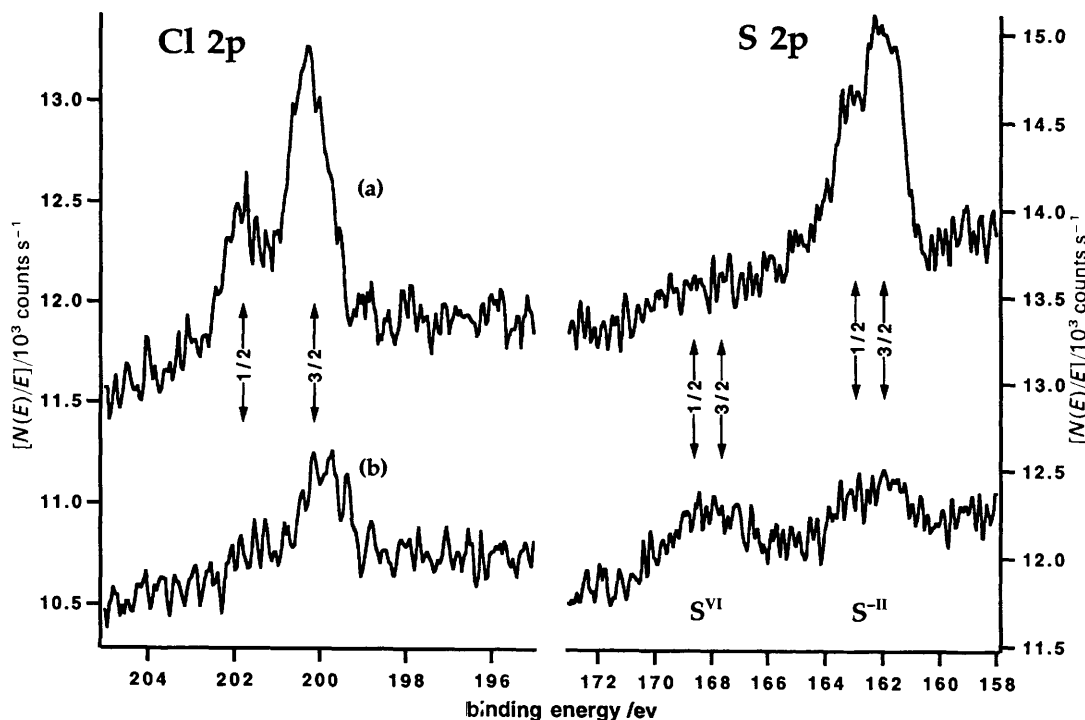


Fig. 2 High resolution XPS in the Cl 2p and S 2p binding energy regions of 8-chlorooctylsulfide SAMs prepared on evaporated gold films using (a) procedure A (excluded from light and O_2) and (b) procedure B (exposed to light and O_2). The positions of the two spin-orbit component of the 2p emission features are indicated by the labels, 1/2 and 3/2.

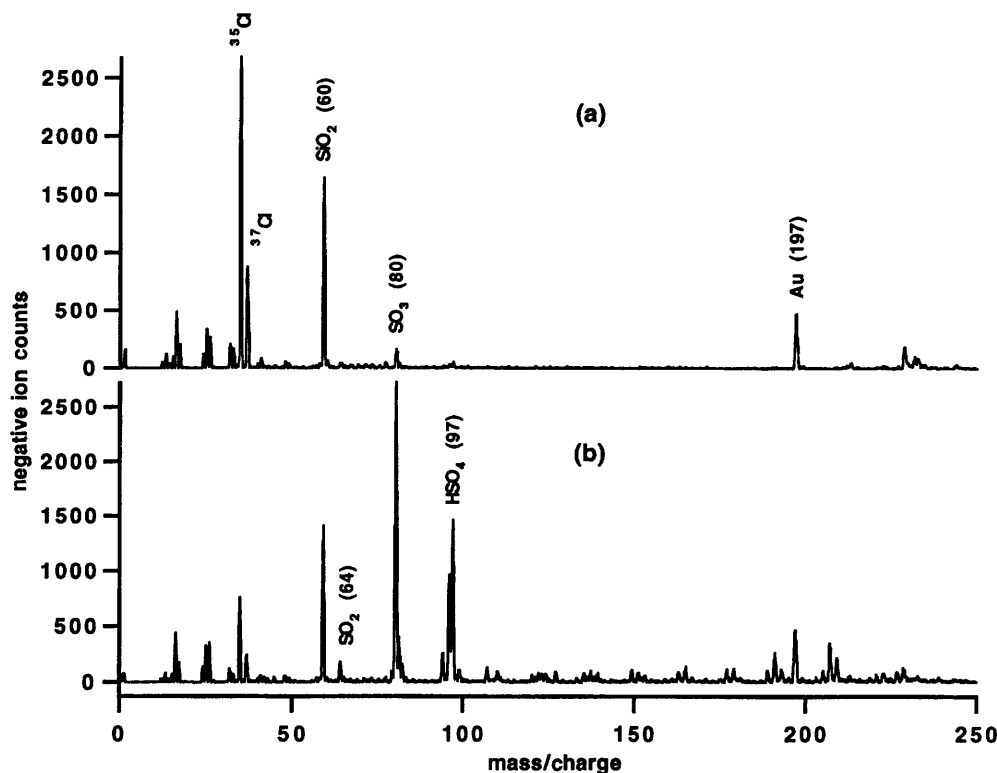


Fig. 3 Negative ion SIMS survey of 8-chlorooctylthiol SAMs prepared on evaporated gold films using (a) procedure A (excluded from light and O_2) and (b) procedure B (exposed to light and O_2). Relevant peaks are labelled according to the likely identity and m/z value of the desorbed negative ion.

and possibly, AuS^- . The identification of the parent species is confirmed by noting the appearance of fragment ions which result either from loss of oxygen from the SO_3 end of the molecule (e.g. the m/z series: 223, 207, 191) or from loss of HCl [leaving $CH_2CH(CH_2)_8SO_3^-$ with $m/z = 191$] followed by loss of an increasing number of CH_2 groups from the chloro-

alkyl end of the molecule (e.g. the m/z series: 191, 177, 163, 149, 135, 121, 107). Other series can be identified in which the fragment mass differs by 2 (corresponding to two hydrogen atoms or, in some instances, due to the ^{37}Cl isotope). The absence of higher mass fragments in the SIMS spectrum of the sample prepared *via* procedure A (excluded from O_2 and light)

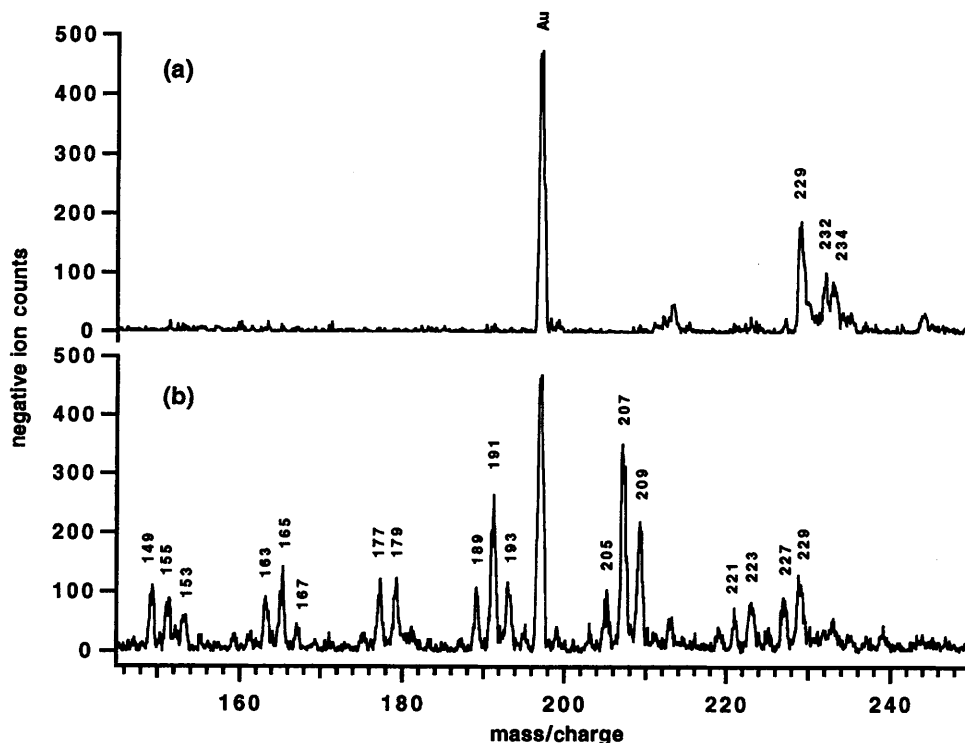


Fig. 4 High mass/charge region (145–2245) of the negative ion SIMS of 8-chlorooctylthiol SAMs prepared on evaporated gold films using (a) procedure A (excluded from light and O_2) and (b) procedure B (exposed to light and O_2). The m/z value of several of the peaks is highlighted to aid reference to the discussion in the text.

is, we believe, due to the instability of the 1-chlorooctylthiolate ion, $\text{Cl}(\text{CH}_2)_8\text{S}^-$, at $m/z = 179$. This ion is not observed in the spectrum of this sample nor does it appear to make a significant contribution to the spectrum of the sample prepared by procedure B, where $m/z = 179$ could arise from fragmentation of 8-chlorooctylsulfonate. This ion clearly fragments to produce Cl^- and a neutral hydrocarbon fragment which remains undetected. The strong Cl^- signal is, therefore, indicative of the presence of $\text{Cl}(\text{CH}_2)_8\text{S}$ at the surface and similarly, the strong SO_3^- feature confirms the presence of $\text{Cl}(\text{CH}_2)_8\text{SO}_3$ in the sample prepared *via* procedure B (exposed to O_2 and light).

NEXAFS measurements also highlight changes in the chemical nature of the SAM–Au interaction on exposure to O_2 and light. Fig. 5 shows NEXAFS spectra of three different SAMs prepared by immersion of pure gold foil in ethanolic solutions of (a) octane-1-thiol, (b) 8-bromooctylsulfide and (c) octane-1,8-dithiol. The first of these was analysed immediately after removal from solution (preparation A) while the last two samples were exposed to the ambient laboratory environment for several hours before analysis (preparation B). Similar to XPS, the energetic position of the S K-level absorption edge is a sensitive indicator of chemical environment, and comparisons with reference compounds¹² allow the assignment of absorption features around 2475 eV and 2483 eV to $\text{S}^{-\text{II}}$ and S^{VI} species, respectively. It is clear that in the case of the octanethiol, prepared *via* procedure A, only $\text{S}^{-\text{II}}$ is evident, consistent with the XPS analysis of a similarly prepared sample of 8-chlorooctylsulfide, shown in Fig. 2(a). In the case of the 8-bromooctylsulfide prepared *via* procedure B,

the NEXAFS in Fig. 5(b) reveals that S is present chiefly as S^{VI} . This tallies with the XPS analysis of Fig. 2(b) in which a significant amount of similarly oxidised S is detected. The octane-1,8-dithiol SAM and the 8-bromooctylsulfide SAM were exposed to O_2 and light for similar periods of time, yet their respective NEXAFS spectra are somewhat different: the former, shown in Fig. 5(b), provides evidence for the co-existence of both $\text{S}^{-\text{II}}$ and S^{VI} species. We attribute the S^{VI} to sulfur at the gold/SAM interface and $\text{S}^{-\text{II}}$ to sulfur at the 'tail' of the adsorbed molecule, *i.e.*, at the SAM/vacuum interface.

Discussion

The data presented allow a direct comparison to be made between SAMs deprived of O_2 and light (procedure A) and those exposed to O_2 and light (procedure B). The XPS spectra recorded at low resolution (Fig. 1) reveal a reduction in the relative atomic concentration of S, Cl and C, which indicates that some desorption of the monolayer has occurred due to exposure to O_2 and light. In addition, the apparent relative increase in the concentration of atomic O suggests that some degree of oxidation has also taken place. This hypothesis is confirmed in the high resolution XPS analysis of the S 2p emission feature (Fig. 2) which provides clear evidence for the oxidation of S from $\text{S}^{-\text{II}}$ to S^{VI} on exposure to light in the presence of O_2 . In this case the oxidation of the 8-chlorooctylsulfide monolayer is not complete since the $\text{S}^{-\text{II}}$ signature of the thiolate species is still observed. The NEXAFS experiment confirms the occurrence of photo-oxidation in the samples exposed to O_2 and light, although

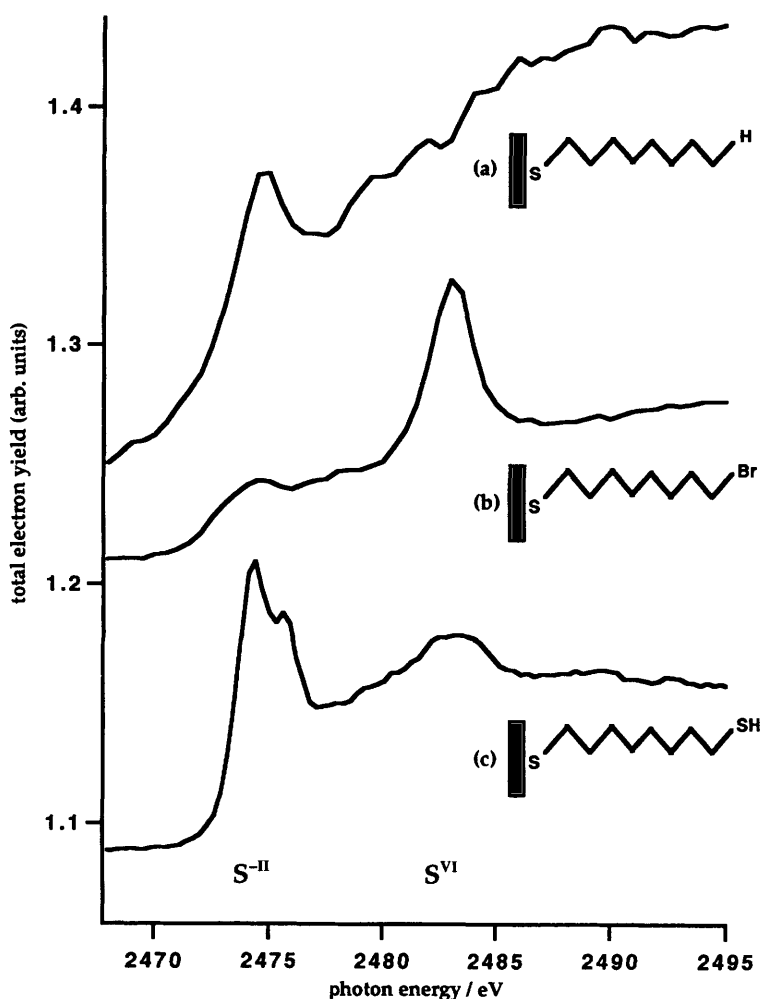


Fig. 5 NEXAFS in the S K-edge region of (a) octane-1-thiol SAM prepared by procedure A, (b) and (c) 8-chlorooctylsulfide SAM and octane-1,8-dithiol SAM, respectively, prepared on gold foils using procedure B (exposed to light and O_2). The accompanying diagrams depict the likely composition of the SAMs following immersion.

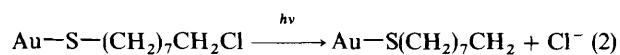
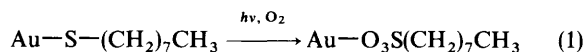
the spectrum of the 8-bromooctylsulfide SAM [Fig. 5(b)] testifies to almost complete oxidation of the SAM in this experiment. Since, after a similar preparation procedure, the octane-1,8-dithiol SAM exhibits both S^{II} and S^{VI} , we conclude that the oxidation of sulfur at the SAM/gold interface in the presence of light, prior to analysis, is mediated by the gold substrate itself.

Photo-oxidation does not cause fragmentation of the adsorbate, according to an examination of the negative ion SIMS analysis of the 8-chlorooctylsulfide SAMs (Fig. 3 and 4). The negative ion fragments observed are consistent with the existence of 8-chlorooctylsulfonate on the gold surface for the SAM which was exposed to O_2 and light but not for the SAM which was excluded from O_2 and light. The spectrum of the latter is consistent with the presence of 8-chlorooctylthiolate, $Cl(CH_2)_8S^-$, which is the likely species formed in the derivatisation. The existence of these species thus explains the appearance of the S^{VI} signature in the XPS and NEXAFS spectra of the photo-oxidised samples and, in addition, the S^{II} feature in the XPS spectrum of the sample excluded from oxygen.

A further striking difference between the SIMS analyses of the two 8-chlorooctylsulfide SAMs is in the intensity of the $^{35}Cl^-$ and $^{37}Cl^-$ signals. The $^{35}Cl^-$ signal from the sample excluded from O_2 and light is a factor of ca. 3.5 greater than that from the exposed or photo-oxidised sample. This difference in chlorine intensity does not appear to be compensated for in the other fragments detected from the oxidised sample. That this represents a genuine reduction in the substrate chloride atom concentration is confirmed in the comparison of the Cl 2p XPS signals from the two samples, which also reveals a reduction in chlorine atom concentration relative to that of sulfur. This suggests that, in addition to the photo-oxidation and partial desorption of the 8-chlorooctylsulfide SAM, photodetachment of the tail-Cl occurs. Since direct photolysis of the C—Cl bond in free chlorocarbons typically occurs around 200 nm,²³ we rule out this process (natural or room lighting has a negligible intensity at this wavelength). The likely explanation is the dissociative attachment of Cl^- by photo-excited or 'hot' electrons from the gold substrate. Using semi-empirical molecular orbital theory we have previously established that the lowest unoccupied molecular orbital (LUMO) of *n*-chloroalkanethiols is sited on the C—Cl moiety, is antibonding in character, and is relatively low lying in energy.¹⁸ We propose that adsorption of the thiol on the gold surface lowers the energy of this LUMO below the vacuum level, thus rendering the orbital energetically accessible to photo-excited but sub-vacuum electrons. When formed, the temporary negative ion has a negative charge residing on the terminal Cl atom, which is spatially separated from its positive image charge at the surface. This allows the dissociating Cl^- ion to escape from the surface.

In summary, we have presented evidence for facile photo-oxidation and photo-reduction in monolayers of 8-chlorooctylsulfide self-assembled on gold. The presence of light with an equivalent energy less than the workfunction of gold is sufficient to promote either process. We conclude that the photo-excitation of hot electrons in the gold is the primary step, followed, in the presence of oxygen, by oxidation at the sulfur/gold interface or dissociative electron attachment (reduction) of chlorine at the monolayer/air interface. In SAMs of 8-chlorooctylsulfide on gold, photo-reduction results in fragmentation of the adsorbate while photo-oxidation yields a weakly adsorbed sulfonate species which is readily desorbed. The processes of photo-oxidation in an

octane-1-thiol SAM and photo-reduction in 1-chlorooctylthiol SAM are summarised in reactions (1) and (2), respectively.



We are currently investigating the detailed mechanisms of these processes through variable-wavelength studies detection of desorbing species and post-irradiative analysis of the gold surface. As a final comment we note that many of the potential applications for SAMs of alkylthiols on gold will rely on the chemical stability of the monolayer. In such cases, care should be taken to avoid exposure of the SAM to oxygen-rich, illuminated conditions.

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