



A New Approach to Generate Thiol-terminated SAMs on Gold

Application Note

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Introduction

Organothiols on noble metals such as gold have been developed as a model system of self-assembled monolayers (SAMs). These organic thin films offer a spectrum of promising applications, including lubricating layers, corrosion inhibitors, lithographic resists, and chemical or biological sensors.

After the immersion of a gold substrate into an alkanethiol solution, thiols will spontaneously bind to the surface with the SH headgroups via a strong gold-sulfur interaction and typically adopt a standing-up configuration in the resulting closely packed monolayer, thus exposing the endgroups at the layer/medium interface. Tailoring the terminated chemical identity of self-organized assemblies renders an effective means to functionalize gold and tune the surface physical or chemical properties to meet specific requirements. In fact, rich endgroup chemistry is one of the primary advantages of SAMs and therefore defines many surface engineering applications. For example, SAMs capped with a polar hydroxyl or carboxylic acid functionality result in hydrophilic surfaces, whereas methyl-terminated layers are hydrophobic.

Due to the high affinity of SH groups to metals, thiol-terminated SAMs have attracted tremendous attention for potential applications such as fabrication of metal films on organic surfaces and construction of molecular electronic devices. From the viewpoint of the molecular formula, α,ω -alkanedithiol molecules are good candidates to produce SAMs presenting free SH groups if dithiols attach to gold through only one end and adopt a standing-up configuration, as in the case of alkanethiols. However, previous results from both spectroscopy

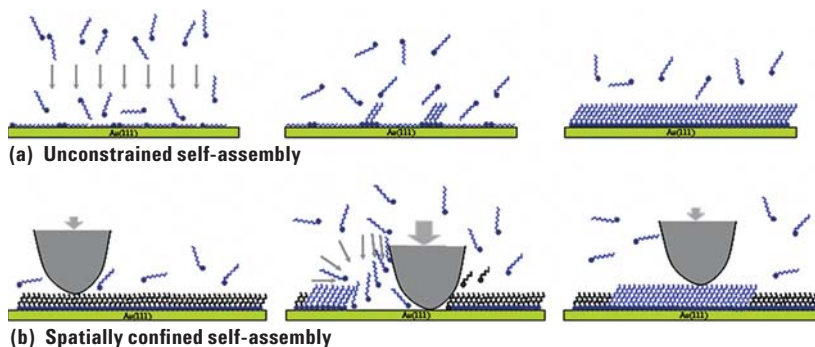


Figure 1. Schematic diagram of two different surface reaction pathways of thiol self-assembly on gold. (a) Unconstrained thiol adsorption occurs during natural self-assembly. (b) Spatially confined self-assembly occurs in nanografting.

and microscopy investigations have revealed that alkanedithiol SAMs are not densely packed when they are prepared from the most widely used approaches, namely, either by direct immersion into a dithiol solution or by exposure to a thiol solution. Indeed, adsorbed layers inevitably contain undesired dithiol molecules, which bind to gold with both ends to form alkanedithiolates and exhibit a lying-down or looped orientation.

The intrinsic cause of yielding dithiolate assemblies to a large extent can be ascribed to the reaction mechanism of thiol self-assembly on gold. Alkanethiols go through a multistep adsorption process to form a SAM in the case of natural growth, as illustrated in Figure 1a. Thiol molecules initially absorb onto gold with the hydrocarbon chains oriented parallel to the substrate. When the surface coverage of this so-called lying-down phase increases to near saturation, continuous collisions by thiols from solution induce a lateral pressure and lead to a two-dimensional phase transition, during which thiols reorient from an intermediate lying-down state to the ultimate standing-up configuration. Since the activation

energy of the phase transition step for organothiols with a single SH group is moderate, molecules can overcome the energy barrier and convert to an upright monolayer readily at room temperature.

Adsorption of alkanedithiols on gold following this self-assembly pathway leads to a different outcome. Like alkanethiols, dithiols lie down on the surface at the early adsorption stage. However, such an orientation allows or favors the dithiol molecules to react with gold to form alkanedithiolates. The additional thiolate bond (20 kcal/mol) dramatically stabilizes the lying-down phase and thus increases the activation energy for conformational transformation to a standing-up one. As a result, subsequent transition beyond intermediate phase is inhibited by this kinetics trap and dithiol molecules end up with the lying-down configuration in the resulting layer.

Effort has been invested to generate better quality thiol-terminated monolayers by preventing the unfavored dithiolates. A widely used approach is the introduction of special organodithiols with designed backbones into the typical SAM



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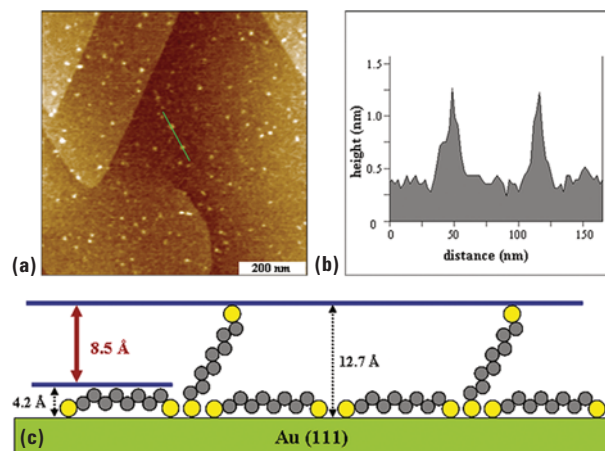


Figure 2. AFM characterization of a C8DT SAM prepared by the natural growth approach. (a) Topographic image showing protrusion dots sparsely distributed on the surface. (b) Cursor profile corresponding to the line drawn in (a). (c) Model of the theoretical height difference between a lying-down C8DT monolayer and a standing-up SAM.

preparation. Restricted molecular bending and rotation derived from inflexible backbones presumably inhibit dithiols from having good coupling of both ends with gold substrate and therefore make the desired upright orientation more likely to occur. Enhancement of molecular rigidity on dithiol species usually is achieved by incorporation of conjugated components such as aromatic rings and double/triple bonds in the molecular linkers. However, such molecular building blocks may involve complex and costly synthetic protocols. Furthermore, the outcome of this method is reduction but not elimination of dithiolates in the resulting SAM because the self-assembly pathway of these particular organodithiols is the same as that for simple n-alkanethiols.

Another alternative to facilitate upright dithiol layers is to immerse a previously formed SAM into an alkanedithiol solution, depending on the exchange/replacement reaction to transpire between adsorbed thiolates and dithiols in solution. Desorption of thiolated molecules from the substrate occurs individually and randomly, leaving the empty sites of gold both ultrasmall and constrained. As a result, backfilled dithiol molecules prefer to stand up upon the adsorption because the surrounding matrix layer sterically prevents them from lying down on the surface. The main drawbacks of this approach are the slow reaction kinetics and incomplete replacement of resist layers with dithiol SAMs.

Recently, a stepwise protection/deprotection strategy was reported by Wöll *et al.*¹ to improve the availability of free SH groups for dithiol SAMs. One of the thiol groups is first protected as the thioester functionality. After the organothiolate adlayer is formed, the protection group can be restored to SH by immersion into a NaOH solution. Instead of using simple alkanedithiols with an alkyl chain, organodithiols with a bulky aromatic linker are chosen in their study in order to avoid a less densely packed adlayer caused by the introduction of larger protected groups. Their approach also involves laborious sample preparation and requires delicate control of reaction conditions.

In this application note, we report a new and effective approach to achieve densely packed thiol-terminated SAMs on gold using simple nonrigid alkanedithiols, without the need for additional chemical treatments. The method applies an Agilent-licensed atomic force microscopy (AFM) lithography method known as nanografting² performed in a dithiol solution. Thiol adsorption on gold during nanografting follows a different reaction pathway (shown in Figure 1b) due to a spatial confinement effect.^{3,4} Unlike the case of natural growth, freshly exposed areas of gold produced in nanografting are confined by the AFM tip and surrounding undisturbed matrix molecules. Under controlled conditions such as with a slow fabrication speed or within a thiol solution with a high concentration, the transient bare gold is sufficiently small that reactive thiol molecules do not have sufficient room to assemble in a lying-down orientation.

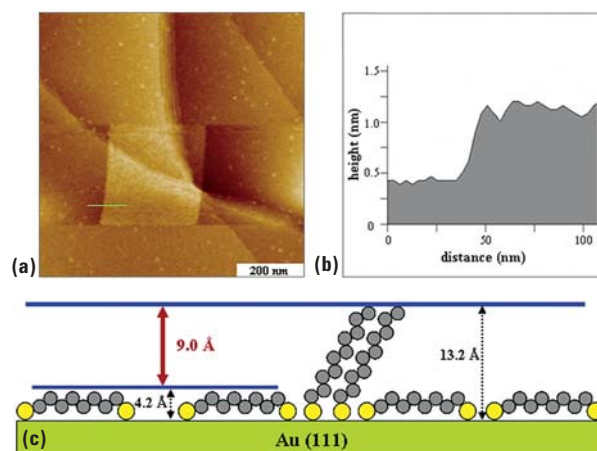


Figure 3. Probing the layer thickness of a naturally grown C8DT SAM. (a) The *in situ* topographic image showing fabrication of a C10 SAM into the C8DT SAM matrix. (b) Cursor profile corresponding to the line drawn in (a). (c) Model of the theoretical height difference between a lying-down C8DT monolayer and an upright C10 SAM.

The spatial confinement enables molecules to bypass the initial lying-down phase and adsorb onto the gold with a favored standing-up configuration directly. Consequently, a high-quality upright dithiol layer is expected.

Naturally grown alkanedithiol SAMs characterized by AFM

Investigations were initiated by characterizing the structure of 1,8-octanedithiol (referred to as C8DT) SAMs prepared by natural growth. The objectives were to validate our study with previous work and more importantly to generate a baseline for later structural comparisons of the same alkanedithiol SAMs formed via nanografting.

A high-resolution AFM topographic image of a C8DT SAM formed by soaking a Au(111) substrate in 0.02 mM C8DT solution for one week is presented in Figure 2a. The sample exhibits heterogeneous surface structures because some randomly distributed bright nanoscopic dots are clearly resolved from the surrounding layer. A cursor profile (Figure 2b) corresponding to the line drawn across two dots indicates that these protrusion islands are about 8 Å taller than the neighboring area. In theory, the thickness of a lying-down C8DT layer can be approximated by the Van der Waals diameter of an all-trans alkyl chain, which is 4.2 Å. Meanwhile, the calculated thickness of a close-packed standing-up C8DT monolayer is about 12.7 Å with the assumption that 1,8-octanedithiols follow the same orientation as 1-octanethiol

(i.e., tilts 30° from the surface normal) because they share the same linker structure and the terminal SH group is not bulkier than a methyl functionality. Therefore, the measured apparent height of islands ($8\text{ \AA}$) corresponds well to the expected theoretical difference in thickness between a standing-up ($12.7\text{ \AA}$) versus a lying-down ($4.2\text{ \AA}$) C8DT monolayer. It implies that the naturally grown C8DT SAM is mainly composed of lying-down molecules interspersed with some nanodomains of upright dithiols.

Another experiment was performed to measure the absolute thickness of the naturally grown C8DT SAM. The same sample was immersed in a dilute decanethiol solution in an AFM liquid cell. Using nanografting, decanethiol molecules (referred to as C10) can be fabricated as closely packed monolayer within the C8DT matrix layer, as in Figure 3a. A nanopattern ($285\text{ nm} \times 300\text{ nm}$) of C10 SAM was produced successfully on gold. The C10 SAM has a well-defined thickness and thus furnishes a molecular ruler for height evaluation. The C10 monolayer is about $8\text{ \AA}$ taller than the neighboring C8DT layer (Figure 3b), which matches the theoretical difference in heights between a lying-down C8DT monolayer and a typical C10 SAM, as illustrated in Figure 3c.

Combined results from AFM characterizations using both high-resolution imaging and nanolithography establish unambiguously that C8DT molecules assemble dominantly with a lying-down orientation for a naturally

grown SAM. The results are in good agreement with previous studies of the same system with other techniques. Using both ultrahigh vacuum scanning tunneling microscopy (UHV-STM) and Fourier transform infrared reflection-absorption spectroscopy (FT-IR-RAS), Kobayashi *et al.* investigated the structures of a C8DT SAM prepared from one-day immersion in a 1 mM ethanolic solution.⁵ In their work, molecularly resolved STM images clearly showed that all of the dithiol molecules within the C8DT SAM were arranged with the molecular axis parallel to the gold surface.

To the best of our knowledge, there are no AFM reports that identify a lying-down conformation of C8DT molecules in naturally grown SAMs. Furthermore, our AFM studies demonstrate the capabilities of the AFM technique to discriminate different molecular conformations of alkanedithiols on gold, since both lying-down and standing-up orientations of C8DT molecules in the monolayer are clearly differentiated. The coexistence of the upright conformation beside the lying-down orientation results from the extended immersion (7 days) used for our sample preparation.

Production of densely packed thiol-terminated SAMs via nanografting

Nanofabrication of C8DT molecules within a hexanethiol (referred to as C6) SAM matrix was performed as a proof-of-concept experiment for achieving high-quality thiol-terminated surfaces.

In situ AFM images before and after fabrication are displayed in Figures 4a and 4b, respectively. A rectangular pattern of C8DT was produced successfully by nanografting. The theoretical height of a C6 SAM is $8.8\text{ \AA}$ whereas that of a lying-down C8DT layer is $4.2\text{ \AA}$. The dithiol area would be lower than the C6 SAM if the C8DT molecules assemble as a lying-down monolayer. Since the pattern is shown to be taller than the surrounding matrix, it indicates that the C8DT molecules adsorb on gold with a desired standing-up conformation and form a SH-terminated surface.

The frictional images (Figures 4c and 4d) provide additional evidence that the functionality exposed on the surface of pattern area is a thiol group. With respect to the surrounding methyl-terminated matrix, the pattern area exhibits a larger difference in contrast for the two images, indicating greater frictional force between the fabricated C8DT SAM and the AFM tip during contact mode imaging. Compared to the methyl endgroup of a C6 SAM, the SH group is more hydrophilic due to higher polarity. The silicon nitride AFM tip is also hydrophilic, therefore a higher frictional force is expected between the SH group and the AFM tip because of the stronger hydrophilic-hydrophilic adhesion interaction.

The cursor profile in Figure 5b shows that the apparent height of fabricated C8DT SAM is about $5\text{ \AA}$, which is close to the theoretical height difference of $3.9\text{ \AA}$ between a C6 SAM and a standing-up C8DT monolayer following the previous

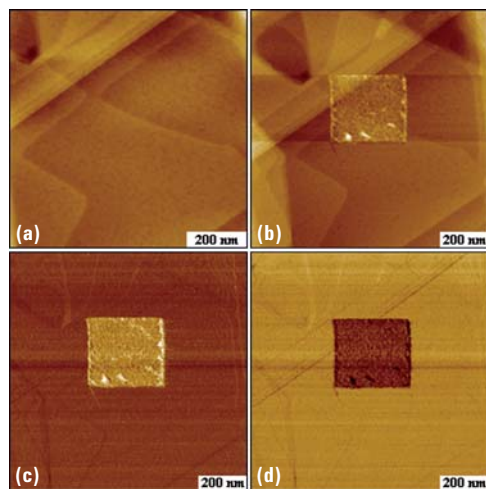


Figure 4. Construction of a SH-terminated SAM via nanografting. (a) Topographic image of the C6 SAM matrix before fabrication. (b) After nanografting, the resulting pattern of C8DT layer is taller than the surrounding C6 SAM. The corresponding friction trace (c) and retrace (d) images of (b).

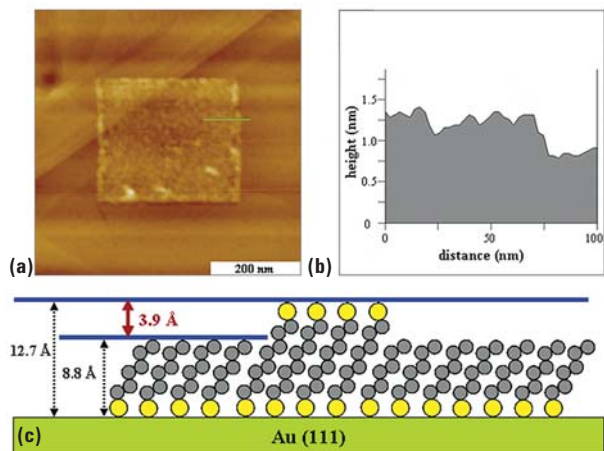


Figure 5. Quantitative measurement of the height of fabricated C8DT SAM. (a) A high-resolution topographic image showing that dithiol molecules are densely packed in the pattern. (b) Cursor profile corresponding to the line drawn in (a). (c) Side view of the orientation of dithiol molecules within the C8DT SAM based on the AFM study.

assumptions of molecular orientation. If the dithiol molecules were not densely packed, the measured height would be shorter. The nanografted C8DT SAM exhibits a different morphology compared to the surrounding n-alkanethiol SAM. The pattern area contains granular nanodomains, whereas the matrix areas are much smoother so that the underlying substrate structures such as the single atomic Au(111) steps are clearly visible. The observed nanodomain feature likely results from the aggregates formed by thiol terminal group interactions.

Conclusions

A new approach to fabricate high-quality thiol-terminated SAMs is reported. It involves a scanning probe lithography method known as nanografting in conjunction with knowledge of self-assembly chemistry. Using C8DT as an example, dithiol SAMs were prepared by both natural growth and spatially confined self-assembly. AFM characterizations clearly demonstrate that the C8DT

molecules of the fabricated SAM nanopatterns are densely packed with a preferred standing-up conformation, leading to a surface presenting free SH groups. The naturally grown layer is mainly composed of lying-down dithiol molecules with both SH endgroups chemisorbed to the gold substrate.

The improved availability of thiol groups from fabricated C8DT SAM is ascribed to the different reaction mechanism of nanografting, which favors the standing-up orientation of dithiols in the resulting SAM. Nanografting also allows the positioning of high-quality thiol-terminated layers on gold with nanometer-scale precision in geometry, size, and location. This capability is highly desirable as patterning of thiol-terminated SAMs with nanometer-scale spatial resolution is critically required in order to use these designed nanostructures as surface templates to direct metal deposition and construct prototype devices for molecular electronics.

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