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SFM Tip-Assisted Hydrolysis of a Dithiobis(succinimido undecanoate) Monolayer Chemisorbed on a Au(111) Surface

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Received May 9, 1997. Revised Manuscript Received September 2, 1997[®]

Abstract: This paper reports on the use of a scanning force microscope (SFM) for the *tip-assisted* base hydrolysis of an ester-terminated alkanethiolate monolayer on Au(111). We have found that contact imaging accelerates the base hydrolysis of a dithiobis(succinimido undecanoate) monolayer relative to the surrounding unimaged area. It is proposed that (1) the mechanical disruption by the SFM probe tip of the steric barrier imposed by the neighboring adsorbates facilitates access of hydroxide ions to the buried acyl carbons in the adlayer, and (2) the surface area hydrolytically transformed by this disruption can be controlled by the SFM imaging conditions. Findings in support of our conclusions are presented, and potential implications to nanotechnology are briefly discussed.

I. Introduction

The scanning probe microscopies have proven invaluable as surface characterization tools to an impressive range of fundamental and technological areas.^{1–4} We have, in parallel with the efforts of others,^{5–15} been exploring the use of the friction and adhesion modes of scanning force microscopy (SFM) as probes of the compositional transformations of interfaces at nanometer length scales.^{16,17} While continuing such investigations,¹⁸ we have discovered that the mechanical interaction between a SFM probe tip and various ester-functionalized

alkanethiolate monolayers can notably accelerate the rate of the base hydrolysis of the ester linkage in small, spatially defined locations. The following describes our initial findings using monolayers chemisorbed at Au(111) from dithiobis(succinimido undecanoate) (DSU). We also briefly speculate on the possible impact of this type of processing^{19–21} to the nanofabrication of surfaces for sensor technology.

II. Experimental Section

A. Sample Preparation. (i) Au(111) Substrates. Substrates were prepared by the resistive evaporation of 300 nm of gold onto freshly cleaved mica sheets. Upon removal from the evaporator, the substrates were oven annealed at 300 °C for 5 h. This processing results in a film with a predominate Au(111) surface crystallinity.¹⁷

(ii) Monolayer Films. Two different types of monolayer samples were prepared. The first type was used in the investigations of the tip-induced acceleration of the base hydrolysis for the DSU monolayers at Au(111). The second type was used as a control for the determination of the differences in the friction at both unhydrolyzed and fully hydrolyzed monolayers of DSU.

The first type of sample was formed by the immersion of the Au(111) substrates into a dilute (0.1 mM) ethanolic solution of DSU for 24 h. These samples were then removed from the formation solution, rinsed with copious quantities of ethanol, and air-dried. The synthesis of DSU followed literature procedures^{22,23} and will be detailed elsewhere.²⁴

The second type of sample was prepared using a more extensive procedure. This procedure, which yielded a compositionally patterned adlayer of both unhydrolyzed and fully hydrolyzed DSU, is composed of three general steps. Step 1 entailed the immersion of a gold-bound DSU monolayer into an alkaline (1 M KOH) aqueous solution for 6 h. This step, as determined with the use of infrared reflection spectroscopy (IRS),¹⁸ fully converts the succinimidyl terminus of the adlayer to a carboxylate moiety. Step 2 utilized “thiolate photolithography”²⁵ to construct a compositionally patterned adlayer. The patterns were

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[®] Abstract published in *Advance ACS Abstracts*, December 15, 1997.

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created by sandwiching a copper transmission electron microscopy (TEM) grid (2000 mesh (hole size $7.5\ \mu\text{m}$, bar size $5.0\ \mu\text{m}$)) between a DSU-coated sample and a quartz plate. A 200-watt, medium-pressure mercury lamp (Oriel) was used as the light source. The beam was collimated, reflected off an air-cooled, dichroic mirror (220–260 nm), focused by a fused silica lens, and passed through the TEM grid before impinging onto the sample surface. The power at the sample was estimated at $550\ \text{mW}/\text{cm}^2$. Exposure times were $\sim 20\ \text{min}$. Overall, this process converts the irradiated gold-bound thiolates to various forms of oxygenated sulfur (e.g., RSO_3^-)²⁶ which are readily rinsed from the surface with most organic solvents. Step 3 involved the removal of the oxygenated sulfur species by rinsing extensively the irradiated samples with deionized water and ethanol. After drying under a stream of argon, the samples were reimmersed into the dilute DSU solution for $\sim 12\ \text{h}$. Overall, the combination of the three-step processing results in a compositionally patterned surface, with DSU adsorbed in the squares and carboxylate-terminated adsorbates confined in the grids.^{18,27}

B. Instrumentation. (i) Scanning Force Microscopy (SFM). All images were collected using a $12\text{-}\mu\text{m}$ tube scanner, SFM fluid cell, and Digital Instruments Multi Mode NanoScope III. The force constant of the triangular Si_3N_4 cantilevers (Digital Instruments) for normal bending was $\sim 0.06\ \text{N/m}$ and for torsional bending was $\sim 80\ \text{N/m}$.¹⁷ Unless noted otherwise, all images (512×512 pixels) were collected in situ in $10\ \text{mM}\ \text{KOH}$ or in deionized water (pH 6.2) at a scan rate of $10.2\ \text{Hz}$.

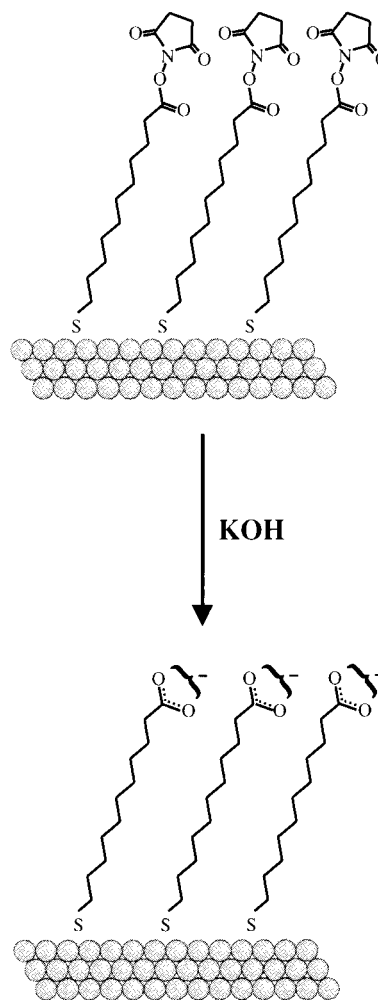
(ii) Infrared Reflection Spectroscopy (IRS). The progression of the base hydrolysis of the DSU monolayers at Au(111) was determined using IRS. These characterizations were performed in an ex situ mode for samples immersed in a $10\ \text{mM}\ \text{KOH}$ solution for varied periods of time. The emersed samples were rinsed with ethanol prior to mounting in the N_2 -purged chamber of a Fourier transform infrared spectrometer. The extent of the base hydrolysis was determined by the appearance of the symmetric ($1446\ \text{cm}^{-1}$) and asymmetric ($1590\ \text{cm}^{-1}$) carboxylate stretching modes that are characteristic of the immobilized product of the reaction.¹⁸

C. Data Analysis. The determinations of the extent of the base hydrolysis from the SFM images were performed using the Bearing Analysis resident in the NanoScope III software. This analysis sets a threshold in the magnitude of a z displacement (i.e., height or friction) and calculates the total percentage of the surface above the reference plane set by the threshold.

III. Results and Discussion

A. Concepts and General Observations. Scheme 1 idealizes the molecular architecture and base-hydrolyzed transformation of an ester-functionalized monolayer that forms at Au(111) from a dilute ($0.1\ \text{mM}$) ethanolic solution of DSU.^{22–24} Characterizations of the rate for the hydrolysis of the ester linkage of the adlayer using IRS indicate that the full conversion of the succinimidyl terminus to the corresponding carboxylate moiety requires more than 2 h for completion in an alkaline ($10\ \text{mM}\ \text{KOH}$) solution.²⁸ This rate is ~ 1000 times slower than found for solution-phase analogs.²⁹ As discussed in investigations of similar systems,^{30,31} this low rate of conversion reflects, in part, the steric hindrance that is imposed by

Scheme 1



neighboring adsorbates upon the attack of hydroxide ions on the acyl carbon of the buried ester groups.³⁰

The remaining sections of this paper present our evidence for the tip-assisted base hydrolysis. We begin by discussing the underpinnings for the analysis of the SFM data in terms of the compositional changes that arise from the base hydrolysis of the DSU monolayers. We then demonstrate that the rate of the base hydrolysis is *enhanced* by the direct physical contact of the probe tip with the DSU adlayer during the SFM imaging process.

B. Detection of the Compositional Changes of DSU Monolayers at Au(111) by SFM from Base Hydrolysis. The analysis of the SFM images regarding the chemical transformation that results from the base hydrolysis of the ester linkage of the DSU monolayers chemisorbed at Au(111) relies on the sensitivity of frictional imaging to the chemical composition of the outermost few angstroms on an interface.^{8–11,17} As recently demonstrated,¹⁷ the observed friction at the microcontact formed between a SFM probe tip with a high surface free energy (e.g., uncoated Si_3N_4) and a sample with a high surface free energy is greater than that for a sample with a low surface free energy.³² Wetting characterizations using water as a probe liquid yield an advancing contact angle for a DSU monolayer and fully hydrolyzed DSU monolayer of 50° and $\sim 0^\circ$, respectively.²² It then follows that the friction measured when an

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(27) Under these conditions, there was no detectable displacement of the carboxylate portion of the patterned surface by solution-based DSU, as judged from IRS.

(28) We have also characterized the base hydrolysis of several other ester-terminated monolayers, including the methyl, ethyl, and butyl mercaptohexadecanoate. In contrast to a DSU monolayer, the rates for the base hydrolysis of the latter adlayers were markedly slower and, because of instrumental drift, were not amenable to in situ imaging. For example, the monolayer of the methyl ester required nearly seven days before complete transformation.

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(32) The torsional response in a SFM friction measurement because of differences in surface composition and packing density can be convoluted with changes in topography and elasticity,^{5,10} respectively.

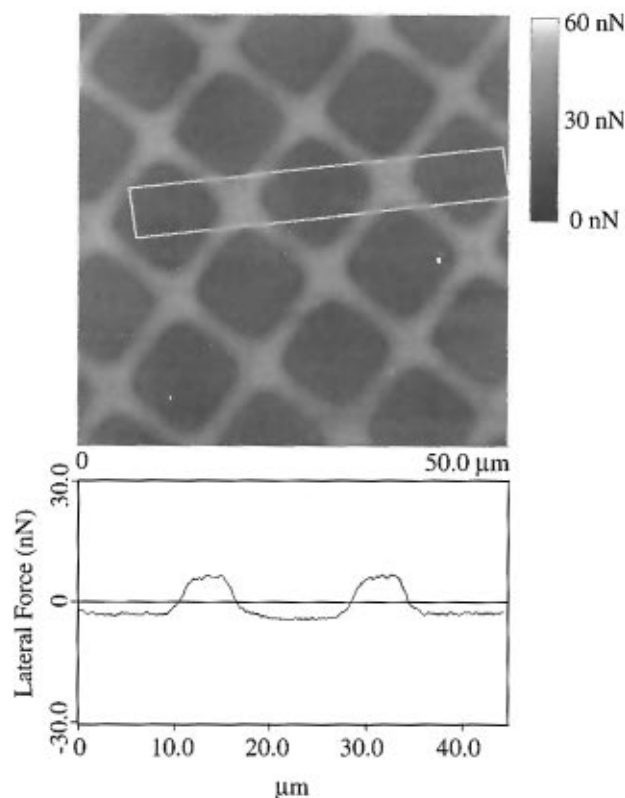


Figure 1. Friction image (50.0 $\mu\text{m} \times 50.0 \mu\text{m}$) of a sample patterned with regions of DSU and fully hydrolyzed DSU monolayers recorded in deionized water (pH 6.2). The light regions (the grids) are areas of high friction and correspond to surface regions terminated with carboxylate adsorbates. The dark regions (the squares) are areas of low friction and correspond to the surface regions with an adsorbed DSU monolayer. The image was acquired at a load of ~ 25 nN and scan rate of 5.5 Hz.

uncoated Si_3N_4 tip is in contact with a DSU adlayer should be lower than that when an uncoated Si_3N_4 tip is in contact with a fully hydrolyzed DSU adlayer.

The in situ image of the compositionally patterned sample in Figure 1 is consistent with the general tenants of the above analysis and quantifies the differences in the friction for an adlayer of DSU and its base-hydrolyzed analog. This sample, which was imaged in deionized water (pH 6.2) at a load of ~ 25 nN, was prepared using thiolate photolithography²⁵ (see Experimental Section) and was patterned to consist of a DSU adlayer in the squares and a carboxylate-terminated adlayer (i.e., regions of fully hydrolyzed DSU) in the grids. As is evident, the observed friction for the adlayer in the squares is ~ 10 nN lower than that for the adlayer in the grids. Furthermore, an analysis of friction loops (not shown) reveals that the friction between an uncoated Si_3N_4 probe tip and unhydrolyzed DSU monolayer is ~ 30 nN, whereas that between an uncoated Si_3N_4 probe tip and fully hydrolyzed DSU monolayer is ~ 40 nN. These observations are consistent with the earlier predictions based on considerations of the differences in the surface free energy of the two types of samples.

It is also important to establish the level at which the observed friction changes can be correlated with the extent of the compositional change induced by the base hydrolysis of the DSU adlayer. As such, compositional changes were followed using IRS via the growth of the symmetric and asymmetric carboxylate stretching modes. These experiments were conducted by immersing a freshly prepared DSU monolayer into 10 mM KOH for differing periods of time, and characterizing the carefully rinsed sample via IRS.³³ These results were then compared to

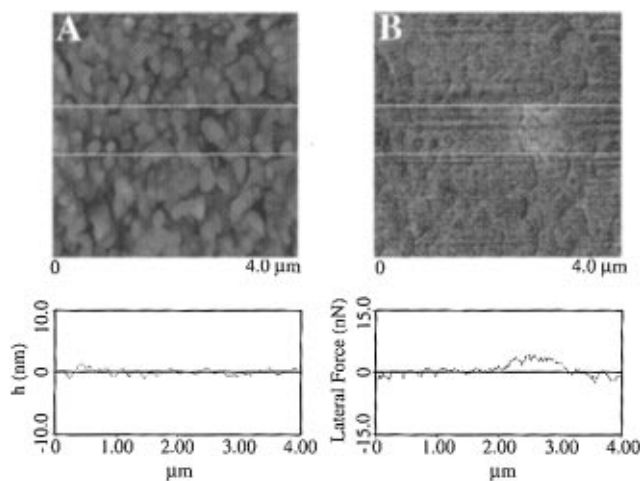


Figure 2. In situ topographic (A) and friction (B) images (4.0 $\mu\text{m} \times 4.0 \mu\text{m}$) and cross sections of a DSU monolayer chemisorbed at Au(111) after immersion for 1 h in an alkaline (10 mM KOH) aqueous solution. The y axis of the cross-sectional profiles for Figure 1A,B are the "height" and "lateral signal", respectively. These images were acquired at a load of ~ 25 nN and scan rate of 10 Hz after repetitively scanning for 1 h at a load of ~ 25 nN the 1.0 $\mu\text{m} \times 1.0 \mu\text{m}$ area that is evident to the right of the center of the friction image. Both cross-sectional plots represent the results of averaging cross-sectional analyses.³⁴

the compositional changes determined using Bearing Analysis from the in situ images of samples (i.e., samples not repetitively scanned) immersed in 10 mM KOH. This comparison, which will be reported in detail elsewhere,¹⁸ indicated that (1) the extent of the transformation determined using the two different techniques differed by no more than 10% for all immersion times, and (2) the detectable difference (i.e., sensitivity) in the extent of the transformation from the analysis of the friction data was 10%. The next section presents evidence for the tip-assisted hydrolysis of a DSU monolayer, with the data examined within the context of the above analytical figures of merit.

C. Tip-Assisted Hydrolysis. Evidence for the *tip-assisted* acceleration of the base hydrolysis for a DSU monolayer chemisorbed at Au(111) that arises from contact imaging is presented by the 4.0 $\mu\text{m} \times 4.0 \mu\text{m}$ images in Figure 2. Figure 2A contains a topographic image and cross-sectional profile,³⁴ with the corresponding frictional image and cross-sectional profile shown in Figure 2B. These images were collected after continually scanning a 1.0 $\mu\text{m} \times 1.0 \mu\text{m}$ area that was located slightly to the right of the center of the images for 1 h at a load of ~ 25 nN. Both images indicate the presence of large (100–300 nm), atomically smooth terraces.³⁵ More importantly, the friction image reveals the effect of both the exposure to and repetitive scanning of the sample in the alkaline solution. The latter two observations, which are discussed below, reflect the sensitivity of frictional imaging to changes in chemical composition as demonstrated in Figure 1.

The friction image provides insight into the compositional changes of the sample in two ways. The first insight develops by examining the image outside the repetitively scanned area.

(33) An assessment of the possible change in the orientation of the adlayer as a function of the extent of the hydrolysis, based on the constancy of the relative absorbance of the symmetric and asymmetric carboxylate structures, indicated that such an effect on the compositional analysis is small (i.e., a few percent).

(34) The cross-sectional analysis was performed by averaging the individual lines in the area bound within the delimiting markers in the images.

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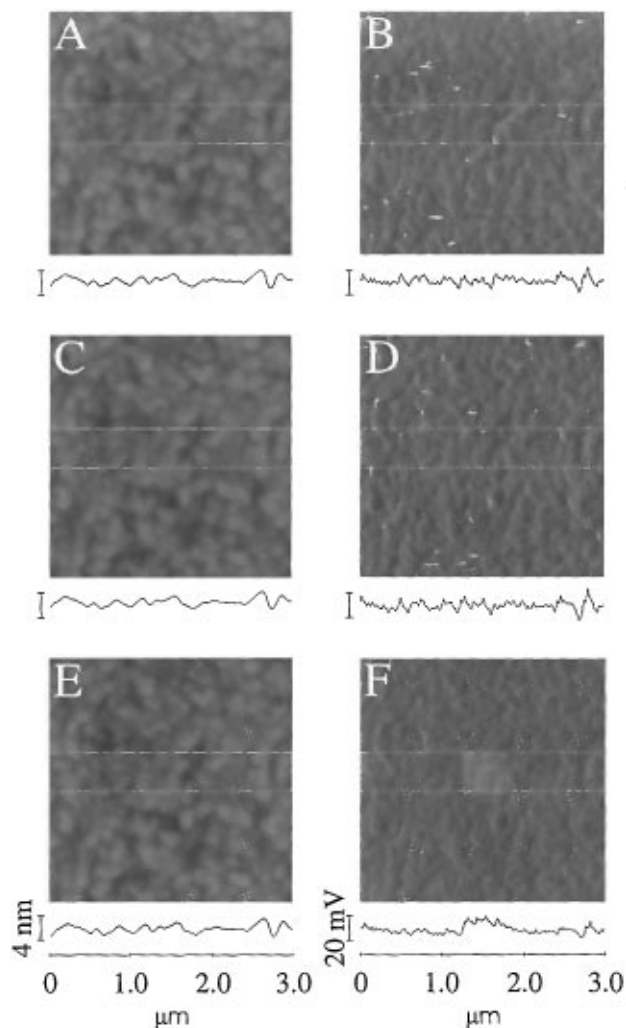


Figure 3. In situ topographic (A) and friction (B) images ($3.0\ \mu\text{m} \times 3.0\ \mu\text{m}$) and cross sections of a DSU monolayer chemisorbed at Au-(111) in the SFM liquid cell filled with deionized water (pH 6.2); in situ topographic (C) and friction (D) images of the same imaged area in A and B after repetitively scanning a $0.50\ \mu\text{m} \times 0.50\ \mu\text{m}$ area located in the center of the images while under deionized water; and in situ topographic (E) and friction (F) images of the same area in A and B after exposing the sample to an alkaline (10 mM KOH) aqueous solution for 30 min (see the caption for Figure 2 for further details).

This examination reveals the presence of small (50–80 nm), localized regions of high friction ($\sim 40\ \text{nN}$) interspersed among identifiable regions of low friction ($\sim 30\ \text{nN}$). These differences, which are superimposed on the response originating from changes in topography, reflect the partial conversion (68%) of the DSU monolayer from an ester to carboxylate end group. That is, the regions of high friction correspond to domains in the adlayer composed largely of carboxylate end groups, and the regions of low friction correspond to domains comprised largely of the ester terminus of the unhydrolyzed DSU adlayer.

The second insight, which is of critical importance to our principal assertion, develops from a comparison of the friction observed in the repetitively scanned region to the area surrounding this region. Importantly, the fraction of the area (87%) in the repetitively scanned area with a high friction is identifiably greater than that found in the surrounding region (68%). Thus, the DSU adlayer in the repetitively scanned region is more extensively hydrolyzed than that in the surrounding region.

At issue, then, is how contact imaging enhances the rate of the hydrolytic transformation. We believe that the probe tip induces a localized disorder in the outer portion of the structure

of the adlayer. This disorder enhances access of hydroxide ion to the acyl carbon of DSU, which accelerates the hydrolysis in the repetitively scanned area. In other words, the repetitive scanning process results in a *tip-assisted* hydrolysis, with the tip acting like a nanoscale stirring bar.

As a further test of this possibility, we repetitively scanned an area on a freshly prepared DSU monolayer under deionized water (pH 6.2). We note that IRS experiments for samples immersed in deionized water for extended periods of time (e.g., 5 h) did not detect the presence of a carboxylate species, indicating that the transformation of the ester linkage of DSU is exceedingly slow at pH 6.2. Figure 3A,B presents the respective $3.0\ \mu\text{m} \times 3.0\ \mu\text{m}$ height and friction images obtained after filling the in situ cell of the SFM with deionized water. Next, a $0.50\ \mu\text{m} \times 0.50\ \mu\text{m}$ region that was located near the center of the images in Figure 3A,B was repetitively scanned at the same rate and load as used for Figure 2. After 1 h of continual scanning, the scan area was increased to $3.0\ \mu\text{m} \times 3.0\ \mu\text{m}$, and the images in Figure 3C,D were acquired. These images, which encompass the repetitively scanned area, are notably devoid of evidence for a change in friction. Importantly, this result shows that the observed change in the friction for the repetitively scanned area in Figure 2B is not from a detectable tip-induced wear of the sample surface.

If, however, the sample in Figure 3C,D is subsequently exposed for 30 min to the alkaline aqueous solution in the absence of scanning, the images in Figure 3E,F are obtained.³⁶ This exposure results in the appearance of a localized, square-shaped region of high friction that coincides with the location of the repetitively scanned area. In this case, the fraction of the area in the repetitively scanned region with high friction is 95%, whereas that in the surrounding region is 32%. We therefore conclude that the enhanced rate of hydrolysis results from a subtle tip-induced disordering of the outer portion of the DSU adlayer that increases the accessibility of hydroxide ion to the acyl carbon of the buried ester functionality. In support of this interpretation, the first results from ongoing experiments have shown that the tip-assisted enhancement of the hydrolysis rate is dependent on the load such that a higher load increases the enhancement and vice versa.

IV. Conclusions

Studies to delineate the range and scope of this new approach to localized surface modification are underway, driven mainly by the possibility of creating chemically inhomogeneous patterns of nanometer scale dimensions for sensor design. We are particularly interested in defining the lower limit in the size of an area that can be transformed and the conditions requisite to confining the modification to only the repetitively scanned area. We are also pursuing experiments aimed at furthering insight into the extent (e.g., contact area and depth of penetration) of which the tip interacts with the sample surface, and whether solvent uptake (i.e., hydration) in the scanned regions plays a role.

Acknowledgment. This work was supported in part by the Office of Basic Energy Sciences, Chemical Science Division, of the U.S. Department of Energy, the National Science Foundation (BIR-9601789), and the Microanalytical Instrumentation Center of Iowa State University. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under contract no. W-7405-eng-82.

JA9715051

(36) Images encompassing the repetitively scanned area that were acquired immediately after the addition of 10 mM KOH into the in situ cell were also devoid of evidence for a frictional change.