



Rapid degradation of alkanethiol-based self-assembled monolayers on gold in ambient laboratory conditions

Trevor M. Willey^{a,b,*}, Andrew L. Vance^a, T. van Buuren^a, C. Bostedt^{a,1},
L.J. Terminello^a, C.S. Fadley^{b,c}

^a Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA

^b University of California, Davis, CA 95616, USA

^c Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Abstract

Self-assembled monolayers (SAMs) consisting of alkanethiols and similar sulfur-containing molecules on noble metal substrates are extensively used and explored for various chemical and biological surface-functionalization in the scientific community. SAMs consisting of thiol- or disulfide-containing molecules adsorbed on gold are commonly used due to their ease of preparation and stability. However, the gold–thiolate bond is easily and rapidly oxidized under ambient conditions, adversely affecting SAM quality and structure. Here, the oxidation of dodecanethiol on gold is explored for various 12-h exposures to ambient laboratory air and light. SAM samples are freshly prepared, air-exposed, and stored in small, capped vials. X-ray photoelectron spectroscopy (XPS) reveals nearly complete oxidation of the thiolate in air-exposed samples, and a decrease in carbon signal on the surface. Near-edge X-ray absorption fine structure spectroscopy (NEXAFS) at the carbon K-edge shows a loss of upright orientational order upon air exposure. Alternatively, the oxidation of the thiolate is minor when SAMs are stored in limited-air-containing small 15 ml vials. Thus, care must be taken to avoid SAM degradation by ensuring alkanethiolates on gold have sufficient durability for each intended environment and application.

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* Corresponding author. Tel.: +1 925 424 6084; fax: +1 925 422 4665.

E-mail address: willey1@llnl.gov (T.M. Willey).

¹ Present address: Technische Universität Berlin, Germany.

1. Introduction

Solution exposure of alkanethiols to gold creates easily formed, relatively stable self-assembled monolayers that can be used for chemically or biologically functionalizing surfaces. The stability of such monolayers to ambient conditions is often taken for granted; however, recent reports have cast the assertions into doubt by suggesting a limited shelf-life for alkanethiols on gold under e.g. biological conditions [1]. This paper first reviews some of the literature on degradation of SAMs under different types of exposure, then presents additional data on alkanethiols exposed to air, and discusses this important aspect in preparing functionalized surfaces.

Early laser desorption experiments first saw oxidation features in hexadecanethiol on gold exposed to air [2] but did not quantitatively explore the stoichiometry and assumed (possibly incorrectly) that the oxidation was small. Other mass spectrometry desorption studies found $-\text{SO}_2^-$ (sulfinate) and $-\text{SO}_3^-$ (sulfonate) species at the ends of oxidized molecular fragments [3,4].

Later, a method for SAM removal using ultraviolet light and the associated ozone (O_3) produced was reported [5], with the ozone allegedly oxidizing the thiolates. Subsequently, photochemical removal methods using wavelengths insufficient to create O_3 from O_2 degraded and removed an oxygen-containing mercaptoundecanoic SAM, but were slow in removing an alkanethiol [6]. These studies concluded that UV light and the presence of oxygen could remove SAMs from gold surfaces. Further exploration supports ozone as a primary culprit for SAM degradation. In one study, SAMs were exposed to N_2 , pure O_2 , H_2O and O_2 , enclosed pressurized air, and O_3 . Only the O_3 exposed thiolates oxidized [7]. Another showed that the presence of light was not required to oxidize the SAMs, and that highly-crystalline, Au(111) substrates fare better than rougher surfaces, but in both cases, sulfur moieties oxidized to both sulfinate and sulfonate [8]. Additional reports conclude that for alkanethiols, oxidation occurs extremely rapidly and efficiently through ozone exposure [7,9–11].

Morphological changes have also been reported for degrading alkanethiols. Scanning tunneling

microscopy measurements found thiolates oxidize first at domain boundaries. The oxidized molecules begin forming a striped phase² [12] between pristine domains. A final “fluid” phase is both disordered and deforms the underlying gold surface [13].

The rapid degradation of sulfur–gold bonding must be understood for the utilization of SAMs, and even more importantly for use of more dilute surface-attached species such as catenanes or rotaxanes with a more exposed Au–S interface [14–17]. Here, we investigate the degradation of alkanethiols on substrates under ambient, atmospheric, laboratory conditions using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). For simple SAMs, the changes in the sulfur, carbon, and oxygen chemistry and stoichiometry using XPS are quantitatively explored for five dodecanethiol-on-gold samples: (1) a freshly prepared sample, (2) a sample stored in capped vials in darkness, (3) a vial-stored sample under fluorescent lighting, (4) a sample simply exposed to air in the dark, and (5) a sample exposed to air in the light. XAS measurements were also carried out to investigate chemical and morphological changes on two samples: a fresh one, similar to sample (1) above, and a second exposed to ambient lighting and atmosphere overnight, in similar fashion to sample (5).

Compared to pristine films, SAMs oxidize readily when exposed to air, while oxidation is minor if the SAMs are stored in closed, air-containing vials. As the film oxidizes, the SAMs lose their ordered, orientationally upright nature.

2. Experimental

2.1. Reagents and materials

Reagents were purchased from commercial sources and used as received. Dodecanethiol (98%) was purchased from Aldrich. Ethanol (200

² Striped phases often appear during the formation (or in this case degradation) of self-assembled monolayers. They consist of molecules prostrate on the surface self-organized into parallel rows. They appear as “stripes” in STM measurements as seen in the two other references listed in this paragraph.

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