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Ozonolysis Is the Primary Cause of UV Photooxidation of Alkanethiolate Monolayers at Low Irradiance

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Self-assembled monolayers (SAMs) of alkanethiols on Au surfaces have been studied extensively since the pioneering work of Nuzzo, Allara, and Whitesides.[1−3] Important potential SAM applications include contact printing and lithography.[4−14] SAM resists have advantages in both conventional and ultrahigh spatial resolution lithography. Use of SAMs avoids both dimensional changes associated with polymer swelling during solvent development and reduces electron backscatter from X-ray or electron beams.

UV irradiation of an alkanethiolate SAM on Au in air has been shown to form alkylsulfonates,[9−11] and UV photopatterning of alkanethiolate SAMs based on this finding has been reported by several groups.[11−13] Prior studies, however, do not distinguish between photooxidation, where the UV radiation leads directly to the photoproduct, and chemical oxidation, where photolysis leads to a reactive oxygen species which subsequently participates in the sulfonation reaction.[10,15−17] We have found that the labilization (or stripping) of HDT SAMs on Au on the minutes time scale under low-irradiance conditions requires both O_2 and UV irradiation at wavelengths competent for O_3 formation, i.e. $\lambda < 200$ nm. In addition, ex-situ generation shows that O_3 accounts for $\geq$10-fold more labilization than do O atoms or $O_2(^1\Delta_g)$. These findings lead us to the conclusion that ozonolysis, from UV-photosynthesized O_3,[18] is the primary cause of the UV oxidation of self-assembled hexadecanethiol (HDT) monolayers and, by generalization, of other alkanethiolate monolayers, on Au at low irradiances, a conclusion consistent with the findings of Norrod and Rowlen from surface-enhanced Raman scattering studies.[19]

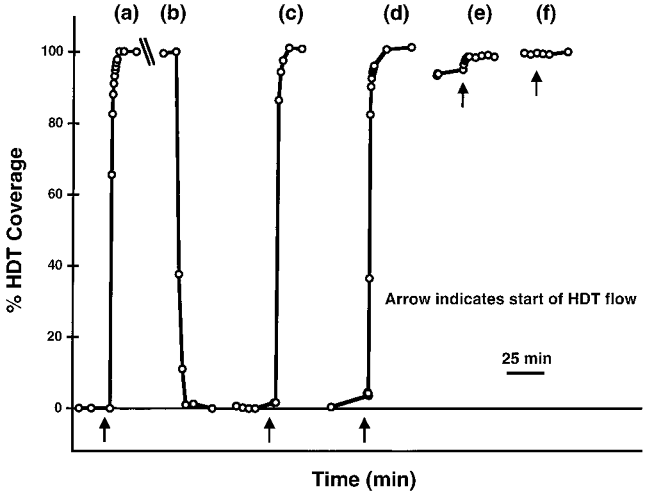

Figure 1. SPR measurements of HDT coverage on Au during assembly (a), stripping (b), or reassembly following UV irradiation or ozonolysis (c−f): (a) typical HDT assembly on a clean surface; (b) stripping with O_3 generated remotely; (c) reassembly following treatment with O_3 in the dark; (d) reassembly following UV irradiation in air; (e) reassembly following UV irradiation under N_2; (f) reassembly following ex situ UV irradiation in high vacuum.

We measure SAM stripping in situ by surface plasmon resonance spectroscopy (SPRS) in a windowed flow-cell configuration.[20] SPRS allows us to monitor the assembly of an HDT SAM from solution in real time, its subsequent removal by UV irradiation or ozonolysis, and then the *re*assembly of HDT onto the Au surface. The SPRS coverage measurement is repeatable within 2% following the cycle of assembly, rinsing, draining, UV irradiation/ozonolysis, rerinsing, and reassembling the HDT film.

Figure 1 shows a single HDT assembly experiment (Figure 1a), stripping (Figure 1b), and a series of reassembly curves (Figure 1c−f) which follow various treatments.[22] Zero coverage represents the clean Au surface, and full coverage represents the SPR position for HDT SAMs soaked in 1 mM HDT/EtOH solution for $t > 12$ h. It is apparent from the figure that saturation coverage is reached in a small fraction of this time. A typical experiment begins with either a freshly evaporated Au surface, or one which has been cleaned with O_3 for 30 min[16] followed by rinsing with EtOH. The SPR position is measured periodically, first in flowing EtOH and then as HDT solution is introduced into the flow cell. Figure 1a is typical for a HDT assembly experiment. Figure 1b is the stripping curve during ozonolysis (with ex situ generated O_3 and in the dark) starting from a full monolayer of HDT. Each datum in Figure 1b represents the HDT coverage obtained by sequentially draining and drying the cell, exposing the HDT film to O_3 for the indicated period of time, then rinsing the exposed film in flowing EtOH and subsequently measuring the SPR position. Ozonolysis and EtOH rinsing clearly

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(1) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481−4483.

(2) Bain, C. D.; Troughton, B. E.; Tao, Y. T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321−335.

(3) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559−3568.

(4) Kumar, A.; Biebuyck, H. A.; Abbott, N. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1992**, *114*, 9188−9189.

(5) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1498−1511.

(6) Kumar, A.; Whitesides, G. M. *Science* **1994**, *263*, 60−62.

(7) Wilbur, J. L.; Kim, E.; Xia, Y.; Whitesides, G. M. *Adv. Mater.* **1995**, *7*, 649−652.

(8) Xia, Y.; Whitesides, G. M. *J. Am. Chem. Soc.* **1995**, *117*, 3274−3275.

(9) Li, Y.; Huang, J.; McIver, R. T.; Hemminger, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 2428−2432.

(10) Huang, J.; Hemminger, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 3342−3343.

(11) Tarlov, M. J.; Burgess, D. R. F.; Gillen, G. *J. Am. Chem. Soc.* **1993**, *115*, 5305−5306.

(12) Huang, J.; Dahlgren, D. A.; Hemminger, J. C. *Langmuir* **1994**, *10*, 626−628.

(13) Gillen, G.; Bennett, J.; Tarlov, M. J.; Burgess, D. R. F. *Anal. Chem.* **1994**, *66*, 2170−2174.

(14) Chan, K. C.; Kim, T.; Schoer, J. K.; Crooks, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 5875−5876.

(15) Lewis, M.; Tarlov, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 9574−9575.

(16) Worley, C. G.; Linton, R. W. *J. Vac. Sci. Technol. A* **1995**, *13*, 2281−2284.

(17) Hutt, D. A.; Leggett, G. J. *J. Phys. Chem.* **1996**, *100*, 6657−6662.

(18) Horvath, M.; Bilitzky, L.; Huttner, J. *Ozone*; Elsevier Science Publishing: New York, 1985; pp 196−201.

(19) Norrod, K. L.; Rowlen, K. L. *J. Am. Chem. Soc.* **1998**, 120, 2656−2657.

(20) The SPR experiments were carried out with 750-nm radiation from an Ar^+-pumped Ti−sapphire laser. The SPR flow cell was constructed with Teflon, and all measurements were made in the Kretschmann configuration.[20] Au films were deposited directly onto a Cr-coated sapphire substrate by thermal evaporation at ca. 1 Å/s at pressures below 1.5×10^{-6} Torr. The thickness of the Au was ~500 Å and the Cr ~10 Å.

(21) Kretschmann, E.; Raether, H. *Z. Naturforsch.* **1968**, *23*, 2135.

(22) UV irradiation was performed with a low-pressure Hg lamp producing 50 μW/cm^2 irradiance. O_3 was generated in an air-flow upstream of the cell using the same UV source. The flow rate was 28.9 mL/min, and the ozone concentration in the ozonolysis experiments was 0.55 ppm, determined by the iodometric method.[22]

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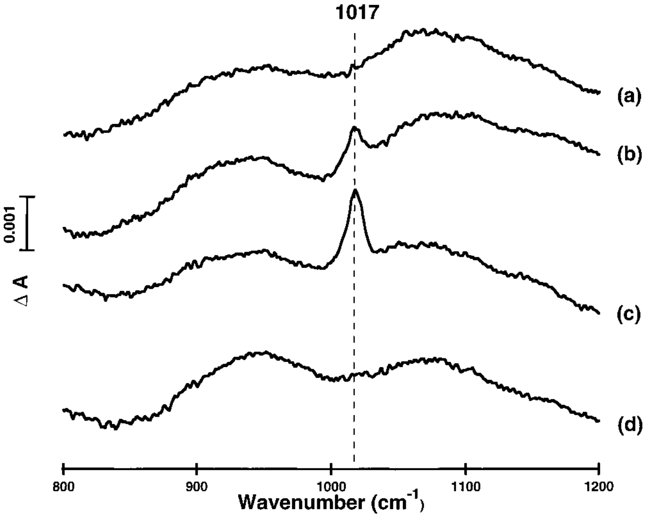

Figure 2. Difference IR spectra (Δ*A*, absorbance of variously treated HDT SAMs minus absorbance of the pristine HDT SAM): (a) exposed to UV for 30 min in N_2; (b) exposed to UV in air for 30 min; (c) exposed to O_3 for 30 min; (d) sample from c following a rinse with H_2O and 2-propanol.

remove HDT and restore the Au surface within the SPR detection limit of ca. 0.02 monolayers.

Figure 1c illustrates the assembly of HDT onto the O_3(30 min)/EtOH cleaned surface and is indistinguishable from Figure 1a, illustrating the complete removal of the HDT SAM by ozonolysis and the repeatability of HDT reassembly after treatment. Figure 1d is the corresponding reassembly after UV irradiation in air of the SAM in Figure 1c. It is evident that exposure of the HDT SAM to ex situ generated O_3 produces results identical to those of direct UV irradiation of the film in air. However, Figure 1e shows that exposure of the SAM to the same UV source for 60 min in flowing N_2 leads to only a small, <5%, amount of stripping. The slow and incomplete stripping in N_2 can be explained by O_2 permeability of the Teflon capillary tubing required in our flow apparatus. Figure 1f is a similar experiment, but in which O_2 is rigorously excluded by UV-irradiating the SAM in a high-vacuum chamber (10^{-6} Torr), for 1 h, then subjecting it to the same sequence of EtOH rinsing followed by HDT−EtOH solution assembly. Clearly, no observable (<2%) HDT SAM was stripped during this treatment, illustrating that in rigorously O_2-free conditions, UV irradiation, at a level sufficient to remove an HDT SAM completely in the presence of O_2, produces no strippable products on an alkanethiol SAM on Au.

The identities of the HDT UV-irradiation products were studied by reflection−absorption infrared spectroscopy (RAIRS). IR difference spectra ($\Delta A = A_{\text{treated}} - A_{\text{untreated}}$) of variously treated HDT SAMs are presented in Figure 2. The unirradiated HDT film shows only background features in the fingerprint region. Figures 2a−d are Δ*A* of a HDT SAMs exposed to (a) UV radiation for 30 min under N_2, (b) UV for 30 min in air, (c) O_3 alone for 30 min, and (d) O_3 for 30 min followed by rinsing in H_2O and 2-propanol. UV irradiation in N_2 produces little spectral change above background. UV irradiation in air or exposure to O_3, however, cause the appearance of a new band at 1017 cm^{-1}. The band at 1017 cm^{-1} is removed by rinsing in H_2O/2-propanol. The band at 1017 cm^{-1} and one not observed in these experiments (a broad doublet ca. 1000−1200 cm^{-1}) have been assigned to sulfonate stretching modes by correlation to XPS for air-oxidized HDT SAMs on silver[24] and by analogy to solid hexadecanesulfonic acid.[25] The fact that this 1017-cm^{-1} band is rinsed away by water/2-propanol is fully consistent with its assignment to a sulfonate species. The CH-stretching bands (2800−3000 cm^{-1}) are also broadened and shifted by UV−air and O_3 exposure, but not UV−N_2 treatment, in a fashion consistent with disordering of the SAM.[26] Disordering in O_3-exposed but unrinsed SAMs probably reflects free volume in the films resulting from alkane chain fragmentation.

We also studied the wavelength dependence of the stripping reaction to examine the possibility that hot electron activation[10] of the sulfur head group or coadsorbed O_2 was responsible for the observed labilization. When long-pass filters with cutoffs at either $\lambda = 305$ or $\lambda = 200$ nm were interposed into the light path, *we did not observe any HDT stripping*. Clearly all the Au interband transitions up to the work function (5.1 eV), including the important $\Delta\epsilon_2$ feature at 2.38 eV, are accessed by radiation at $\lambda > 200$ nm.[27] If electron generation in the Au substrate played an important role in the resultant photochemistry, we would expect to see effective labilization at these longer wavelengths. However, only wavelengths short enough to generate O_3, e.g. $\lambda = 185$ nm[18,28] from the low-pressure Hg lamp resulted in SAM stripping.

Excited-state (singlet) molecular oxygen, $O_2(^1\Delta_g)$, is also a likely[29,30] byproduct of the UV irradiation of oxygen. Because $O_2(^1\Delta_g)$ is an aggressive oxidant toward sulfur,[31,32] we exposed a HDT SAM to flowing O_3-containing air with and without O_2-$(^1\Delta_g)$.[33] The exposures yielded 0.52 ± 0.02 and 0.49 ± 0.02 monolayer stripping, respectively, indicating little, if any, action attributable to $O_2(^1\Delta_g)$ and, by extension, to O atoms.

The results presented here demonstrate that, at the low irradiances typical of low-pressure Hg lamps, (a) both O_2 and irradiation below 200 nm are required for UV-photolytic generation of strippable products in HDT SAMs, (b) UV irradiation of HDT SAMs in the presence of O_2 has an effect similar to that of exposure to O_3 generated ex situ, (c) O_3 is at least 1 order of magnitude more effective than other active oxygen-containing species at generating labile products under these conditions, and (d) the products of reaction in either O_3 exposure or UV irradiation appear to be oxidized sulfur head groups, which are easily removed by subsequent rinsing in a polar solvent. Taken together these results are convincing evidence that UV photooxidation of HDT SAMs proceeds principally by generation of O_3 and subsequent ozonolysis of the sulfur head group. The results clearly have important implications for high spatial resolution patterning. Since O_3 molecules are mobile on or near the surface and will attack Au−S bonds randomly, successful patterning strategies employing UV photolysis of alkanethiolate SAMs in the presence of O_2 must prevent diffusion of photogenerated O_3 away from the desired patternable area.

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(23) *Standard Methods for the Examination of Water and Wastewater,* 16th ed.; APHA, AWWA, and WPCF: Washington, DC, 1985.

(24) Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y. T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7152−7167.

(25) Pouchert, C. J., Ed. *The Aldrich Library of FT.-IR Spectra*; Aldrich Chemical Co.: Milwaukee, WI, 1985; pp 257−888.

(26) Terrill, R. H.; Tanzer, T. A.; Bohn, P. W. Manuscript in preparation.

(27) (a) Monroe, B. M. In *Singlet O_2*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. 1, pp 177−224. (b) Christensen, N. E.; Seraphin, B. O. *Phys. Rev. B* **1971**, *4*, 3321.

(28) Herzberg, G. *Atomic Spectra and Atomic Structure*; Dover: New York, 1944; p 202.

(29) Valentini, J. J.; Gerrity, D. P.; Phillips, D. L.; Nieh, J. C.; Tabor, K. D. *J. Chem. Phys.* **1987**, *86*, 6745−6756.

(30) Sparks, R. K.; Carlson, L. R.; Shobatake, K.; Kowalczyk, M. L.; Lee, Y. T. *J. Chem. Phys.* **1980**, *72*, 1401−1402.

(31) Gu, C.; Foote, C. S.; *J. Am. Chem. Soc.* **1982**, *104*, 6060−6063.

(32) Sheu, C.; Foote, C. S.; Gu. C. *J. Am. Chem. Soc.* **1992**, *114*, 3015−3021.

(33) Reaction conditions: reagents generated ex situ; 6 min reaction time, $O_2(1\Delta_g)$ stripped by passage through a 10-cm water cell.