Study of the Photooxidation Process of Self-Assembled Alkanethiol Monolayers

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Patterned self-assembled monolayers on solid substrates are being investigated for applications in material science, microelectronics, and biotechnology.[1] A UV-photolithographic method was recently reported for patterning alkanethiol self-assembled monolayers (SAMs) on Au and Ag surfaces with micrometer resolution.[2,3] It was shown that upon exposure to UV light, thiolate head groups are photooxidized to sulfoxide species. The oxidized sulfur species are weakly bound to the surface relative to thiolates and thus are easily displaced from the monolayer by immersion in a solution containing a second alkanethiol molecule.[4] Although some of the oxidation products from the UV photolysis procedure have been identified using X-ray photoelectron spectroscopy and laser desorption mass spectrometry, many questions still remain about the mechanism of the photooxidation reaction. In this report, we present surface-enhanced Raman spectroscopy (SERS) results acquired from UV-irradiated SAMs on Ag. We show that the photooxidation of the alkanethiol monolayer proceeds essentially by a two-step mechanism. First, UV exposure causes C−S bond scission and subsequent desorption of the hydrocarbon chain. Second, the exposed sulfur is oxidized to sulfite and sulfate species.

SERS was used to monitor the disappearance of Raman bands associated with S−C and C−C bonds of the *n*-alkanethiols and the appearance of bands associated with S−O species. Because of the relatively high Raman cross sections for the C−S and S−O vibrations, SERS was found to be a highly sensitive technique for characterizing the effects of UV exposure on alkanethiol monolayers. SAMs comprised of *n*-alkanethiols [$CH_3(CH_2)_nSH$, where $n = 5$, 9, and 17] were formed on electrochemically roughened Ag substrates.[5] SER spectra[6] from as-formed SAMs were qualitatively similar to those reported previously,[7] indicating the presence of densely-packed, high-quality monolayers. UV exposure of a sample was performed in air without removing the sample from its initial position, ensuring that the identical sample area was probed following each exposure. The low-pressure Hg pen-lamp (~3 mW/cm^2) used for irradiating samples was shut off during acquisition of SER spectra. A 2 min delay occurred between UV lamp exposure and acquisition of SER spectra. In a typical experiment, the sample was UV irradiated for 1 min intervals for the first 10 min, followed by 5 min intervals. No decrease of SERS intensities associated with the SAMs was observed following UV exposure; thus, the total accumulated time of UV exposure is reported.

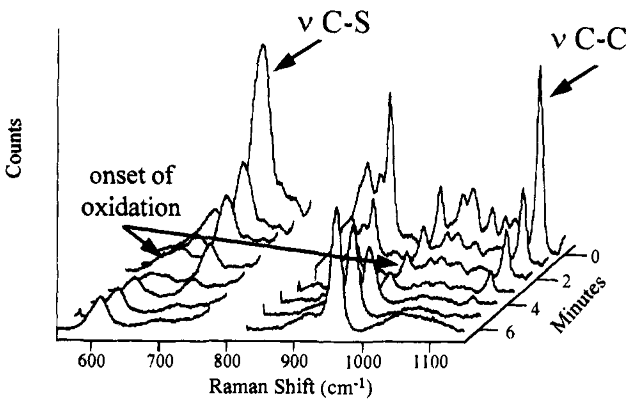

Figure 1. SER spectra acquired from a hexanethiol SAM on Ag after total UV exposure times of 0, 1, 2, 3, 4, 5, and 6 min. See text for description.

Figure 1 contains SER spectra from 550−1150 cm^{-1} acquired from a hexanethiol (C6) monolayer at short UV exposure times (0−6 min). Monolayer peak assignments follow those of ref 7. The peaks at 1112, 1076, 1062, and 1042 cm^{-1} are C−C stretching vibrations originating from the hydrocarbon backbone of the monolayer. The peak at 702 cm^{-1} is assigned to the C−S stretch of the monolayer. Upon UV irradiation, a decrease in the intensity of all monolayer peaks is clearly seen. Also apparent in Figure 1 are new features at 958, 917, and 612 cm^{-1} that increase in intensity with exposure time. We attribute these new bands to the formation of oxidized sulfur species. The intense peak at 958 cm^{-1} is characteristic of the totally symmetric stretch of adsorbed or coordinated sulfate ion ($SO_4^{=}$).[8-10] Corresponding sulfate peaks are also found at 460, 618, and 1132 cm^{-1}. The weak shoulder found at 917 cm^{-1} and the peak at 606 cm^{-1} are assigned to a sulfite ion ($SO_3^{=}$).[11] Although the sulfate species is clearly the dominant oxidation product, the Raman cross section for the symmetric stretch of the sulfite species is smaller than that of the sulfate species. Therefore, the concentrations of the two species are not directly related to the ratio of the intensities. The intensity of the sulfite peaks increased initially, reached a plateau, and then decreased. Concomitant with this decrease, we see growth in peaks at 684,

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(1) For example, see: Stenger, D. A.; Georger, J. H.; Dulcey, C. S.; Hickman, J. J.; Rudolph, A. S.; Nielsen, T. B.; McCort, S. M.; Calvert, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 8435−8442. Abbott, N. L.; Folkers, J. P.; Whitesides, G. M. *Science* **1992**, *257*, 1380−1382. Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498−1511.

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(5) Electrodes were polished with 0.05 μm grit alumina, rinsed with 18 MΩ deionized water, and sonicated for 5 min to remove all traces of the powder. Electrochemical roughening was done in a 1.0 M $NaClO_4$ solution and consisted of three cycles from −0.5 to +0.6 V (vs Ag/AgCl) with the potential poised for 30 and 10 s at the negative and positive potential extremes, respectively. The electrode was sequentially rinsed with water and ethanol and incubated in a 1−5 mM alkanethiol−ethanol solution for a minimum of 24 h.

(6) The Raman configuration consisted of a SPEX 1404 double monochromator converted to single stage use, connected to a SPEX Spectrum One CCD camera cooled to 140 K. (The identification of certain commercial products is done to adequately describe experimental procedures and in no way implies endorsement by NIST.) Integration times of 50 s were used for each SERS spectrum. He−Ne (632.8 nm) excitation was used with power at the sample ~10 mW. SERS signals from SAMs were found to be stable for >2 h at this exposure power. Data were acquired using SPEX DM3000 software and analyzed with GRAMS/386 software (Galactic Industries).

(7) Bryant, M. A.; Pemberton, J. E. *J. Am. Chem. Soc.* **1991**, *113*, 8284−8293.

(8) The intensity observed for the 958 cm^{-1} sulfate peak after >1 h of UV exposure is an order of magnitude greater than that of the most intense monolayer peak.

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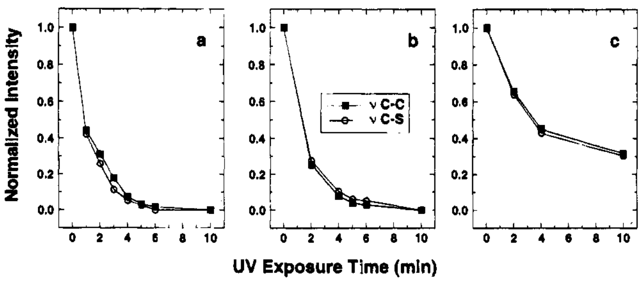

Figure 2. Plot of normalized SERS peak intensities as a function of UV exposure time for (a) C6, (b) C10, and (c) C18 SAMs on Ag. The peak intensities are normalized to the peak intensity before UV irradiation (*t* = 0). The frequencies of the C−C and C−S stretching peaks for the C6 SAM are 1112 and 702 cm^{-1}, respectively. The C−C and C−S frequencies are slightly shifted for the C10 and C18 monolayers but reflect the same band assignments.

708, 1052, and 1432 cm^{-1}. The new peaks indicate a conversion of the sulfite species to new products that may result from reaction of sulfites with water vapor to form acids such as HSO_3^- or HSO_4^-.

Figure 2 shows the decrease in intensity of the 1112 cm^{-1} C−C and 702 cm^{-1} C−S stretches as a function of UV exposure time for the C6, C10, and C18 SAMs. A noteworthy feature of these data is that the decay in the C−C peak intensity closely resembles that of the C−S peak intensity. The similarity of the C−C and C−S decay transients suggests that the same reaction is responsible for the loss of these two features. Thus, we conclude that UV exposure results in the cleavage of C−S bonds, followed by desorption from the surface of the resulting hydrocarbon fragments. Direct scission of C−C bonds by UV exposure cannot be ruled out, but we believe this reaction pathway to be of secondary importance. No loss of monolayer intensity was observed with the UV lamp off, indicating that SAM removal results from a photochemical process, as opposed to postexposure secondary radical reactions. An additional important observation is that no oxidation peaks are detected until after a significant decrease in the intensity of the monolayer bands is observed. In fact, the onset of sulfur oxidation is not observed until the monolayer peaks have diminished to ~25% of their initial intensity.[12] This observation is consistent with the densely packed nature of alkanethiol SAMs. It is likely that oxidation of sulfur head groups requires the removal of hydrocarbon chains to allow easier access by oxygen. Thus, the UV photoreaction of alkanethiol SAMs involves two processes occurring in series: the removal of the alkane chain by C−S bond scission, followed by oxidation of the exposed sulfur atoms.

Rate constants for the photoreaction were determined by plotting the logarithms of the normalized C−S stretching intensities vs UV exposure time.[13] The rate of depletion of the C6 and C10 SAMs fits simple first-order kinetics, with observed rate constants of (1.2 ± 0.03) × 10^{-2} and (1.0 ± 0.05) × 10^{-2} s^{-1}, respectively.[14] In contrast, a first-order kinetic model does not adequately describe the C18 monolayer data. We do not believe that a fundamentally different mechanism occurs for this system. Instead, the deviation from first-order kinetics can be rationalized by considering the magnitude of chain−chain interactions for the C18 SAM. Longer chain SAMs are stabilized relative to those of shorter chain alkanethiols because of greater van der Waals interactions. The greater attractive energy of these interactions may lock the alkyl chain fragment in place after C−S bond scission for the longer chain monolayer, increasing the probability for bond re-formation. In the case of the shorter chain monolayers, C6 and C10, interchain interactions are lower so that desorption of the alkane chain is more facile when C−S bond cleavage occurs, thereby allowing easy oxidation of the S group. A qualitative comparison of the oxidation rates for the three SAMs shows that the rate of oxidation decreases with increasing chain length.

From the SERS data, we propose a two-step mechanism for the photooxidation of the alkanethiol SAMs. In the first step, the C−S bond is cleaved, and the alkane chain, no longer attached, desorbs from the surface. After desorption of the alkane chain, the exposed sulfur is then oxidized. In support of this interpretation are XPS and ellipsometry results from our laboratory acquired from UV-irradiated SAMs on Au surfaces that indicate depletion of carbon from the surface along with a monotonic decrease in film thickness. We also note that there is precedence for facile C−S bond cleavage from previous photochemical studies of thiols and sulfides.[15] Thiol and sulfide molecules absorb in the range of 220−240 nm, and it has been established that C−S scission is a primary photochemical reaction pathway with UV irradiation. Moreover, the existence of adsorbed sulfur oxidation products strongly supports C−S bond scission. The delay in the appearance of oxidation peaks reflects the volatilization rate of the alkane chain after bond scission, with greater delays observed for the longer chain thiols.

In summary, we have found that UV irradiation in air of alkanethiol SAMs on Ag surfaces results in photochemically induced C−S bond scission, desorption of alkyl chain fragments, and oxidation of surface-bound sulfur. In addition, we have demonstrated that SERS is uniquely suited for studying SAM photochemistry because of its excellent sensitivity to C−S, C−C, and S−O vibrations. Studies are underway to examine the wavelength dependence of the photoreaction and to determine if a similar mechanism holds for alkanethiol SAMs on Au.

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Supporting Information Available: Plots of the logs of the normalized SERS intensities of the C−S stretching bands (C6, C10, C18 SAMs) and ellipsometric thicknesses (C10, C18 SAMs) against UV exposure time used to determine rate constants of the photoreaction (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) A monolayer peak at 975 cm^{-1}, tentatively identified as a CH_3 rocking mode, overlaps with the 958 cm^{-1} oxidation peak. Deconvolution of the peak reveals a contribution due to the oxidation peak after 2 min of UV exposure.

(13) Monolayer features were completely absent within 10 min for the C6 and C10 SAMs and within 25 min for C18 (the growth of a background feature in this area made it difficult to determine the exact point at which the monolayer is completely removed for the C18 SAM). The intensity of the largest sulfate peak continues to increase up to ~2 h total elapsed time for C6, 3 h for C10, and 7 h for C18.

(14) The error associated with the rate constants is the standard error for a 95% confidence interval from a linear regression fit.

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