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Oxidation of Self-Assembled Monolayers by UV Light with a Wavelength of 254 nm

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Self-assembled monolayers (SAMs) formed by the adsorption of alkanethiols onto gold surfaces have attracted widespread and growing interest, as model materials for fundamental investigations of adhesion, tribology, biological interfacial interactions, and other interfacial phenomena, and as novel templates for the fabrication of molecular, biomolecular, and cellular structures and devices. Recently there has been much interest in the oxidative chemistry of SAMs. Although in general SAMs exhibit remarkable chemical stability, there have been concerns about their possible susceptibility to oxidation by atmospheric agents such as ozone.[1,2] Understanding the fundamental chemistry of SAM oxidation is thus of general importance. There have also been a number of reports of the photochemical oxidation of SAMs,[3,4] and several groups have utilized photolithographic methods to produce micropatterned materials.[5−8] Recent papers by Bohn and co-workers[9,10] and by Rowlen and co-workers[11,12] have demonstrated that exposure of SAMs to ozone leads to oxidation of the thiolate headgroup to a sulfonate, the species reported to be formed in SAM photooxidation studies, and Poirier et al. have provided elegant STM data to support this.[13] However, Bohn and co-workers and Rowlen and co-workers go further and assert that ozonolysis is the *only* mechanism of SAM oxidation during exposure to UV light sources. Specifically, they claim that light of wavelength 185 nm is necessary for oxidation to occur. This is an important claim, because of its relevance to the questions concerning SAM oxidation, and because it casts some doubt on the general feasibility of photolithographic processes for SAM patterning and for the manipulation of SAM chemistry.

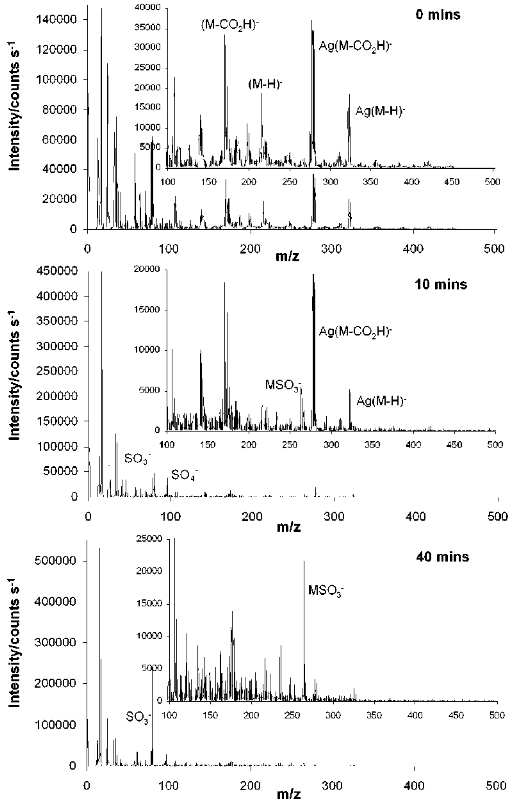

Figure 1. Static SIMS spectra of MUA SAMs on silver following exposure to the UV lamp.

To test this claim, we have used an ozone-free UV lamp (Model R-52G, UVP Inc, Cambridge, UK) to study the photooxidation of SAMs.[14] Using static secondary ion mass spectrometry (SIMS), we have demonstrated that such a light source is capable of rapidly photooxidizing SAMs of mercaptoundecanoic on both gold and silver. These data emphatically refute the conclusion of Bohn et al. and Rowlen et al. that light of shorter wavelengths is *necessarily* required to oxidize SAMs. However, we have found that the behavior of dodecanethiol is very different, suggesting that the photochemistry of SAMs of alkanethiols on gold and silver is rich and varied.

In earlier studies, we have provided clear evidence for the power of static SIMS for probing surface reactions in SAMs.[15] In particular, we have used SIMS to quantify rates of photooxidation of SAMs on both silver[16] and gold.[17] SIMS spectra show unequivocal changes that are due to oxidation,[18] and provide a highly reliable indication of whether photooxidation has occurred. Figure 1 shows SIMS spectra of SAMs of mercaptoundecanoic acid (MUA) on Ag as prepared and following exposure to UV light for periods of 10 and 40 min.[19] The spectrum of the as-prepared SAM exhibits characteristic molecular fragments, in-

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(14) The majority of emission from this lamp occurs at 254 nm (power 1.25 mW cm^{-2} at a distance of 15 cm). To confirm that the manufacturer's specification was correct, we tested for the emission of ozone using a Draeger Tube (Draeger Safety, Northumbria, UK). Ozone was undetectable at the lower sensitivity limit of 0.005 ppm.

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(19) SAMs were prepared according to well-established procedures. Gold (∼30 nm) was thermally evaporated onto chromium (∼10 nm) primed glass microscope slides that had previously been cleaned using piranha solution (CAUTION: pirhana solution is a strong oxidising agent and reacts violently with organic materials). Freshly prepared gold films were immersed in 1 mmol solutions of the appropriate thiol in degassed ethanol for 18 h. After removal from the solution, the slides were rinsed in copious amounts of degassed ethanol and dried under flowing nitrogen. Static SIMS was performed using a Vacuum Generators SIMS system equipped with a Ga liquid metal ion source and an MM 12−12 quadrupole mass analyzer. Typically, a primary particle flux of ca. 2 nA cm^{-2} was employed and the primary particle dose was $<5 \times 10^{12}$ ions cm^{-2}, well within the static regime.

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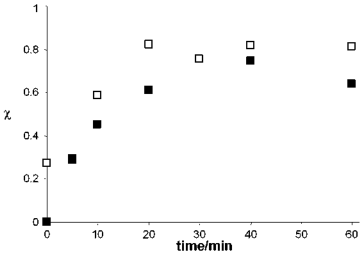

Figure 2. Variation in the extent of oxidation, χ, with the time of exposure to UV light for SAMs of MUA on gold (filled squares) and silver (open squares) substrates.

cluding the peak at m/z 217 due to the molecular alkanethiolate species, designated $(M-H)^-$, and the peaks due to a complete silver thiolate complex, $Ag(M-H)^-$ at m/z 324 and 326 (due to the two isotopes of silver, ^{107}Ag and ^{109}Ag). Loss of a CO_2 fragment from these molecular species appears to be facile, as might be expected, because peaks are observed corresponding to $(M-CO_2H)^-$ (m/z 173) and $Ag(M-CO_2H)^-$ (m/z 280/282).

After exposure to light from the UV lamp for 10 min, a new peak appeared at m/z 265, due to the sulfonate of MUA, designated MSO_3^-. A new peak was also observed at m/z 221, due to the loss of CO_2 from this ion. In our previous studies of the photooxidation of SAMs of MUA on gold following exposure to a medium-pressure mercury arc lamp,[17] the intensity of the MSO_3^- peak was reported to be small. The intensity of the peak at m/z 221 was substantially greater. In the present study, the intensity of the MSO_3^- ion was found to be much greater than that of the m/z 221 ion for monolayers of MUA on both gold and silver. This may indicate a difference in the mechanism of oxidation. For example, there may be lines in the spectrum of the medium-pressure arc lamp that excite oxidative degradation of the terminal end of the adsorbate.

In addition to the sulfonate species, peaks are observed at m/z 80 and 96, due to SO_3^- and SO_4^-, respectively. These peaks, and the sulfonate fragments at m/z 221 and 265, increased in intensity as oxidation progressed, and dominated the spectrum after 40 min of exposure. At the same time, the intensities of the molecular fragments that were prominent in the spectrum of the as-prepared SAM were observed to decline. It was previously shown that the ratios of these peak areas may be used to quantify the extent of oxidation χ.[16] In particular, the ratio

$$\chi = \frac{[MSO_3^-]}{[MSO_3^-] + [(M-H)^-]}$$

was calculated, where [X] is the peak area corresponding to species X in the SIMS spectrum. Figure 2 shows χ as a function of time of exposure to UV light for monolayers of MUA on both gold and silver. It is clear that oxidation is both rapid and extensive. The rates of photooxidation of MUA on silver and gold surfaces are strikingly similar. The efficacy of photooxidation by light of wavelength 254 nm is further demonstrated by the preparation of patterned SAMs. Figure 3 shows a SIMS image of a pattern formed following exposure of an mercaptopropanoic acid (MPA) SAM to 254 nm light through a mask (an electron microscope grid) for 5 min and subsequent emersion in a 10 mmol ethanolic solution of octanethiol. Octanethiol has displaced oxidized MPA, leaving MPA intact in the masked regions of the surface. Good contrast is observed between the masked and exposed regions of the sample, indicating effective oxidation and displacement of MPA in exposed regions. Given that an ozone-free light source has been employed in these experiments, it is clear that these data indicate that photochemical oxidation (not ozonolysis) has occurred.

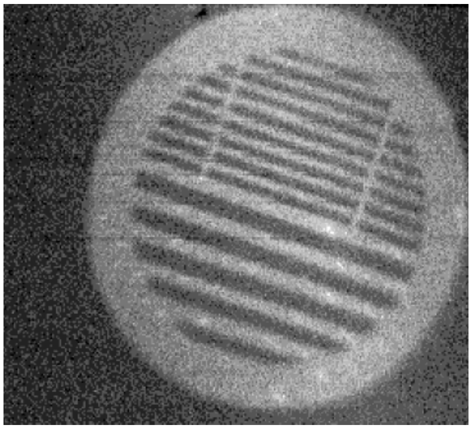

Figure 3. SIMS image of a photopatterned SAM, formed by mapping the O^- intensity. Acid terminated regions contain oxygen and thus exhibit bright contrast, while methyl terminated regions exhibit dark contrast.

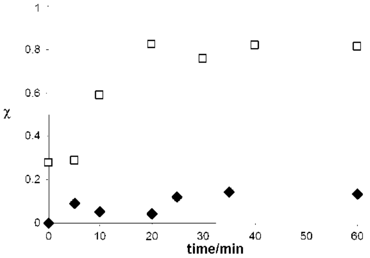

Figure 4. Variation in the extent of photooxidation of SAMs of MUA (squares) and DDT (diamonds) on exposure to UV light.

Monolayers of dodecanethiol (DDT) were also exposed to 254 nm UV light, and SIMS spectra recorded. In contrast to the MUA SAMs, the DDT SAMs oxidized very slowly (Figure 4). This is consistent with the observation of Ferris and Rowlen that decanethiol SAMs did not appear to oxidize when exposed to 254 nm light in the absence of ozone. Our data do not necessarily contradict theirs, therefore, but indicate the diversity of behavior that may be observed with different thiols under different conditions. The clear difference in the behavior of DDT and MUA SAMs on exposure to UV light represents a stark contrast with the behavior observed in an earlier study with a medium pressure arc-lamp, when much more rapid oxidation was observed for DDT SAMs than for MUA SAMs.[17] It may be concluded that the photochemistry of SAMs may be strongly influenced by the chemistry of the terminal functional group and the nature of the light source. One possible explanation for the different behavior is that hydroxyl radicals are formed by the interaction of UV light with water adsorbed onto the hydrophilic MUA SAMs. However, this remains a speculative hypothesis. What is clear from these data is that SAMs exhibit a diverse range of behavior during exposure to UV light. Previous studies have already highlighted the role of the alkyl chain length and terminal group chemistry in controlling photooxidation of SAMs on gold, and the present work supports this, emphasizing the importance of examining an adequately large range of SAM structures when conducting fundamental studies.

In summary, UV light with a wavelength of 254 nm leads to the rapid and complete photochemical oxidation of monolayers of mercaptoundecanoic acid. When a mask is employed during photooxidation, clear patterns may be formed. These data undermine the conclusions of previous studies that light of wavelength 185 nm is necessary to cause SAM oxidation. Different behavior is observed for monolayers of DDT, pointing to a diverse photochemistry for these important materials.

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