Hydrogen Sulfide-Induced Desorption/Reorganization of Self-Assembled Monolayers of Alkanethiol and Its Derivatives

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Abstract: Self-assembled monolayers of alkanethiolate on gold were shown to desorb or be replaced from the gold surface by exposure to H_2S vapor. Under the same conditions, the desorption occurred faster with shorter chain length thiols than with longer ones. The thiolate moiety desorbed mainly in the form of a free thiol, which underwent various structural reorganizations depending on the chain length as well as the terminal functional group it carries. For nonpolar, methyl-terminated thiols, the assembly either randomized to give a disordered liquid state (for chain length $<$C16) or maintained a well-ordered but physisorbed monolayer state (for chain length $\geq$C18). With polar terminal groups such as hydroxyl, ester, acid, amide and, cyano groups, the desorbed molecules reorganized into discrete clusters of the corresponding thiol compound. The results demonstrate the important role of the terminal functional group at the film−air interface in determining the ultimate structure of a molecular assembly.

Introduction

The self-assembled monolayers (SAMs) of alkanethiol on metal surfaces have been developed into a useful system both for fundamental structural studies of interfacial phenomena as well as technological applications of miniaturized dimensions.[1] An important feature of this system is the robustness of the adsorbed film due to the polar covalent bonding between the sulfur atom and the underlying metal (mainly gold, silver, and copper).[2] Nevertheless, the Au−S bond is not as sturdy as it was generally perceived. For example, it has long been known that the thiolate adsorbate can be exchanged by a second thiol molecule present in a contacting solution.[3] The thiolate can also be removed readily by electrochemical oxidation or reduction.[4] Upon UV irradiation, a much less adhering sulfonate species can be generated.[5] Oxidation by a trace amount of ozone in air to give sulfonate has been the subject of many studies recently.[6,7] The stability of the monolayer film under various environments is certainly an important issue that should be faced.

We reported previously that the structure of a monolayer formed from *n*-alkanoic acid on metal oxide surfaces could be readily perturbed by simple exposure to certain chemical vapor.[8] An interesting structural reorganization was manifested by the *n*-alkanoate monolayer on silver surface. The process is believed to originate from the competition for the silver ion by the chemical agent (for example, HCl or H_2S) so that free *n*-alkanoic acids were released from the surface binding sites and underwent further reorganization. Similar reorganization was found for the thioacid monolayer on gold surface, after ambient hydrolysis of the gold thiocarboxylate group to a carboxyl group and gold sulfide.[9] In all these cases, the ultimate structure of the assembly was determined by the balance of various interactions, including intermolecular interactions, substrate−adsorbate interactions, and the H-bonding of carboxylic acid molecules.

The alkanethiolate on gold surface is generally considered stable and robust because of the strong polar covalent Au−S bond. Nevertheless, it has been noted that a trace amount of sulfide impurity present in the solution can compete with 4-pyridinethiol effectively during the monolayer adsorption of the pyridinethiol onto gold surface and even replace the monolayer completely.[10] It was contemplated that an alkanethiol monolayer may also be vulnerable to a competing hydrogen sulfide vapor at the gold surface. It is of interest to understand the molecular process for the thiolate monolayer under H_2S atmosphere. Here we wish to report the observation of displacement of the alkanethiolate moiety from the gold surface by exposure to H_2S vapor and the reorganization of the monolayer assembly thereafter. It was found that the displacement/reorganization process depends on the chain length of the thiolate involved, as well as the terminal functional group it carries. With polar terminal functional groups such as hydroxyl, ester, acid, amide, and cyano groups, the thiolate moieties desorbed and reorganized into discrete clusters of the corre-

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sponding bulk thiol materials. For nonpolar methyl-terminal thiols, the assembly either randomized to a disordered liquid state (for chain length <C16) or maintained a well-ordered physisorbed monolayer state (for chain length ≥C18), which is similar to that of a physisorbed Langmuir-type film transferred from the air/water interface. The results are rationalized as a minimization of surface energy at the substrate surface.

Experimental Section

Materials. Gold (>99.99%) and chromium (>99.99%) were obtained from Johnson Matthey Company. One-side polished silicon wafers were purchased from Semiconductor Processing Company. Absolute ethanol and GR grade THF were obtained from Merck and used as received. Saturated alkanethiols were obtained from Aldrich. Hydrogen sulfide (99.5+% lecture bottle) was obtained from Aldrich. The thiols 16-mercaptohexadecanoic acid, methyl 16-mercaptohexadecanoate, 16-mercapto-1-hexadecanol, and 16-mercaptohexadecanamide were prepared according to literature procedures.[11,12] 17-Mercaptoheptadecanenitrile was prepared from 16-bromohexadecanol by reacting with sodium cyanide in DMSO. The resulting 17-hydroxyheptadecanenitrile was treated with *p*-toluenesulfonyl chloride and then sodium thioacetate. Hydrolysis of the thioester gave the desired product. Fractional recrystallization gave the 17-mercaptoheptadecanenitrile as a white solid: ^{1}H NMR δ 2.52 (2H, q), 2.34 (2H, t), 1.26 (28H, br s), mp 38−39 °C.

Monolayer Preparation. The gold substrates were prepared by vacuum deposition of ~7 nm of chromium and then 200 nm of gold onto 2-in. silicon wafers under a vacuum of 2×10^{-6} Torr at a rate of ~0.5 nm/s. An ethanolic solution (~1 mM) of each thiol was prepared under ambient condition. A monolayer of respective thiol was prepared by soaking the gold substrate in the solution for at least 4 h before being withdrawn from the solution and rinsed three times with pure ethanol and once with THF then blown dry with a stream of pure nitrogen. The thiol monolayer was subjected to IR or other characterization within 3 h after preparation. No sign of structural change could be detected by reflection−absorption IR during this period of ambient storage.

Exposure Experiment. The film-covered substrate surface was placed in a 1-L chamber and purged with a slow stream of N_2 for 10 min. The H_2S vapor (10 mL) was injected via a syringe to make up a 1% H_2S atmosphere in the chamber. After the sample was exposed for various amounts of time, it was retrieved and characterized directly (as in the case of IR) or soaked in ethanol and THF consecutively before characterization for the presence of the monolayer material.

Electrochemical Studies. All electrochemical studies were carried out using a BAS 100B Electrochemical Analyzer (Bioanalytical System USA). A three-electrode-cell system with a single compartment was used. A 2000 Å gold-coated silicon wafer with ~70 Å chromium as an adhesion layer was used as a working electrode and a platinum spiral wire served as a counter electrode. An Ag/AgCl (3M NaCl) electrode acted as the reference electrode. A 0.5 M KOH solution was used as the supporting electrolyte. Samples were purged with purified argon gas for 10 min before starting the experiments. All potentials were recorded against the Ag/AgCl reference. For electrochemical study, the freshly prepared Au substrates were annealed at 300 °C for 3 h in a muffle furnace followed by treatment with UV irradiation for 1 h to remove organic impurities on the gold surface. After the UV treatment, substrates were washed with ultrapure water and then rinsed with ethanol and dried in a stream of nitrogen prior to monolayer formation. For the H_2S-induced desorption studies, the monolayer-modified Au substrates were exposed to the H_2S for various periods of time and then rinsed with ethanol before the cyclic voltammogram experiments.

X-ray Photoelectron Spectroscopy. The X-ray photoelectron spectroscopy experiments were performed on an Omicon ESCA system with an Al Kα monochromator X-ray source and EA 125 Hemispherical analyzer. The X-ray power suppliers were run at 14 kV and 12 mA at a pressure of 2×10^{-10} mbar. The pass energy of the analyzer was set at 20 eV for sulfur and 50 eV for others. A freshly prepared Au substrate was used as a reference. All peaks were corrected against Au 4f$_{7/2}$ (BE = 84.0 eV). Four elements were collected on each sample: Au, C, S, and O with an acquisition time of 1000, 400, 12000, and 400 s for each respective element. Curve fitting was done with Omicon-Presents using Marquardt-Levenburg method.

Quartz Crystal Microbalance. A SEIKO EG&G quartz crystal analyzer (Model QCA 917) was used to record the mass changes upon adsorption/desorption. The 9 MHz AT-cut quartz crystals (supplied by SEIKO EG&G) with a surface area of 0.3 cm^2 Au electrodes were used for all the studies. The crystals were cleaned for a few seconds with a 1:1 mixture of hot concentrated H_2SO_4 and H_2O_2 (30%) solution, followed by washing with Milli-Q water, THF, and hexane and finally drying in a stream of nitrogen. Monolayers were prepared by immersing the gold-coated quartz crystal in a thiol solution for 1 day and rinsing with ethanol and drying with nitrogen. The H_2S-induced desorption studies were conducted by the ex situ method. The monolayer-modified quartz crystals were placed in an H_2S chamber for different periods of time and the frequency change was measured after the sample was washed with ethanol and THF. The resolution of the frequency change is within ±2 Hz. All experiments were conducted in a closed Faraday cage system to avoid noise and external disturbance.

Reflection−Absorption IR Spectroscopy. Reflection−absorption IR spectra were taken on a Digilab FTS60 Fourier transform IR spectrometer equipped with a liquid nitrogen-cooled MCT detector. Single reflection with a grazing angle of 86° of the incident beam was used. Spectra were taken with p-polarized light. An ozone-cleaned gold wafer was used as the reference sample.

Results and Discussion

The displacement of alkanethiolate from the gold surface by hydrogen sulfide was evidenced by a variety of techniques, which are presented in the following.

Electrochemical Reductive Desorption. It has been established that alkanethiolate can be reductively desorbed from the surface of a gold electrode.[5] The potential at which the adsorbate desorbs depends on the packing as well as the chain length of the thiolate moiety and the pH of the medium. Figure 1 shows the typical reductive wave for a hexadecanethiol monolayer on gold (abbreviated as Au/SC15CH$_3$) at −1.36 V vs Ag/AgCl (3M NaCl) in 0.5 M KOH in the first scan. The sharp peak will shift to lower potential and broaden in successive cycles, due to the partial loss of the thiolate moiety into the electrolyte solution during the desorption−readsorption cycle.[13] In contrast, the cyclic voltammogram of a gold surface exposed to H_2S vapor gave a very sharp reductive desorption wave at −0.88 V. A small anodic peak was observed during the reverse scan. It is noted that a similar reductive peak (−0.9 V) was observed for the Na_2S-treated gold surface, and it was attributed to atomic and/or oligomeric sulfur adlayer.[10] The reduction peak current increases linearly with increasing scan rate, indicating a surface-confined species.[14] When Au/SC15CH$_3$ was exposed to H_2S for various periods of time and rinsed, the cyclic voltammogram showed that a peak around −0.9 V was growing with time, while the peak associated with a closely packed C16 thiolate was lost within the first 2 h of exposure. The peak at around −0.9 V gained its full intensity after exposure to H_2S for around 6 h, together with some broad peaks present between −1.1 and −1.2 V. This clearly suggests the replacement of the long-chain thiol by the small H_2S molecules.

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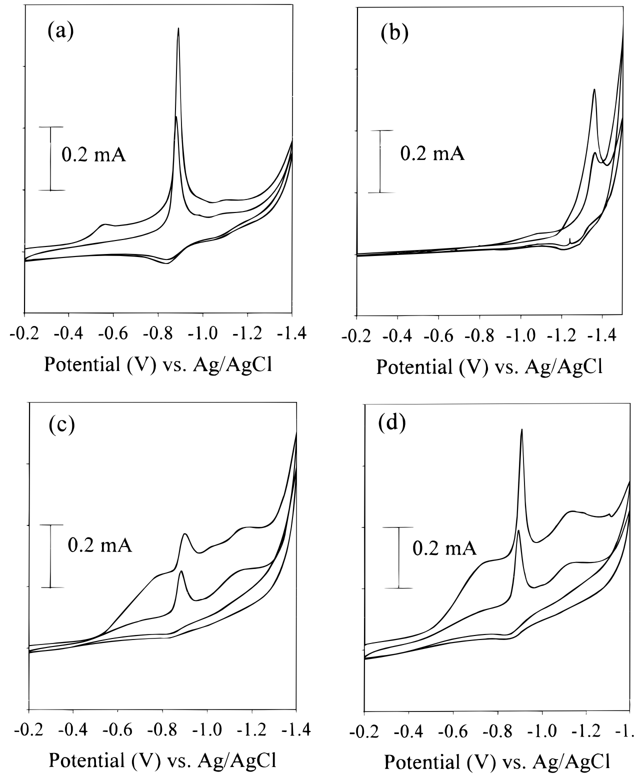

Figure 1. Cyclic voltammogram of (a) H_2S-modified gold, (b) Au/$SC15CH_3$, (c) the monolayer exposed to H_2S for 2 h, and (d) the monolayer exposed to H_2S for 6 h.

Quartz Crystal Microbalance (QCM). QCM provides a convenient way to observe the mass change occurring on the gold/quartz surface as the change of vibration frequency for the oscillating quartz crystal is linearly related to the mass change resulting from the adsorption of other species.[15] Use of QCM to follow the growth kinetics of the monolayer formation of alkanethiol has been documented.[16] In the case of C16 thiol, the monolayer adsorption process is completed within 20 min, shown by a stabilized frequency following a quick drop. Control experiments with bare gold surface exposed to H_2S vapor exhibited a frequency decrease over a much longer period and leveled off only after several hours. The mass increase corresponds to multilayer adsorption of the hydrogen sulfide species on the surface. This agrees with the previous observation that a roughening effect resulted from H_2S exposure.[17] The displacement of alkanethiolate was monitored for SAMs of three different chain length by following the frequency change upon H_2S exposure. A fast *increase* of frequency was noted for all these SAM-covered surfaces after exposure and rinsing with organic solvent. In the case of C12 thiol, the frequency started to decrease again after 2 h. The C16 thiol gave similar behavior only at a later stage. In the case of C20 thiol, the gradual increase of frequency continued after 10 h of exposure. In all cases, the maximum mass loss estimated from the frequency increase is less than that expected for the loss of a full monolyaer. The interpretation of these data has to take into account the fact that the displacement of a long-chain alkanethiol is accompanied by the adsorption of H_2S. In the earlier stage, the mass loss of alkanethiol outweighed the mass gain from the adsorption of the small H_2S molecules and thus a net loss of mass was noted. After much of the long chain has been displaced, net mass increase due to multilayer adsorption of H_2S resumed. From the slope of the curve, it is suggested that the rate of the frequency change and thus the displacement rate decreased in the order of C12 > C16 > C20. The longer chain thiol resisted the displacement more effectively than the shorter chain thiol. This chain length effect is similar to the anticorrosion effect of thiol monolayers against aqueous Br^- ion.[18]

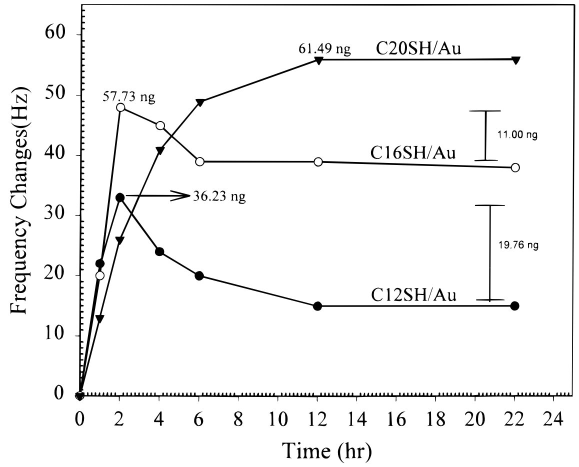

Figure 2. QCM frequency change as a function of the exposure time for the alkanethiol-cover gold surface.

X-ray Photoelectron Spectroscopy. The displacement process for Au/$SC15CH_3$ by H_2S was also examined by XPS spectroscopy. Before being exposed to H_2S, the monolayer gave S(2p) peaks at 161.5 eV for $S(2p_{3/2})$ and 162.8 eV for $S(2p_{1/2})$ respectively in about a 2:1 ratio (Figure 3a), which is in agreement with the reported binding energies of the surface-bound sulfur from alkanethiolate.[19,20] A strong C(1s) peak occurred at 284.7 eV for the alkyl chains (Figure 4a). No O(1s) peak was detected, which indicated the thiolate was the only binding headgroup species. In contrast, the H_2S-exposed bare gold gave a broad and complicated S(2p) region, with two apparent peaks at 161.1 and 162.1 eV (Figure 3c). Deconvolution gave two sets of split peaks, each separated by ~1.2 eV with a 2:1 ratio, which implies more than one sulfur species may be present. This may correlate to a mixture of atomic and/or oligomeric surfur species and sulfhydryl groups, the latter of which was suggested to exist in the H_2S-exposed Au(110) surface.[21] A carbon (1s) peak at 284.0 was found, presumably due to the residue carbonaceous contaminants on the surface (Figure 4c). The higher binding energy for C(1s) for ordered SAM than that of disordered carbon species was also documented.[19] After the SAM surface was exposed to H_2S vapor for 6 h and rinsed with ethanol, the C(1s) shifted to 284.2 eV, a position similar to the C(1s) peak observed for contaminant carbonaceous species, yet the intensity has dropped to a similar level as the H_2S-exposed bare gold surface (Figure 4b). The sulfur region also gave a similar pattern as that of H_2S-exposed

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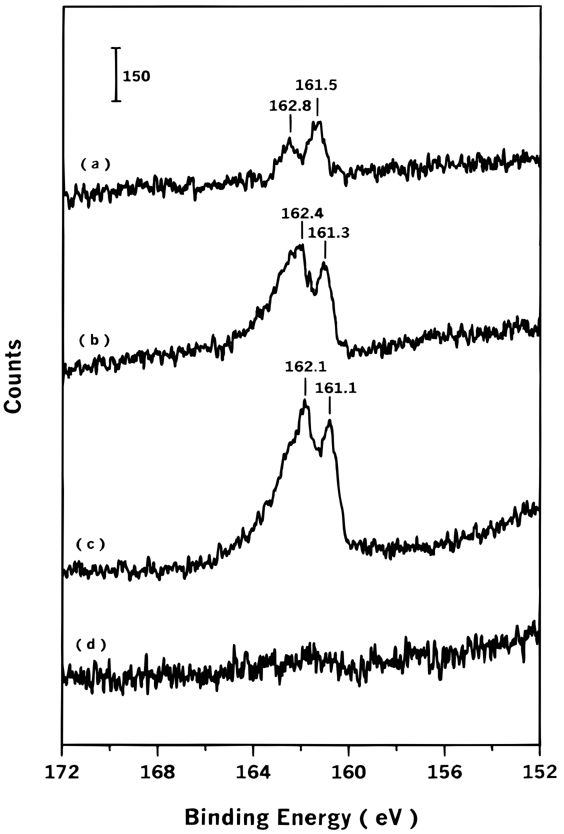

Figure 3. XPS spectra of the C(1s) region of the (a) Au/SC15CH$_3$ monolayer before H$_2$S exposure, (b) after H$_2$S exposure for 6 h, (c) bare gold exposed to H$_2$S, and (d) the bare gold surface.

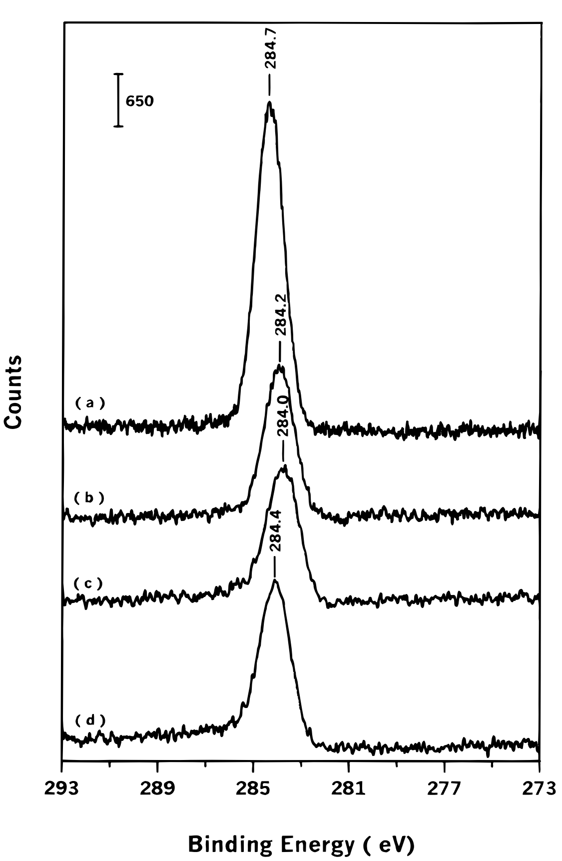

Figure 4. XPS spectra of the S(2p) region of (a) the Au/SC$_{15}$CH$_3$ monolayer before H$_2$S exposure and (b) after H$_2$S exposure for 6 h, (c) the bare gold exposed to H$_2$S, and (d) the bare gold surface.

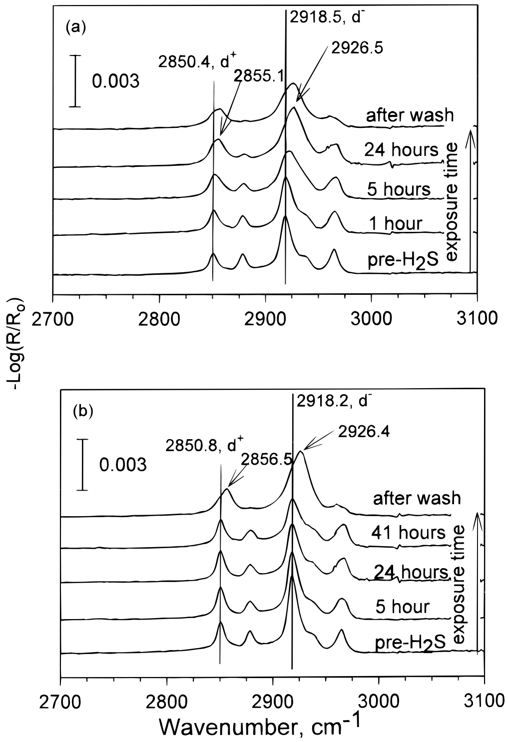

Figure 5. Reflection−absorption IR spectra as a function of H$_2$S-exposure time for the monolayer of (a) Au/SC15CH$_3$ and (b) Au/SC19CH$_3$.

bare gold surface (Figure 3b). It is concluded that the monolayer material was lost after exposure to H$_2$S vapor.

The Reflection Absorption IR Spectroscopy. While the above characterizations require or result in the removal of desorbed species from the surface, the reflection−absorption IR spectroscopy examines the surface *as is* after H$_2$S exposure. It provides rich information regarding the detailed structural change of the assembly upon H$_2$S exposure. Depending on the group exposing at the surface, two types of behavior were observed:

(a) Monolayers with a nonpolar terminal group: Figure 5a shows the spectra for the monolayer of Au/SC15CH$_3$ before and after H$_2$S exposure for various intervals of time. Before the exposure, the vibrational frequencies for CH$_2$ symmetric and asymmetric stretches occurred at 2850.4 and 2818.5 cm^{-1}, respectively, indicative of a densely packed and crystalline assembly of the alkyl chains.[12] With ambient storage, the spectrum and thus the structure is stable to organic solvent wash. However, upon exposure to H$_2$S, the peaks start broadening on the higher side. After several hours, the peaks shifted to 2855.1 and 2926.5 cm^{-1}, respectively, indicating a disordered, liquidlike film has resulted. Washing the surface with organic solvent removed much of the material from the surface, as indicated by ellipsometry measurement. The IR spectrum remained that of a disordered film; nevertheless, the intensities did not decrease by much. It should be noted that in the reflection mode, the peak intensity is highly orientation-dependent.[22] The intensity change is complicated if both the amount and the orientation are changing during the washing process.[23] For C18 and longer thiols, the situation is somewhat different. As shown in Figure 5b for C20 thiol, after exposure to H$_2$S the intensities of the two methylene stretches decreased, but the frequencies very much maintained at the same positions as the starting film. This implies that the film retained a crystalline packing and ordered

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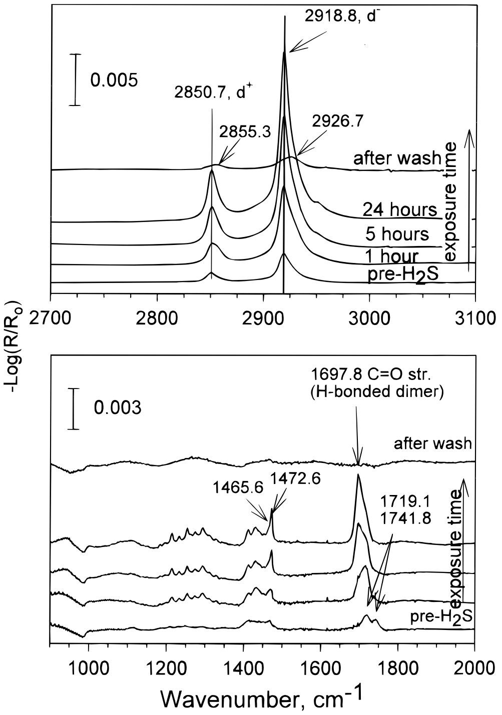

Figure 6. Reflection−absorption IR spectra as a function of H_2S-exposure time for the monolayer of Au/SC15COOH.

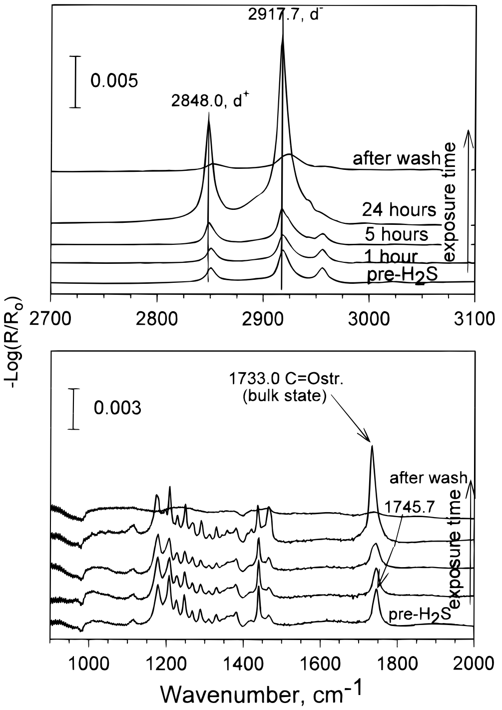

Figure 7. Reflection−absorption IR spectra as a function of H_2S-exposure time for the monolayer of Au/SC15COOCH$_3$.

structure. The decreasing intensity can be attributed to orientational change, with the alkyl chains being even closer to the surface normal.[22] When the film surface was washed with organic solvent, a disordered film resulted as suggested by the frequencies at 2856.5 and 2926.4 cm^{-1}. Material loss is again indicated by ellipsometry measurement.

(b) Monolayer with a polar terminal group: In contrast to the saturated alkanethiols, monolayers carrying a polar terminal group gave quite different results. For example, the result of a monolayer of 16-mercaptohexadecanoic acid (Au/SC15COOH) is shown in Figure 6. The film before H_2S exposure gave the expected spectrum, with the carbonyl stretch occurring at 1719.1 and 1741.8 cm^{-1}, representing the hydrogen-bonded and isolated carbonyl group, respectively.[12] The C−H stretches occur at 2850.7 and 2918.8 cm^{-1}, respectively, indicative of a well-ordered packing of the chains. Upon exposure to H_2S, the peaks for the C−H stretches broaden toward the higher side in the beginning but then narrow down again, with the peak position maintained around 2919 cm^{-1} and intensities growing substantially with time. The absorption for the carbonyl group also grew and shifted to a single peak at around 1697.8 cm^{-1}, which is assigned as the carbonyl stretch for the H-bonded dimer of carboxylic acid.[24] Also growing in intensities are the deformation bands for CH$_2$ at 1472.6 and 1465.6 cm^{-1} and a series of "progressional bands" between 1300 and 1150 cm^{-1}. These peak positions virtually match with the peak positions of the KBr transmission spectrum of the bulk sample of the original 16-mercaptohexadecanoic acid. The assembly was apparently physisorbed as the material on the surface can be readily removed now by organic solvent. Acid-terminated thiols of different chain length (C12 and C20) gave similar spectral change, except that the time required to reach the ultimate spectrum varied. With C12 acid, the spectrum after 1 h of exposure is similar to that after 24 h, implying the desorption process may have completed in a rather short period (1−2 h), while for C20 acid, the spectra kept changing even after 20 h of exposure.

The dramatic spectral change was reminiscent of the spectral change when a SAM of *n*-alkanoic acid on Ag was exposed to HCl or H_2S vapor.[8] In those cases, the adsorbed carboxylate molecules were believed to be protonated and released from the specific surface sites and reorganized into discrete, hydrogen-bonded dimer crystallites, all resulting from a competition for silver ion by the HCl or H_2S. The dramatic increase in the intensities of methylene stretching modes was due to a preferential orientation of the chain axis of the crystallites to be parallel to the surface.[8] The similar observation seen here implied that the carboxyl-terminated thiol underwent similar desorption/aggregation as happened on the acid/silver surface.

Other SAMs with polar terminal functional groups, such as ester, amide, cyano, and hydroxyl, gave similar spectra changes upon H_2S exposure, i.e., a substantial increase in the C−H stretch intensities with peak frequencies characteristic of crystalline chain packing. Although these polar functional groups do not form dimeric forms such as that of the carboxyl group, analysis of the IR spectra also indicates that the polar end group has experienced a change in the local environment, from that in an isolated environment to that in a bulk material. For example, Figure 7 shows the spectral change of methoxycarbonyl-terminated monolayer upon exposure to H_2S. The ν(C═O) for the ester group in the monolayer occurs at 1745.7 cm^{-1}, 13 wavenumbers higher than that observed for bulk crystals of the parent compound. This has been attributed to the fact that the ester functionality is exposed to ambient in the oriented monolayer.[25] Groups in such an environment are surrounded by fewer neighboring groups, while after exposure

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(23) In fact, a bare gold surface went through similar H_2S exposure and solvent wash yielded a similar spectrum, presumably due to the tenaciously bound contaminant. Thus it is not possible to assess quantitatively the loss of material from the IR spectra.

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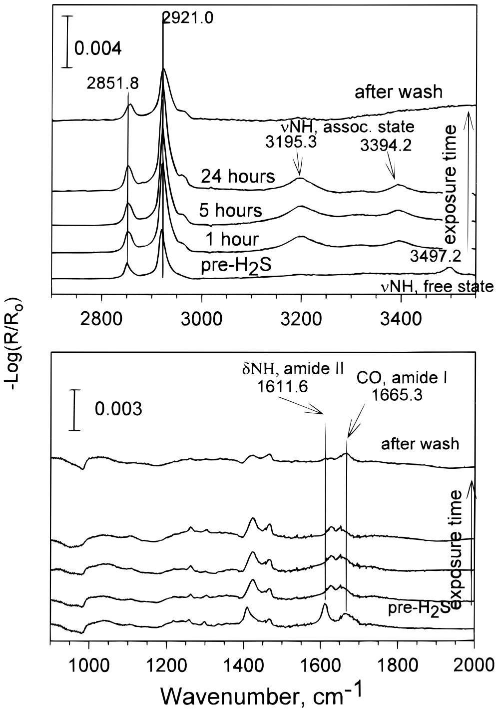

Figure 8. Reflection−absorption IR spectra as a function of H_2S-exposure time for the monolayer of Au/SC15CONH$_2$.

to H_2S the ν(C═O) shifted to 1733.0 cm^{-1}, the same as the carbonyl stretch frequency in bulk sample. This implies the ester group is in the local environment of a bulk state. In conjunction with the intensity change and crystalline-like peak positions (2917.7 and 2848.0 cm^{-1} for ν_a(CH$_2$) and ν_s(CH$_2$), respectively) of the methylene vibration modes, formation of discrete crystallites of bulk material is suggested. Again, all of these characteristic peaks were lost after solvent wash, apparently due to the loss of film materials by washing. Figure 8 shows the spectral change of amide-terminated alkanethiol monolayer Au/SC15CONH$_2$. The ν(NH) for the terminal amide group changed from 3497.2 cm^{-1} for the free state to 3394.2 and 3195.3 cm^{-1} for the associated state. Shifts in amide I and II bands in the 1600−1700 cm^{-1} region (smaller separation of the two bands in the associated state compare to the wider separation in the isolated state) lead to the same suggestion that the amide functional group experienced a local environment change from that of the interfacial state to that of a bulk state.[24] Substantial increase of the methylene intensities again implied molecular chains lying closer to the surface. The IR spectra for Au/SC16OH and Au/SC16CN are shown in Figures 9 and 10. Substantial growth of methylene intensity was also observed.

On the basis of the above results, we propose that the alkanethiolate moiety was displaced by H_2S from the surface and then reorganize according to the nature of the end group and chain length. The observation that a small H_2S molecule can displace long-chain alkanethiolate is interesting. The concentration effect (large excess of H_2S present) should not be the major reason. It has been known that the monolayer of a long-chain thiol is more stable than that of the shorter chain thiol, which is reflected by the reduction desorption potentials. The potential required to desorb alkanethiolate shifted from −0.77 V for ethanethiolate to −1.36 V for hexadecanethiolate. The more negative potential is due to the contribution of the van der Waals interaction of the alkyl chain. However, it is noted that the reductive desorption potential for the sulfide species resulting from H_2S is around −0.89 V, more negative than that of the short ethanethiolate. This would suggest the binding of the sulfide species is intrinsically stronger than that of an alkylthiolate.

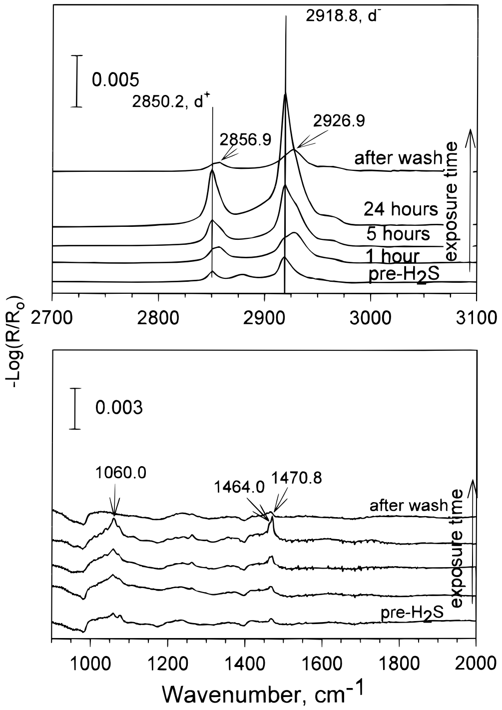

Figure 9. Reflection−absorption IR spectra as a function of H_2S-exposure time for the monolayer of Au/SC16OH.

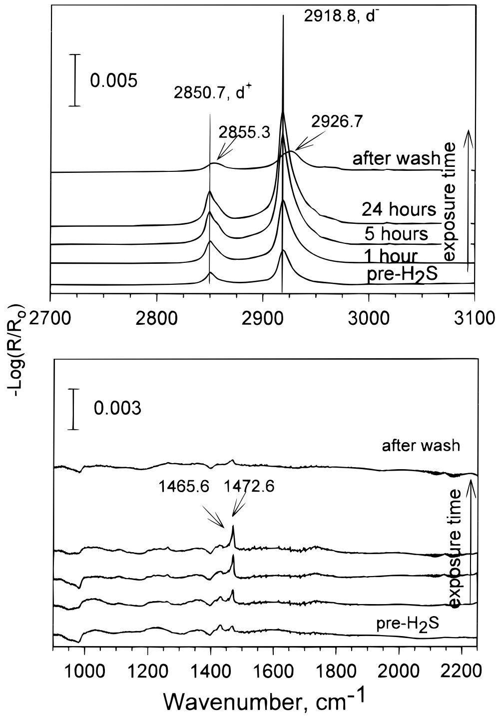

Figure 10. Reflection−absorption IR spectra as a function of H_2S-exposure time for the monolayer of Au/SC16CN.

In the exchange study of alkanethiolate by another alkanethiol in solution, it was suggested that the exchange start from defect sites and there are sites that are not exchangeable and sites that are exchangeable.[3b,c] Disulfide was implied, but not rigorously proven, to be the form desorbed under exchange conditions.[26]

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(26) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528−12536.

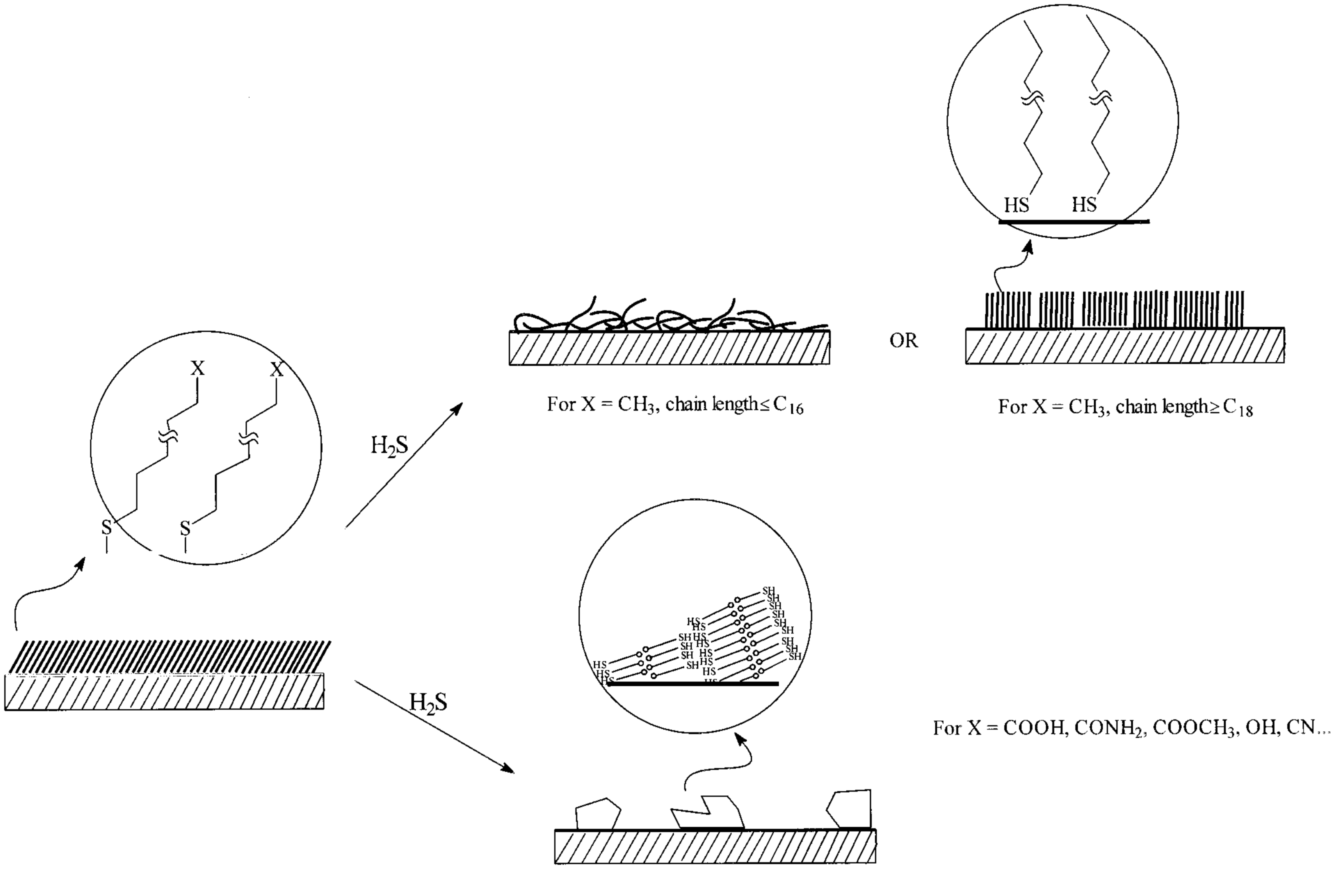

Figure 11. Schematic representation of reorganization of the self-assembled monolayer of alkanethiol derivatives as induced by H_2S exposure.

In the current case, we found from XPS data that most of the thiolate can be desorbed by H_2S. To delineate the form for which thiolate is desorbed, we used the closely related system, the SAM-capped gold nanoparticles,[27] which allows the use of NMR spectroscopy to characterize the product. Close analogy in structure between the SAM on a gold nanoparticle surface and on a planar surface was suggested.[28] Thus a similar exposure experiment was carried out on the C16 thiol-covered nanoparticle system. After H_2S exposure, the nanoparticles were washed with $CDCl_3$ and filtered. The organic filtrate collected was analyzed by the NMR technique. The NMR results[29] indicated that the alkanethiol was the major component released from the surface, together with disulfide as a minor product. It is noted that a similar conclusion was made when the place-exchange reaction was carried out on a nanoparticle system.[30] Thus the following reaction is implied

$$\mathrm{AuSR(s)} + \mathrm{H_2S(g)} \rightarrow \mathrm{AuSH(s)} + \mathrm{RSH}$$

where s means a surface adsorption site.

More interesting is the fate of the assembly after desorption. An overall picture is shown in Figure 11. Before desorption, the thiol molecules were pinned on the surface via a strong covalent Au−S bond, which dictates the spacing of the headgroups. The chain−chain interaction provides the driving force for a well-ordered packing of the assembly. The end groups constitute the third contributing interaction. For nonpolar end groups, such as methyl, a low interfacial energy is implied whereas for polar end groups, the interfacial energy will be higher. When the molecules are replaced by H_2S, the strong pinning interaction no longer exists. The system is open to a new equilibrium state. Here the end groups apparently become a determining factor. For all systems carrying a polar functional group, the assembly undergoes a de-wetting type of reorganization to give discrete crystallites, the size of which is determined by the mobility of the molecule and the intermolecular forces. In the case of nonpolar end group such as methyl, chain length and thus the interchain interaction is the prevailing factor. With C16 and shorter chains, a liquidlike disordered film was obtained, reflecting the physical state of the parent molecule. There is no strong enough interaction to sustain a well-ordered packing. For C18 and longer chains, the oriented monolayer state is still the most favorable state. Without a strong pinning to specific binding site, an even more perpendicular alignment of the chains and thus higher interchain interaction is implied by the lower intensity yet crystalline-like IR characteristics. Such is also the most favored orientation by calculation.[31] Thus the chemisorbed monolayer literally changed into a physisorbed, Langmuir-type monolayer. The tendency for various functionalized monolayers to reorganize can also be understood in terms of optimization in interfacial energy. Those monolayers exposing the polar terminal functional group have a higher surface free energy. If the molecules are released from the binding sites, a

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(27) (a) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802. (b) Hostetler, M. J.; Wingate, J. E.; Zhong, C. J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, G. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14,* 17−30.

(28) Terrill R. H.; Postlethwaite, T. A.; Chen, C. H.; Poon, C. D.; Terzis, A.; Chen, A.; Hudchison, J. E.; Clark, M. R.; Wignall, G.; Londono, J. D.; Superfine, R.; Falvo, M.; Johnson, C. S., Jr.; Samulski, E. T.; Murray, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 12537−12547.

(29) A quartet at δ 2.50 was assigned as the CH_2 next to the SH of the thiol whereas a triplet at δ 2.66 was assigned as the CH_2 next to the S−S of a disulfide. The two sets of signals exist in a ratio of ∼8:2.

(30) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782−3789.

(31) Ulman, A.; Eilers, J. E.; Tillman, N. *Langmuir* **1989**, *5*, 1147−1152.

lower free energy state is achieved by having the molecules reorganizing into bulk material, where the polar end groups are buried in the bulk, a phenomena suggested to occur even in the covalently attached state of a self-assembled monolayer upon ambient storage.[32] Attempts to image the reorganization process by AFM have not been successful, presumably due to the inherent rough morphology of polycrystalline substrate used in the study. One may argue the role of the roughened surface on the structure. It is contended that the roughened surface might influence the kinetics of a surface reaction.[33] Our conclusion on the structure change was drawn mainly from thermodynamic considerations and should hold irrespective of how fast it is attained.

Conclusion

In summary, it is shown that the self-assembled monolayer of alkanethiol derivatives on gold can be displaced from the surface by exposure to H_2S vapor. The process requires the H_2S to penetrate down to the metal surface and thus exhibit a chain length effect, where a longer chain provides better protection against the attack. The desorbed molecules seek a new equilibrium structure, which very much depends on the terminal functional group. With polar end groups such as carboxyl, ester, amide, and hydroxyl groups, a reorganization of the assembly into discrete but bulk-like clusters is suggested. This can be seen as a process of minimization of surface energy, such that the polar group can be removed from the very outer surface. With a nonpolar end group such as the methyl group, the oriented assembly is still the favored structure given enough chain length.

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(32) Evans, S. D.; Sharma, R.; Ulman, A. *Langmuir* **1991**, *7*, 156−161.

(33) For example, the rate of oxidation of alkanethiolate by ozone depends on the roughness of the gold surface: Lee, M. T.; Hsueh, C. C.; Freund, M. S.; Ferguson, G. S. *Langmuir* **1998**, *14*, 6419−6423. The growth rate of polymethylene on Au depends on the roughness of gold: Seshadri, K.; Sundar, V. A.; Tao, Y. T.; Lee, M. T.; Allara, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 4698−4711.