Assembly of Covalently-Coupled Disulfide Multilayers on Gold

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Abstract: We report on the spontaneous organization of up to eight covalently attached layers formed on gold from solution phase (α,ω)-dithiols 1,6-hexanedithiol (C_6), 1,8-octanedithiol (C_8), and 1,9-nonanedithiol (C_9). The linking chemistry between layers is the oxidative formation of a sulfur−sulfur bond that competes successfully with intralayer S−S bond formation. We have used optical null ellipsometry, FTIR, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV) to characterize the multilayers. Once formed, the multilayers are stable when washed with 1 M KCl, water, ethanol, $CHCl_3$ and *n*-hexane solutions, before and after prolonged exposure to ambient laboratory conditions. In addition to the formation of multilayers, our data point to the efficient oxidation of the interlayer disulfide bond to an oxidized sulfur moiety where the S−S bond remains intact. Extensive oxidation produces a sulfonate-terminated surface that reacts with Zr^{4+} and alkanebisphosphonates to form a hybrid multilayer assembly.

Introduction

Alkanethiol/gold self-assembled monolayers (SAMs) are a highly reproducible and well-characterized model system for understanding organic monolayer interfaces.[1,2] Much of the pioneering work on the synthesis and macroscopic characterization of these SAMs was done in the 1980s by Whitesides, Nuzzo, and Allara.[3−28] External reflection FTIR spectroscopy has been used extensively to study SAMs, and from these measurements we know that, for long alkanethiols (>10 carbons), the predominantly all-trans chains are oriented at ~30° with respect to the surface normal.[16,25] This organization was shown to decrease only for short chain alkanethiols, where interchain interactions were insufficient to induce macroscopic ordering. Surface wetting studies showed that the polar character of the interfaces depends on the chemical identity of the organic terminus of the surface modifier. Polar-capped modifiers produce hydrophilic surfaces while alkanethiol surfaces are hydrophobic. Helium diffraction studies of these SAMs indicate that the organization intrinsic to the substrate is carried through to the ends of the aliphatic chains.[26−28] More recently, a wealth of atomic microscopy measurements (STM, AFM) have shown that the thiol sulfur headgroups adsorb in a pattern related directly to the structure of the gold substrate, and that the monolayer exhibits large scale structural change over several minutes.[29−40] Our recent thermodynamic data

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indicate that the labile nature of the SAM is a direct consequence of the small free energy of adsorption for these systems,[41,42] and this finding, based on gravimetry, is in excellent agreement with the relevant electrochemical data.[43] In more recent years, there have developed many potential applications for SAMs including lithography, contact printing, corrosion resistance, and biotechnology.[44] We are able to use this considerable body of knowledge to understand the formation of the multilayers we report here.

The wealth of information on SAMs and their intrinsic high degree of ordering make them an appealing starting point for more complicated chemical structures. Despite their desirable features, perhaps the most significant limitation of SAMs is their inability to form robust, covalent multilayer structures without the use of reaction schemes requiring several steps to form each layer.[45] While there have been several reports of multilayer formation of thiols on gold, the layers are thought to be physisorbed upon one another and not bonded covalently.[46,47] There is passing reference in the literature to the formation of dithiols into layered assemblies,[48,49] but we are not aware of any detailed reports on the formation of covalent multilayers directly from dithiols on a gold substrate. We report here on the synthesis and characterization of covalent multilayers formed on gold from the (α,ω)-dithiols 1,6-hexanedithiol (C_6), 1,8-octanedithiol (C_8), and 1,9-nonanedithiol (C_9), from ethanol and hexane solutions. The linking chemistry between layers is the oxidative formation of a S−S bond, and this process competes successfully with intralayer S−S bond formation. We do not find evidence for "looping" where both thiol termini bond to the gold substrate. The simple synthetic route we report here is reminiscent of the metal−phosphonate (MP) chemistry pioneered by the Mallouk,[50−55] Thompson,[56,57] and Katz groups[58−63] and the cobalt−isocyanide chemistry developed by the Page group,[64] except our approach is to use direct covalent chemistry without a metal coordination center. In addition to the formation of multilayers, our data indicate efficient oxidation of the S−S and SH groups within the layers to a family of oxidized sulfur moieties. We consider the various forms of oxidized sulfur that can be expected for this structural motif. Our findings are consistent with recent reports on the facile ozone-mediated oxidation of thiols[65−67] and offer a potential new route to the formation of sulfonate-terminated surfaces. We have shown that for oxidized multilayer surfaces, it is possible to grow additional layers using metal ion coordination chemistry. This growth can occur only when the terminal functionality is a sulfonate. The S−S bonds within the multilayers appear to "protect" the Au−S bond from oxidative attack based on photolysis experiments we report here.

Experimental Section

Substrates and Reagents. The gold slides used as substrates were made by evaporation of 200 nm of Au on 20 nm of Ti on Si(100) wafers.[68] 1,6-Hexanedithiol, 1,8-octanedithiol, and 1,9-nonanedithiol were purchased from Aldrich Chemical Co. and used as received. The multilayers were formed on gold by immersing the substrate in a 10 mM ethanolic solution of the dithiol at 20 ± 1 °C for 12 h or in a 1 mM solution of the dithiol in *n*-hexane for 1 h at the same temperature. Immersion for longer periods produced more than one statistical layer for synthesis from ethanol solution, as measured ellipsometrically. Solutions were purged with dry N_2 and the multilayer interfaces were stored either in air or under dry N_2 and covered with aluminum foil to minimize their exposure to UV light.[65]

Optical Null Ellipsometry. Layer thicknesses were measured by using optical null ellipsometry. The instrument is a Rudolph Auto-EL II equipped with a He−Ne laser light source operating at 632.8 nm. The software used for data acquisition and reduction is from Rudolph. For all measurements, the layer refractive index was assumed to be $\mathbf{n} = 1.45 + 0i$. For thin films such as these, the dependence of the recovered thickness on the real part of the refractive index is modest for physically realistic values of $\mathbf{n}$.

Infrared Spectroscopy. The vibrational spectroscopic response of the multilayers was characterized with a Nicolet Magna 550 FTIR spectrometer. Resonances in the C−H and S=O stretching regions were measured by using a Harrick grazing incidence attachment with a beam incidence angle of ~80° with respect to the sample surface normal. Spectral resolution for all measurements was 2 cm^{-1}.

X-ray Photoelectron Spectroscopy. XPS measurements were made on multilayer samples with a PHI Model 5400 X-ray spectrometer. The X-ray source is the Al Kα line and all values reported are referenced to the C1s line at 285.0 eV.

Electrochemistry. Cyclic voltammograms were recorded by using a standard three-electrode cell containing an Ag/AgCl (3 M KCl) reference electrode and a Pt-wire counter-electrode. The working electrode was the gold-coated substrate used in the synthesis of the multilayer, mounted in a sealed plastic holder. The exposed area of the gold substrate/multilayer was 0.1 cm^2. A CH-Instruments electrochemical analyzer was used to perform the cyclic voltammetry (CV) measurements.[68]

Photolysis. Multilayer samples were photolyzed with a Hg lamp in the presence of air or N_2 in an optically isolated mount. The Hg light source produces UV output with an intensity of 4.5 mW/cm^2 (all

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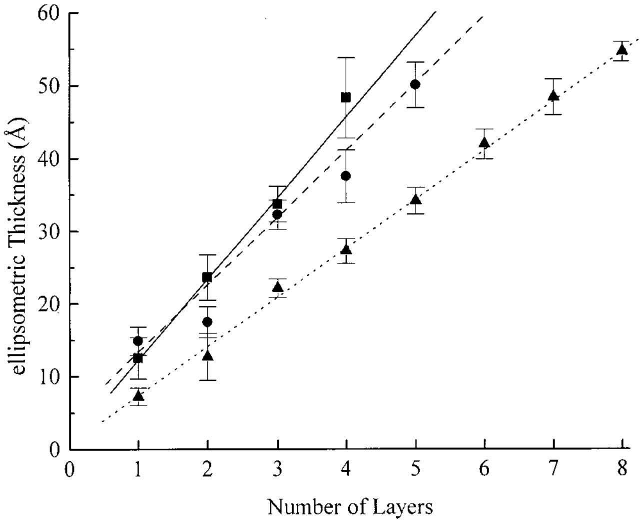

Figure 1. Ellipsometric thicknesses of multilayers of 1,6-hexanedithiol (▲), 1,8-octanedithiol (●), and 1,9-nonanedithiol (■). For all cases, the thickness depends linearly on the exposure time to dithiol solution. Slopes for these dependencies are 7 Å/layer for C_6, 8.9 Å/layer for C_8, and 10.8 Å/layer for C_9.

lines). The samples were mounted 45 mm from the lamp for all photolysis experiments.

Results and Discussion

The primary issues we focus on in this paper are the formation of multilayer structures using (α,ω)-dithiols, determining the nature and chemical speciation of the interlayer bonding, and the response of these layers to exposure to selected solvents and UV light. It is important to note that, when we discuss multilayer assemblies in the context of these materials, we are not referring to the discrete deposition of individual uniform layers at a given point in time. Rather, because of the interlayer linking chemistry used in the synthesis of these assemblies, the growth is statistical, and the thickness measurements represent an average of a given number of layers in the area illuminated by the ellipsometer beam.

Optical null ellipsometry is a useful method for the characterization of these multilayers. The slope of the best-fit line through the ellipsometric thickness data yields an average thickness of 7 Å per layer for C_6, 8.9 Å per layer for C_8, and 10.8 Å per layer for C_9 (Figure 1). Molecular mechanics calculations predict lengths of 9.3, 11.8, and 13.0 Å for all-trans C_6, C_8, and C_9, respectively. With the assumption of a 30° tilt angle, we predict an 8 Å layer thickness for C_6, 10.2 Å for C_8, and 11.3 Å for C_9. It may be tempting to relate any small differences between calculation and experimental results to slight variations in the average tilt angle. Because we have not determined the fractional coverage of the surface and we know that multilayer growth does occur for these systems, it is not possible to distinguish between tilt angle and surface coverage contributions to the ellipsometric data. This limitation, in addition to the good agreement between experiment and calculation, precludes our ability to discern any even−odd effect, which was the initial reason for our use of C_6, C_8, and C_9. The regular growth of these layers argues strongly against significant "looping" of dithiols on the gold surface and against efficient intralayer S−S bond formation between neighbors. The uncertainties in the ellipsometric readings are significant relative to the absolute values (Figure 1), consistent with the formation of regions containing different numbers of adlayers. Such heterogeneity is an unavoidable consequence of the statistical nature of this polymerization chemistry and the extended immersion times required to form these structures. Our ellipsometric data demonstrate the formation of multiple layers of dithiol. We are interested in understanding the nature and chemical speciation of the interlayer bonds and, indeed, whether they exist. To address these points, we offer two bodies of data. The first is wet chemical data in concert with ellipsometry to determine the susceptibility of the multilayers to solvent attack. Significant solubility would imply the absence of covalent interlayer bonding. The second body of data is focused on understanding the chemical identities of the interlayer linking functionalities. This information is provided by XPS measurements. We discuss these bodies of information separately.

To establish whether layer constituents are bound to adjacent layers covalently or are physisorbed, we have performed a series of washing experiments. The experimental procedure was to measure the thickness of the multilayer assembly ellipsometrically, immerse it in a solution for a specific period of time (typically 1 h), remove, rinse, and dry the sample, and take an ellipsometric measurement of the thickness. The solutions used for these experiments were neat *n*-hexane, absolute ethanol, and 1 M KCl(aq). These solutions were chosen because they represent nonpolar, polar, and ionic solvating systems. For all experiments, we observed no change in the ellipsometric thickness of the multilayer, indicating that the interlayer bonding is covalent and not physical. This is a physically reasonable conclusion based on the strength of hydrogen-bonding interactions that characterize thiols. The reported value of dimer formation in H_2S is 1.7−1.8 kcal/mol.[69,70] van der Waals interactions are unlikely to be sufficiently strong to account for our findings either, and it would be difficult to envision a layered structure dominated by these interactions given the orientation of the initial layer, assuming it to be the same as that of alkanethiols on gold.

With the covalent nature of the interlayer bonding supported by the washing studies, we consider the chemical speciation of that bonding, to the extent that such information can be obtained. X-ray photoelectron spectroscopy (XPS) is sufficiently sensitive for this purpose and this technique provides significant information on the oxidation state(s) of the adsorbed species. We show in Table 1 the relative concentrations of the elements present in the substrate and interface. Before describing these results, we offer a few cautions on the interpretation of XPS data. The atomic composition determined experimentally is sensitive to the energy of the incident X-ray beam, variations in photoionization cross-section with chemical structure, the takeoff angle, the elemental distribution perpendicular to the surface, and the actual composition and density of the monolayer. Thus elemental composition derived from XPS is, at best, semiquantitative.[71,72] Experimentally, because we use the same conditions for all measurements, our results vary little but the band ratios offer the best comparisons between samples. By comparing selected ratios for multilayers exposed to different experimental conditions such as UV light or air, it is possible to examine the effect of synthesis and sample treatment on the extent of S−S group oxidation.

To establish the susceptibility of these multilayers to oxidation, we have investigated changes in formed layers as a function

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Table 1. Element Composition

sample	Au4f (%)	C1s (%)	O1s (%)	S2p (%)	C1s/Au4f	C1s/S2p	C1s/O1s	O1s/S2p	S_r/S_o[a]
2 layers C_6 (16 Å, 2 weeks old)	27.1	56.0	12.0	4.8	2.1	11.7	4.7	2.5	1.5
6 layers C_6 (42 Å, 2 weeks old)	10.7	60.6	20.0	8.7	5.7	7.0	3.0	2.4	5.3
7 layers C_6 (48 Å, relatively fresh)	8.5	66.5	18.6	6.4	7.8	10.4	3.6	2.9	8.3
7 layers C_6 (45 Å, 2 weeks old)	9.6	60.0	22.8	7.6	6.2	7.9	2.6	3.0	3.3
4 layers C_9 (42 Å, air)	13.3	68.0	9.4	8.5	5.1	8.0	7.2	1.1	6.4
3 layers C_9 (34 Å, N_2)	14.6	66.3	11.4	7.7	4.5	8.6	5.8	1.5	6.2
3 layers C_8 (photolysis, 11 Å, air)	28.4	54.1	13.7	3.9	1.9	13.9	4.0	3.5	1.6
3 layers C_8 (photolysis, 10 Å, N_2)	22.9	59.2	13.0	5.3	2.9	11.2	4.6	2.5	1.5

[a] S_r/S_o represents the ratio of the sum of the areas of the reduced form of sulfur having peaks at 161.7 and 163.6 eV to the oxidized form of sulfur with a peak at 168.3 eV. All the peak positions are referenced to a C1s binding energy of 285.0 eV.

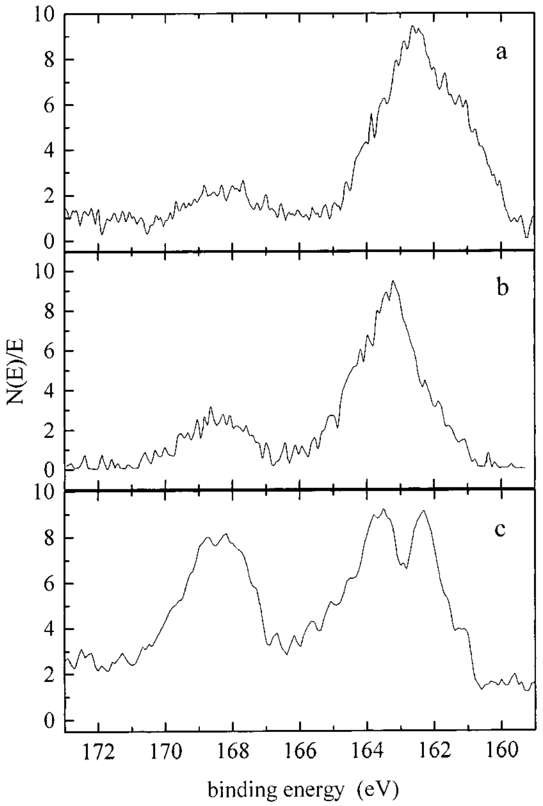

Figure 2. XPS data in the S2p region for films. All values are referenced to the C1s line at 285.0 eV. (a) 7-layer C_6 film measured immediately after formation, (b) 7 layer C_6 film exposed to air for 2 weeks, (c) 10 Å thick C_8 film following UV irradiation in an N_2 atmosphere.

of exposure to both air and light (Table 1). The most notable feature in these spectra is the dependence of the S2p resonances on sample history (Figure 2). These data show the progressive oxidation of the S−S functionalities. For fresh multilayer samples, we observe the dominant S2p resonance to be at 163.6 eV with a weak sideband at 161.7 eV (Figure 2a). The 163.6 eV resonance is associated with gold-bound thiolate and interlayer disulfide bonds. There is not sufficient spectral resolution with the system we used to distinguish the contributions from these two forms of sulfur. The 161.7 eV band is known to arise from gold-bound thiolate at a site that is inequivalent to the 163.6 eV thiolate.[73−75] The reported S2p chemical shifts of a thiolate in alkanethiol SAM on gold,[46] docosanethiol,[76] didocosyl disulfide,[76] and sulfonate[77] are 161.7, 163.6, 163.3, and 168.3, respectively. Figure 2b shows the S2p region of a seven-layer C_6 film on a gold substrate. In addition to the thiolate peaks at 163.6 and 161.7 eV, we find an additional peak at ∼168.3 eV that is seen only after exposure to air. Exposure to air causes slow oxidation with time, and even after 2 weeks of exposure (Figure 2b), there remains a significant amount of reduced S at 163.6 eV. The data in Figure 2c, showing the effect of exposure to UV light, demonstrate that the oxidation of the S−S moiety is, at the very least, assisted by UV light. These findings are consistent with the work of the Pemberton,[67] Bohn,[65] and Rowlen[66] groups on the oxidative attack of the Au−S bond by O_3. It is likely that photoproduced O_3 is the dominant oxidizer in our work as well, although the details of the photodegradation of the multilayers point to the initial photolysis of the S−S bond (vide infra). The photolysis data indicate a reduction in multilayer thickness for photolysis in N_2 and in air. What remains unresolved from the ellipsometric data is whether the dominant process is oxidative Au−S bond cleavage and subsequent desorption or S−S bond cleavage within the assembly. We discuss these data in more detail below.

The oxygen concentration in the multilayers, as measured by XPS, increases after exposure to air for extended periods. For example, maintaining a seven-layered gold substrate in laboratory conditions for about 2 weeks, the C1s/O1s ratio decreased from 3.6 to 2.6 (Table 1). Thiols on gold are oxidizable to some types of SO_x species.[65−67,78] The S_r/S_o ratio reduces significantly from a value of 8.3 to 3.3 for a 7-layer C_6 film after keeping the sample in ambient laboratory conditions for 2 weeks. Despite this oxidation, these films are stable with respect to washing in polar, nonpolar, and ionic solutions.

It is important to consider the R−S−S−R moiety in more detail. Organosulfur compounds are known to exist in a variety of different oxidation states.[79−82] Most experiments on organosulfur systems focus on either the fully reduced thiol or the fully oxidized sulfonate forms. The initial step in the interlayer bonding chemistry we report here is the oxidation of two thiols to form a disulfide, and our time-resolved experiments on the growth of these layers point to the need of an oxidizer to allow the reaction to proceed. Specifically, for growth from *n*-hexane, a single layer forms within minutes, and is stable in solution despite the presence of excess dithiol. Once the substrate is removed from solution, exposed to air, and reintroduced to the solution, another layer forms and remains stable. This same

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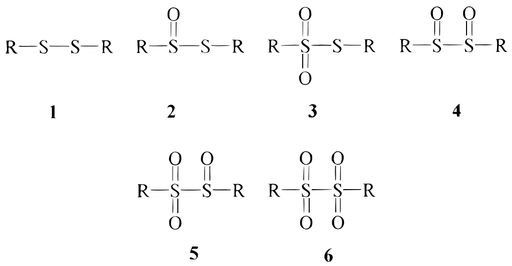
Chart 1. Structures of Various Disulfide Derivatives that May Be Present within the Multilayers[a]



[a] **1**, disulfides; **2**, thiosulfinates; **3**, thiosulfonates; **4**, α-disulfoxides; **5**, sulfinyl sulfones; and **6**, *vic*-disulfones. All species are known except **4**.

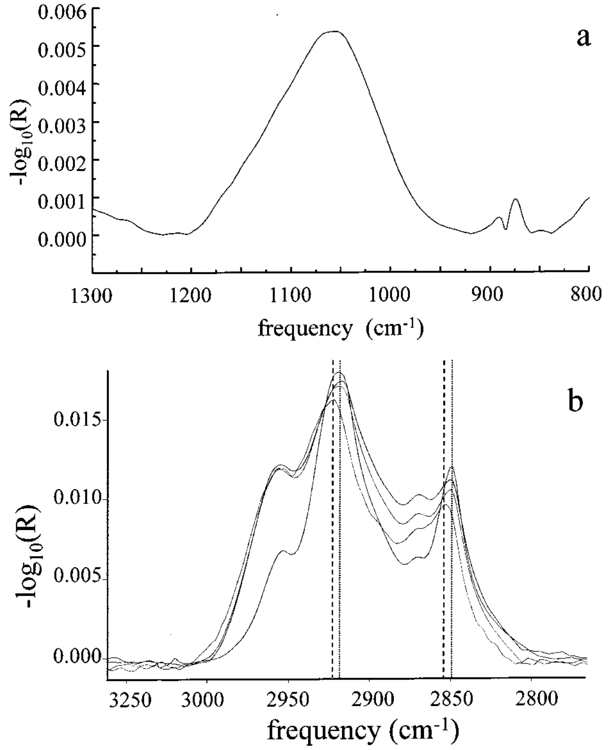


Figure 3. FTIR spectra of C_6: (a) S=O stretch and (b) CH stretching region as a function of the number of layers. The dashed lines are set at 2921 and 2852 cm^{-1} while the dotted lines are set at 2919 and 2850 cm^{-1}.

behavior is not observed for growth from ethanol solution, presumably because of the greater solubility of oxygen in that solvent. Once the oxidation process has been initiated, the product distribution will necessarily be statistical. Under conditions of excess oxidizer, the form of the thiol will be a sulfonate, and this functionality terminates the multilayer growth process, unless certain metal ions are introduced to the reacting system. There are, however, a variety of sulfur oxide compounds that exist where the S−S bond remains intact or where an S−O−S functionality is formed.[79−82] The S−S moiety can exist in the form of disulfides, thiosulfinates, thiosulfonates, α-disulfoxides, sulfinyl sulfones, and *vic*-disulfones (Chart 1). In general, the oxidation of the disulfide moiety proceeds through the series **1** to **6**, with only α-disulfoxides (**4**) being unstable.

The XPS data are not the only indication of oxidized sulfur in these multilayer assemblies. A prominent IR band at 1056 cm^{-1} is consistent with the SO stretching mode (Figure 3a). We believe that the thiols at the multilayer/air interface have been oxidized to SO_x, consistent with recent reports on the oxidative sensitivity of alkanethiol/gold monolayers.[65]

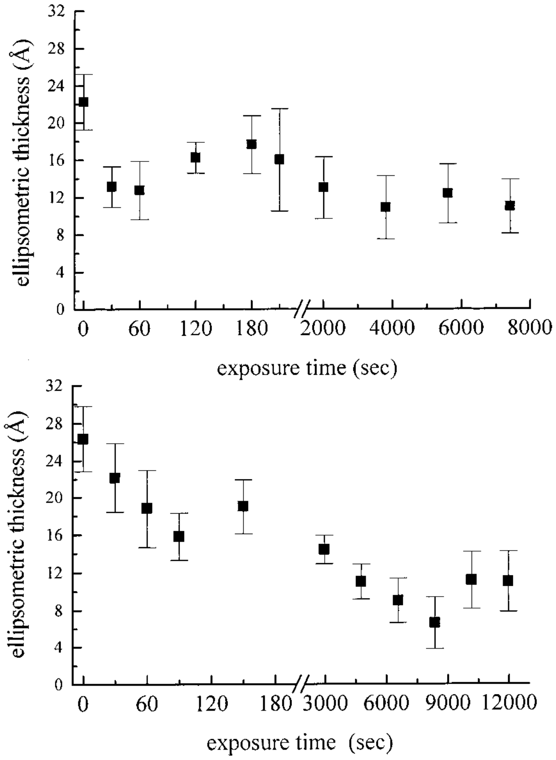


Figure 4. Photolysis experiment showing the thickness of the C_8 multilayer film as a function of UV exposure time: (a) in N_2 and (b) in air.

In an effort to verify the chemical identity of at least the most extensively oxidized form, we have used ionic coordination chemistry. The growth of metal phosphonates is well-known.[50−63] It is also possible to form hybrid metal phosphonate−sulfonate structures with use of Zr^{4+}, and we have used this chemistry as a test for the presence of RSO_3^- on the surface of a multilayer exposed to air for an extended period of time and for which immersion in dithiol solution does not produce additional layer formation. When this film is immersed in a 5 mM $ZrOCl_2$ solution for 0.5 h followed by immersion in a 1 mM 1,12-dodecanebisphosphonic acid (DDBPA) ethanolic solution for 12 h, a 10 Å thick layer is formed on top of the original multilayer. For a full monolayer of DDBPA, we expect a thickness of ∼17 Å. Our data indicate not only the presence of RSO_3^- at the multilayer surface, but also submonolayer coverage. To verify that the 10 Å thickness is not a consequence of the hybrid interlayer bonding scheme, we formed a second DDBPA layer on top of the first and recovered the same 10 Å/layer thickness. This finding reinforces our assertion that the RSO_3^- is present at less than a full layer.

After having discussed the chemical nature between interlayer bonding and the partial oxidation of the multilayers, we now consider the XPS and ellipsometry data on photolyzed multilayers formed from C_8 in air and N_2 atmosphere. Table 1 reports the elemental composition of photolyzed C_8 multilayers. After 5.6 h of photolysis, the thickness of the SAM is decreased to 10 Å from 28 Å (photolysis in air) and 22 Å (photolysis in N_2) (Figure 4). The photolysis data exhibit two distinct time dependencies. The first is characterized by a rapid decrease in thickness with initial exposure to UV light, followed by the second regime, where there is either no change for photolysis under N_2 (Figure 4a) or a slow decrease in thickness for photolysis in air (Figure 4b). We believe that the initial loss of thickness is due to direct photolytic cleavage of the S−S bond and the slower decrease in slope for the air-exposed sample is associated with the oxidative degradation of the Au−S bond.[65,66] Figure 2c shows the S2p region after photolysis which is fitted to three bands each having a doublet corresponding to $S2p_{3/2}$ and $S2p_{1/2}$ of an area ratio of 2:1. Three distinct peaks at 161.7, 163.6, and 168.3 eV are seen and their area ratio is 1.0:2.0:1.9. Even after photolysis of multilayers for 5.6 h, the layers are stable to ethanol washing, indicating that the remainder of the SAM is covalently bonded.

Ideally, the characterization of these multilayers would include a measurement of the distribution of sulfur oxide species within the layers, but this task is, at present, beyond the capabilities of XPS or vibrational spectroscopies. For XPS measurements, the spectral resolution required to achieve this level of speciation is not available. For Raman and IR spectroscopies, the limiting factor is primarily sensitivity. The most relevant resonance to study would be the S−S stretch in the region of 500 cm^{-1}.[23] For IR spectroscopy, the S−S stretch would be nominally forbidden for the disulfide and, in any event, the MCT-A detector required for monolayer IR measurements cuts off near 700 cm^{-1}, rendering this spectral region inaccessible. Raman spectroscopy could also, in principle, be used, but it is not clear that the S−S stretch is a sufficiently strong Raman scatterer to provide a useful signal from a few molecular layers. Surface enhanced Raman scattering may prove useful in future investigations, but we do not have sufficient control over the gold surface morphology at the present time to make these experiments feasible.

Measurement issues aside, any experimental information on the distribution of sulfur oxide species in the multilayer assembly is not likely to tell the complete story on the structure of these systems. There will likely be a variation in the extent of oxidation of the S−S bonds as a function of depth within the multilayer. The primary reason for this variation will be the permeability of the multilayer to oxidizers. Understanding the depth profile of each sulfur oxide form could provide additional insight into the chemical limits on the maximum film thickness achievable with this chemistry.

In addition to the interlayer linking chemistry, we can also gain some insight into the extent of organization of the aliphatic portions of the dithiol multilayers. The organization of the aliphatic chains can be probed with FTIR spectroscopy. The position of the methylene C−H stretching resonances is a sensitive measure of the order within the SAM.[2] For C_6, the first two layers yield the peak position of asymmetric and symmetric CH_2 stretching modes at 2921 and 2852 cm^{-1}, respectively, while for more than two layers, these resonances are shifted to lower frequencies, 2919 and 2850 cm^{-1} (Figure 3b). For the first two layers, the chains are partially disordered, consistent with data on alkanethiols indicating that for chain lengths less than 9 carbons, interchain ordering is not well established.[2] For the thicker multilayers, the positions of the bands are the same as those seen for long-chain SAMs, indicating that the dominant conformation of the aliphatic chains is fully extended, all-trans, and in a quasi-crystalline environment. We also note that, as the number of layers increases, the width of the bands at 2919 and 2850 cm^{-1} decreases. The peak position and width of the CH stretching resonances indicate that order within the films increases with the number of layers. The narrowing of the resonances with increasing thickness suggests either cooperative, multilayer structural organization or a variation in layer density with increasing number of layers. If the latter explanation is operative, the formation of islands would be required to achieve the density enhancement. For C_8 and C_9 multilayers we observe resonances only at 2919 and 2850 cm^{-1}, even for single layers.

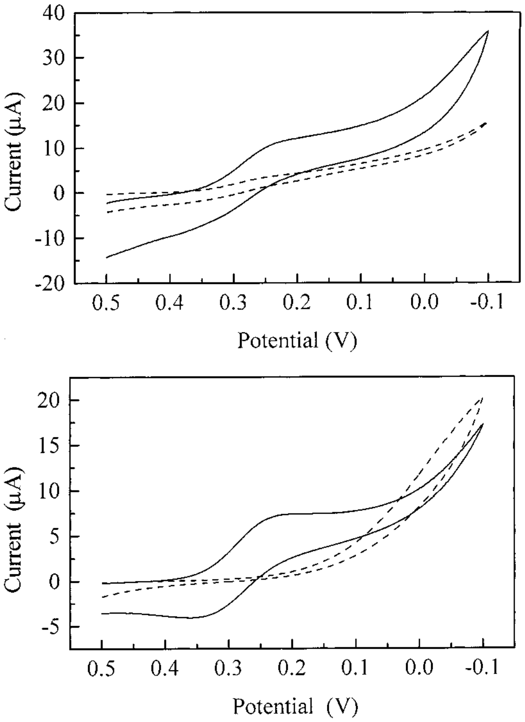


Figure 5. Cyclic voltammetry data for reduction of $Fe(CN_6)^{3-}$ using a gold electrode covered with mono- and multilayer assemblies. Curves for monolayers are solid lines and for multilayers are dashed lines. Data were recorded at (a) pH 3 and (b) pH 10.

Electrochemical methods are well established in the characterization of alkanethiol/Au SAMs.[43] The electrochemical data point to a potentially complex surface morphology for these layers. Cyclic voltammograms of 5 mM $Fe(CN_6)^{3-}$ in 1 M $Na_2SO_3(aq)$ were recorded with gold electrodes coated with monolayers or multilayers of C_9 dithiol. These CVs show a reduction in the current allowed through the bilayer relative to the monolayer, at both pH 3 and pH 10 (Figure 5). This is an expected result, indicating that the layers do indeed provide significant coverage of the Au surface. To gauge the extent of coverage requires the examination of absolute currents, and there is the potential for misinterpretation associated with unaccounted-for leakage paths and an incomplete understanding of the surface roughness, thereby allowing only an estimate of the expected tunneling current. These difficulties notwithstanding, currents greater than 10 μA are seen near −0.1 V. These currents exceed tunneling currents by orders of magnitude and indicate that our layered assemblies are characterized by substantial defects. We believe that the dominant form of defect is likely a vacancy, given the currents we measure.

Conclusion

The results presented here demonstrate the facile formation of robust multilayer films where interlayer bonding proceeds through a covalent S−S linkage. The chemistry is spontaneous and, at the high dithiol concentrations we use, formation of nonlooped layers is favored and interlayer oxidative thiol → disulfide chemistry competes efficiently with intralayer S−S bond formation. XPS measurements reveal that the S−S moiety is readily oxidized without loss of overall multilayer robustness, consistent with the presence of multiple sulfur oxide species with the S−S bond intact. UV photolysis measurements indicate the susceptibility of the S−S bond to photolytic cleavage. Based on our ability to form a hybrid (RSO_3−Zr−O_3PR) layered structure, this approach to multilayer growth will likely provide a useful means of constructing more functionally complex, ordered interfaces than has been attainable with alkanethiol/gold monolayer chemistry.

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