Kinetics of Exchange of Alkanethiol Monolayers
Self-Assembled on Polycrystalline Gold

Gabriel G. Baralia, Anne-Sophie Duwez, Bernard Nysten, and Alain M. Jonas*

Unité de Physique et de Chimie des Hauts Polymères and Research Center on Micro- and Nanoscopic Materials and Electronic Devices, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

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We report on the exchange between a hydrophilic thiol (11-mercapto-1-undecanol) in a liquid or gas phase and a hydrophobic thiol (dodecanethiol) of similar length self-assembled on a polycrystalline gold surface for a wide range of temperatures and times. The molecular composition of the mixed monolayers is determined by the static water contact angle and X-ray photoelectron spectroscopy measurements. Atomic force microscopy in lateral force mode is used to characterize the molecular domains at the nanometer level. The exchange first occurs rapidly at the gold grain boundaries, with an activation energy of about 66 ± 4 kJ/mol. Then, boundaries of ordered thiol domains are progressively replaced, and the exchange is slowed because only regions of increasing perfection are left untouched. Higher temperatures lead to faster kinetics of replacement and the removal of larger amounts of the original thiol. No significant difference could be detected between exchange occurring in an ethanol solution or in the gas phase, and the initial rate of exchange was found to be similar for the displacement of dodecanethiol by 11-mercapto-1-undecanol molecules and for the converse displacement.

Introduction

Self-assembled monolayers (SAMs) on metallic surfaces, especially gold surfaces, have been extensively studied because of their relevance to scientific and technological applications such as corrosion inhibition, lubrication, and chemical and biological sensing. Molecular device fabrication, and surface patterning. Other advantages are their ease of preparation, well-defined structure, and capacity to incorporate a wide range of functional groups by the proper selection of the backbone and end group of their constituent molecules. SAMs are also increasingly employed to fabricate surfaces patterned on the micrometer or nanometer scales, which are subsequently used to direct the location of processes such as adsorption, microphase separation of block copolymers, and so forth. The fabrication of such binary nanopatterned surfaces frequently involves the deposition of a first SAM at specific locations, followed by the deposition of a background SAM in remaining regions of the substrate. This raises the issue of possible exchange reactions occurring during the second deposition, especially for SAMs based on the chemisorption of thiols on gold, which are characterized by a relatively weak bonding energy. In this article, we investigate kinetic parameters controlling this exchange reaction for alkanethiols identical in chain length but different in terminal functionality and grown in SAMs on gold either from the liquid or gas phases. Data were acquired by analytical techniques able to measure ensemble properties of the sample (i.e., X-ray photoelectron spectroscopy, XPS, and contact angle measurements) and a technique able to distinguish nanometer-level properties of the sample (i.e., atomic force microscopy in lateral force mode, AFM-LFM).

Previous works on thiol exchange concentrated on the structure of SAMs after exchange. An important issue investigated by previous researchers is whether mixed or separated domains are formed during the exchange. The first studies pointed out that alkanethiols with different chain lengths or terminal functional groups form mixed monolayers after exchange rather than discrete domains. However, subsequent studies essentially pointed to the formation of separated domains after thiol exchange. Chadsey et al. studied the replacement of ferrocene-terminated alkanethiols by a long-chain...
ankanethiol and concluded that fast replacement occurs on domain boundaries of the first SAM, whereas a slower replacement of ferrocene-terminated ankanethiols is detected inside the domains. Collard and Fox also reported, for ferrocene-terminated ankanethiols, fast replacement near defect sites and a much slower replacement in the inner part of crystalline domains of the SAM. Similar results were obtained by Aizenberg et al. using condensation figures for SAMs of ankanethiols supported on micropatterned metal substrates. Likewise, Lin and Guyot-Sionnest established that the replacement of di- (phenylethynyl)benzenethiol by decanethiol on Au(111) starts at domain boundaries. Arenethiol domains can be progressively suppressed and disappear completely for very long replacement times. Kakihuchi et al. showed domainwise replacement of hexadecanethiol monolayers by 12-mercaptodecanoic acid and also significantly slower replacement of 12-mercaptodecanoic acid by hexadecanethiol, suggesting the importance of lateral hydrogen replacement of 12-mercaptodecanoic acid by hexadecanethiol and also significantly slower domainwise replacement of hexadecanethiol monolayers to ease characterization.

**Experimental Section**

**Chemicals.** Ethanol (spectroscopy grade, Merck), dodecanethiol (98%, Acros), 11-mercapto-1-undecanethiol (95%, Aldrich), H2SO4 (98%, Fisher), and H2O2 (30%, Merck) were used as received. Water was purified (resistivity = 18.2 MΩ cm) using a Milli-Q Plus water system (Millipore).

**Preparation of Template-Stripped Gold Surfaces (TSGs).** We adapted a procedure reported by Wagner et al. Substrates of Si (100) (ACS—France) wafers are cut into ca. 2 cm × 2 cm pieces, washed for 30 min in piranha solution (1:1 concentrated H2SO4:30% H2O2) rinsed with deionized water, and then dried under a flow of ultrapure argon. (Caution: piranha solution reacts violently with organic compounds and should be handled with great care!) A 100-nm-thick layer of gold followed by a 200-nm-thick layer of titanium was vapor deposited on the silicon wafers in an Edwards Auto 306 vacuum coating system. Next, a 400-nm-thick layer of silicon dioxide was deposited by power enhanced chemical vapor deposition (PECVD) to enhance the mechanical properties of the multilayer. The Au—Ti—SiO2-deposited silicon pieces were glued face down onto glass slides with an epoxy glue (EpoTek 377, Gentek—Benelux). Curing was finished by holding the multilayered stack at 160 °C for 2 h. These Si—Au—Ti—SiO2—epoxy-glue glass slides can be stored for months without any loss of quality. Detachment of the Au—glass sandwich from the original silicon wafers can be done mechanically because gold does not adhere strongly to silicon wafers, thereby exposing the gold film. Immediately thereafter, the mechanically stripped fresh gold surfaces were washed abundantly with ethanol and used for monolayer preparation.

**Formation of the SAMs.** TSG films were immersed for more than 18 h in a 2 mM solution of dodecanethiol in ethanol. Similar homogeneous monolayers were obtained by gas-phase thiolization after 1 h of reaction. In this case, the thiolization was performed in a heated homemade glass reactor with an oversupply of pure argon to minimize the contamination of the samples. The reactor is similar to a setup reported previously for the gas-phase silanation of silicon. The thiol was lying on the bottom of the reactor, whereas the sample was placed on a platform to avoid contact with the thiol except through the gas phase. After removal from the thiol solution or from the reactor, the samples were rinsed abundantly with pure ethanol and blown dry with pure argon.

**Kinetics Studies.** Data and plots of the exchange kinetics were obtained on individual samples. Samples were removed from the dodecanethiol—ethanol solution, quickly rinsed with ethanol, blown dry with pure argon, and immersed again in a 2 mM solution of 11-mercapto-1-undecanethiol in ethanol for the case of liquid-phase exchange. Gas-phase exchange reactions were performed in the thiolization reactor at 60 °C. After each exchange reaction, the samples were rinsed with ethanol and blown dry with pure argon once again. The properties of these SAMs were investigated by contact angle measurements, lateral force microscopy (LFM), and X-ray photoelectron spectroscopy (XPS).

**Contact Angle Measurements.** Contact angles of water were measured at room temperature on the samples using the sessile drop method and an image analysis of the drop profile. The water droplet volume was 0.3 μL (Milli-Q water). Each determination was performed by averaging the results obtained on 5–10 droplets. The standard deviation associated with a set of measurements was about 0.8°; this value was taken as a higher bound for the error in the measurements. The values of the water contact angles presented in this article are static water contact angle values, θ (H2O).

**Lateral Force Microscopy.** LFM experiments were conducted with a PicoSPM equipped with a fluid cell and an environmental chamber (Molecular Imaging, Phoenix, AZ) controlled by Nanoscope III electronics (Digital Instruments, Santa Barbara, CA). The images were obtained in ethanol to reduce the capillary forces and enhance the chemical contrast using UV–ozone-cleaned silicon nitride cantilevers with a nominal spring constant of 0.05 N/m. LFM trace and force images were recorded for each sample. The two LFM images were superposed using a homemade procedure developed under Igor Pro (WaveMetrics, Portland, OR) that is based on the correlation between the two images. Briefly, the superposition
involves computing the shift (due to the hysteresis of the scanner) between the two LFM images. This shift can be obtained as the location of the maximum of the cross-correlation function of the two images. After the shifting of the retrace image, the two images were subtracted or added to produce two new images. The subtraction provides an image where each pixel value is related to the friction, with only limited incorporation of topography effects. The addition provides an image where each pixel value is proportional to the topography derivative (“slope”) without friction effects. This procedure allows us to separate the topographical and chemical (friction) information that is entangled in the raw LFM images. Typical LFM images and the result of this treatment are given as Supporting Information.

X-ray Photoelectron Spectroscopy. XPS spectra were collected on an SSX-100/206 spectrometer (Surface Science Instruments) using monochromatic Al Kα X-rays (1486.6 eV). The spectra were referenced to Au(4f7/2) at 84.0 eV. All of the spectra were recorded at a takeoff angle of 35° (angle between the plane of the surface sample and the entrance lens of the analyzer) with a 150 eV pass energy. Intensity ratios were converted into atomic ratios by using the sensitivity factors proposed by the manufacturer (Scoffield photoemission cross section). The XPS spectra were converted into atomic ratios by using the sensitivity factors proposed by the manufacturer (Scoffield photoemission cross section). The XPS spectra were referenced to Au(4f7/2) at 84.0 eV. All of the spectra were recorded at a takeoff angle of 35° (angle between the plane of the surface sample and the entrance lens of the analyzer) with a 150 eV pass energy. Intensity ratios were converted into atomic ratios by using the sensitivity factors proposed by the manufacturer (Scoffield photoemission cross section).

Results and Discussion

Homogeneous monolayers of dodecanethiol on poly-crystalline template-stripped gold (TSG) surfaces were first prepared from the gas or liquid phase as described in the Experimental Section. The exchange of self-assembled dodecanethiol molecules with 11-mercaptop-1-undecanol molecules in the liquid or gas phase was subsequently studied for various temperatures and times by water contact angle measurements, lateral force microscopy (LFM), and X-ray photoelectron spectroscopy (XPS) to obtain a multiscale view of the process.

The variation of water contact angle with exchange time is plotted for different temperatures in Figure 1, where open and closed symbols refer to exchange in the liquid and gas phases, respectively. (For comparison purposes, we also show data related to the exchange of self-assembled 11-mercaptop-1-undecanol molecules by dodecanethiol molecules (open triangles).) The decrease of the water contact angle mirrors the higher hydrophilicity resulting from the exchange of hydrophobic dodecanethiol by hydrophilic 11-mercaptop-1-undecanol molecules. After a rapid decrease of the contact angle with time, the rate of decrease is slowed, and the contact angle slowly approaches a limiting lower value for exchange times larger than 20 h.

The contact angle data were converted into a surface fraction of exchanged molecules, f, using Cassie’s equation

\[ \cos(\theta) = (1-f)\cos(\theta_1) + f \cos(\theta_2) \]  

where \( \theta_1 \) and \( \theta_2 \) are the contact angles of the starting and resulting surfaces, respectively, and \( \theta_1 \) is the contact angle of a homogeneous SAM of displacing molecules (i.e., 11-mercaptop-1-undecanol molecules for most experiments). The results are presented in Figure 2 (bottom). The data were fitted to exponential relationships, taking into account error bars on f computed from the 0.8° error associated with the measurement of contact angles. The initial rate of increase of the exchanged surface fraction, \( \frac{df}{dt} (t=0) \), corresponding to the initial slope of the fits in Figure 2 (bottom) is also plotted in Figure 2 (top) versus reciprocal temperature. Error bars were obtained from the diagonal components of the covariance matrix associated with the fits. The activation energy calculated from the five obtained values of \( \frac{df}{dt} (t=0) \) using the Arrhenius equation shows that this first stage of the process is thermally activated with an activation energy...
of 66 ± 4 kJ/mol over the probed range of temperatures. The initial rates of increase measured in the gas and liquid phases are identical within experimental error, indicating that the process does not depend on the affinity of the molecules of the SAM for the solvent used for the exchange. In addition, identical initial rates of increase of are found for the replacement of dodecanethiol by 11-mercapto-1-undecanol molecules and for the reverse situation where dodecanethiol molecules displace molecules of a SAM of 11-mercapto-1-undecanol.

XPS was used for selected samples to check quantitatively the validity of Cassie’s law. The number of dodecanethiol molecules exchanged by 11-mercapto-1-undecanol molecules in ethanol was estimated in two different ways. First, the surface fraction of OH-ended molecules was calculated from the ratio between the intensity of the O 1s peak from each sample (O) and the intensity of the O 1s peak from the monolayer adsorbed from a solution containing 11-mercapto-1-undecanol only (O_{oh,only}). (See Supporting Information for details.) Second, the ratio between the O 1s and S 2p components was also used to estimate the surface fraction of OH-ended molecules. The intensity of sulfur is attenuated by the 12-carbon-atom overlayer and must be corrected following the classical equation

\[ S = S_0 e^{-d(S/d)} \sin \alpha = 0.55S_0 \]  

where \( S \) is the measured intensity of the S 2p peak, \( S_0 \) is the intensity of sulfur photoelectrons in the absence of attenuation, \( d \) is the thickness of the dodecanethiol monolayer (12 × 1.27 cos 30° = 13.2 Å), where 1.27 Å is the incremental chain length per methylene group, \( S_0 \) is the typical tilt angle of the molecules in the SAM, \( \lambda \) is the attenuation length (39 Å at 1324.6 eV), and \( \alpha \) is the angle between the surface and the analyzer axis (takeoff angle). Table 1 compares the surface fraction of OH-ended molecules computed from the XPS data and S_{oh,only} ratios to the surface fraction of OH-ended molecules obtained from the application of Cassie’s law to contact angle values (\( f_c \)). XPS values are systematically larger than the values obtained from the contact angle data, with larger deviations being observed for samples where the exchange is more severe, which indicates that the relationship between the composition and the cosine of the contact angle may not be linear. However, because the activation energy for thiol exchange was computed from the data close to zero exchange time, the deviations from Cassie’s law should not significantly affect the so-derived value of the activation energy. Our data clearly indicate that SAM scrambling due to exchange can be limited to values below 5% by working at 5 °C for times shorter than 4 h. Other conditions result in significant displacement of the original thiol molecules, corresponding to surface fractions between 10 and 25%.

AFM—LFM experiments were performed to elucidate the reason for the slowing of the exchange kinetics with time and to visualize the location of the exchanged molecules. LFM was used because of its enhanced detection capability for features that are not visible in the topographic imaging mode. Figure 3 presents friction and slope images of a dodecanethiol monolayer before exchange. Gold grain boundaries are clearly revealed in the slope image. In addition, a much lighter and finer fluctuation in topography can be observed in single grains, which we ascribe to single domains of well-packed and organized dodecanethiol molecules separated by gold vacancy islands. Figure 4 shows similar images after exchange at 5 and 20 °C for various times in the liquid phase. After 4 h of exchange at room temperature (Figure 4A and B), bright stripes appear in friction images, corresponding to regions rich in 11-mercapto-1-undecanol that are of higher friction. The location of these stripes essentially coincides with gold grain boundaries (as revealed by the correspondence between slope and friction images), even though dodecanethiol molecules start to be replaced in other regions as well. For a longer exchange time (Figure 4C and D), 11-mercapto-1-undecanol-rich regions appear inside the grains of gold, where they decorate boundaries between ordered domains of dodecanethiol. If the temperature of exchange is reduced to 5 °C (Figure 4E–H), then a similar pattern of replacement is detected, albeit less marked. Whereas hardly any change can be detected after 4 h of exchange (which corresponds to only a 2° decrease of the contact angle), gold grain boundaries become decorated for longer exchange times at 5 °C.

For a higher exchange temperature (60 °C, Figure 5), 1 h of exchange is sufficient to replace a very large number of dodecanethiol molecules. Here again, 11-mercapto-1-undecanol-rich regions decorate the borders of remaining ordered domains of dodecanethiol, indicating that the exchange process still consists of the progressive eating away of dodecanethiol domains, starting from their more defective edges. These images confirm that a rapid exchange first occurs at locations where the packing of dodecanethiol molecules is less perfect, as on the boundaries between gold grains. With time, other regions are replaced as well, starting from domain boundaries and proceeding inward.

<table>
<thead>
<tr>
<th>exchange conditions (time, temperature)</th>
<th>surface fraction of OH-ended molecules (XPS)</th>
<th>water contact angle, experimental value (deg)</th>
<th>surface fraction of OH-ended thiols (contact angle), ( f_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 h at 5 °C</td>
<td>0.05&lt;sup&gt;a&lt;/sup&gt;</td>
<td>107</td>
<td>0.03</td>
</tr>
<tr>
<td>4 h at 20 °C</td>
<td>0.11&lt;sup&gt;a&lt;/sup&gt;</td>
<td>104</td>
<td>0.07</td>
</tr>
<tr>
<td>24 h at 5 °C</td>
<td>0.16&lt;sup&gt;a&lt;/sup&gt;</td>
<td>102.5</td>
<td>0.10</td>
</tr>
<tr>
<td>24 h at 20 °C</td>
<td>0.24&lt;sup&gt;a&lt;/sup&gt;</td>
<td>99.5</td>
<td>0.13</td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined from XPS based on the ratio between the O 1s signal and the S 2p signal corrected for attenuation according to eq 2.  
<sup>b</sup> Determined from XPS based on the ratio between the O 1s signal from each sample and the O 1s signal from a homogeneous 11-mercapto-1-undecanol layer.  
<sup>c</sup> Computed from the experimental contact angles using Cassie’s equation (eq 1).
As proposed previously,27,28 exchange thus occurs predominantly and more quickly in defective regions, where the structure is less ordered and where interchain van der Waals forces are weaker. Hence, because of the distribution of packing quality on real world gold surfaces, the exchange will proceed with different rates for different dodecanethiol molecules, giving rise to the complex kinetic behavior shown in Figures 1 and 2 (slowing of the exchange rate). Because the most defective regions correspond to gold grain boundaries, they may be associated with the initial fast replacement process of ~66 kJ/mol activation energy. For the slowing of the exchange at 60 °C, a number of phenomena can be acting concurrently. For instance, it is known that SAMs of alkanethiols in solution undergo significant desorption at high temperatures.19 Dry annealing also induces defects in monolayer domains.50 Moreover, increased temperature is known to favor the mobility of the molecules on the gold surface (lateral diffusion) and the formation of vacancy islands.51 This may also promote the coalescence between domains of freshly exchanged thiols.52 The balance between these different processes, together with the distribution of packing quality, results in the progressive slowing of the exchange kinetics and its apparent convergence toward a temperature-dependent limiting value for long exchange times.

Conclusions

In summary, we have studied the exchange between two thiols of identical length for a range of experimental conditions. The exchange first occurs rapidly in the most defective regions of the sample (i.e., the grain boundaries of gold), with an activation energy of about 66 kJ/mol. Then, boundaries of ordered thiol domains are progressively replaced, and the exchange is slowed as only regions of increasing perfection are left untouched. Higher temperatures lead to faster kinetics of replacement and the removal of larger amounts of the original thiol, and there is little difference between exchange occurring in an ethanol solution or in the gas phase. From a practical point of view, the exchange between dodecanethiol and 11-mercapto-1-undecanol can be minimized by working at lower temperatures using reduced contact times. From our value of activation energy, we predict that the initial rate of exchange can be decreased by a factor as large as 20 by working at -15 °C instead of at room temperature and by working at 5 °C for times shorter than 4 h; these are conditions that can be used now for the fabrication of unscrambled binary nanopatterned surfaces, as demonstrated elsewhere.18

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Supporting Information Available: Treatment of raw AFM images and XPS data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.