Fluorescence Detection of Surface-Bound Intermediates Produced from UV Photoreactivity of Alkylsiloxane SAMs

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Molecular-level engineering of surfaces, in studies ranging from wetting, 1,2 protein adsorption, 3 cell adhesion, 3,4 and chemical and bio-sensors, 5 often requires the determination of surface concentrations of chemical functional groups. However, the quantification of these surface functionalities can be a daunting task, a direct result of the small concentrations of surface species. Common surface characterization techniques, e.g., FTIR and XPS, have difficulty detecting surface groups below 0.01 of monolayer (ML, the maximum surface concentration of packed alkyl chains, 4.2 × 10^14 cm^−2). 6 Where concentrations are on the order of 10^{12} cm^−2. In addition, some techniques induce damaging perturbation. 7 In the area of biological 8–12 and polymer chemistry, 13–17 fluorescent labeling has long been used to both qualitatively and quantitatively monitor functionality. Fluorescent probes have also been used to study the structure and reactivity of self-assembled monolayers (SAMs). 18–21 An open question is whether the inherent sensitivity of fluorescence can be exploited to identify and quantify low concentration surface functionalities. In the present report, we show that covalent fluorescent labeling of surface species (FLOSS) can identify and detect low concentration, surface-bound intermediates resulting from exposure of alkylsiloxane SAMs to a UV/O_3 environment. 22

Although we suspected the presence of oxygen containing functionality in UV-irradiated siloxane SAMs, 22 FTIR and XPS measurements were inconclusive due to low signal levels. FLOSS enabled the detection of surface chemical groups in the range of 10^{11} to 10^{13} molecules/cm^2 by specific covalent attachment of fluorescent chromophores to surface functionalities, confirming the presence of oxygen containing functionality (OH, CO_2 H, CHO) as proposed earlier. 22 A significant advantage of this method was its ability to probe surface concentrations in the 10^{-4} to 10^{-2} ML range. Moreover, FLOSS did not require a UHV environment commonly needed for highly sensitive surface techniques such as XPS or SIMS.

UV irradiation of octadecylsiloxane (ODS) SAM in ambient resulted in a reduction of the contact angle and a loss of IR absorbance in the CH stretch region. 22 We hypothesized that UV irradiation of the SAM surface resulted in the formation of oxygenated functionalities. Three chromophores (pyrene, naphthalene, and trityl), with appropriate functionalities, were selected to covalently label CHO, OH, and CO_2 H groups, respectively. In all cases, the fluorescence from irradiated SAMs, that presumably contained oxygen functionality, was more intense than that from the unirradiated SAMs, which underwent the same derivatization reactions.

The specificity of the detection was demonstrated explicitly in the case of the derivatization of OH groups by triphenylmethyl chloride. The bare silicon control substrate displayed specific reactivity due to the existence of silanol groups, SiOH, on the native silicon oxide layer 6 (Figure 1). The presence of OH groups on the UV-irradiated SAM was also detected. In addition, the presence of CHO and CO_2 H on UV irradiated SAMs was indicated by 1-pyrenemethylamine (Figure 2) and 2-naphthaleneethanol (Figure 3), respectively. Reinhoudt et al. found that the fluorescence from ~0.3 ML pyrene attached to a NH_2-terminated SAM was dominated by excimer emission around 480 nm, 21 while in Figure 2 the emission was dominated by monomer emission near 390 nm. This provided evidence that the surface coverage of the attached pyrene was less than 0.1 ML. Therefore, little aggregation could occur.

Estimates of residual, nonspecific adsorption were made by adsorbing unsubstituted pyrene and naphthalene to the surfaces. Nonspecific adsorption on the bare SiO_2 was minimal. In the case of the irradiated SAMs, particularly with the pyrene moiety, we saw residual absorption consistent with surface concentration of (1–2) × 10^{11} cm^−2. The increased residual absorption was probably a result of roughening of the SAM surface upon photooxidation.

Having determined qualitatively the nature of the surface bound intermediates, we calibrated the fluorescence by measuring the peak fluorescence intensities for known amounts of chromophores de-
intermediates containing CHO, COH, and CO$_2$H groups. Carbonyl detection limits in cm$^2$ were determined to be 2.5 for CO$_2$H, and 0.5% by OH groups. CHO groups peaked at about 1.3% ML, consistent with Figure 2 that showed that little chromophore aggregation occurred. The CHO concentration dropped to 1.0 ML. The lower detection limit may be further improved by reducing nonspecific adsorption.

To gain a better understanding of the UV photooxidation process and the evolution of surface groups, the surface concentrations of the CHO, OH, and CO$_2$H were determined as a function of UV irradiation time in Figure 4. Up to 4.3% ML was functionalized by CO$_2$H groups and 0.5% by OH groups. CHO groups peaked at about 1.3% ML, consistent with Figure 2 that showed that little chromophore aggregation occurred. The CHO concentration dropped to 1.0 ML. This trend was expected since the concentrations of the intermediates produced by the photooxidation of CH groups should have also decreased as 80% of the CH groups in the SAM were depleted after 50 min of UV irradiation.22

In conclusion, FLOSS results suggested that the UV photoreactivity of siloxane SAMs proceeded through the formation of intermediates containing CHO, COH, and CO$_2$H groups. Carbonyl containing functionality comprises at most 5% of the surface during UV irradiation. This method was suitable for detecting low concentration surface groups (0.0001–0.1 ML). The lower detection limit may be further improved by reducing nonspecific absorption of chromophores. The upper limit was determined by the footprint of the chromophores used (3–4 surface sites of close-packed alkyl chains). The chromophores may not be able to attach to all the closely packed surface groups, and dye aggregation and fluorescence quenching at high concentrations makes quantification complicated.21 Nor did we expect the chromophores to attach to functional groups buried deep in SAMs. On the other hand, this limitation could potentially be an advantage of FLOSS, since one could use chromophores with different geometries to access information about lateral and vertical spatial distributions of functional groups, (e.g., phase segregation), which is difficult to achieve with XPS or SIMS. FLOSS opens the door to addressing biophysical,3 aerosol chemistry,23 and nanoscience questions that are in need of detecting low surface concentrations of chemical functionalities.

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Supporting Information Available: Mechanisms of labeling reactions, experimental details, XPS and IR results, and additional calibration plots (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References


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