Nanografting Sodium Dodecyl Sulfate under Potential Control: new insights into tip-directed molecular assembly

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Abstract:

We have demonstrated that under potential control, sodium dodecyl sulfate can form ordered and stable patterns within nanoscale regions of a pre-existing SAM where thiol molecules have been mechanically removed. The results offer novel insights into the mechanism of nanografting and new routes to fabricating diverse chemical structures on surfaces.

Keywords: nanografting | sodium dodecyl sulfate | nanoshaving | self-assembled monolayer

Article:

Scanning probe-directed assembly of adsorbed molecules into well-ordered chemical structures on surfaces^{1,2} enables some of the highest-resolution chemical patterning techniques available. In particular, nanografting^{1,3-7} is capable of producing kinetically trapped patterns of alkanethiol monolayers with sub 10 nm feature sizes by using an AFM tip to mechanically desorb thiol molecules with large local forces (nanoshave) from a pre-formed alkanethiol self-assembled monolayer (SAM); a second thiol from solution ($\sim\mu\text{M}$) then rapidly forms an ordered and compact structure on the exposed gold surface.³ A remarkable phenomenon in nanografting is the accelerated self-assembly of thiol molecules: the ordered patterns of the second alkanethiol typically form within the desorbed regions before the surface can be imaged again by AFM. By

contrast, the formation of a SAM on an unpatterned gold surface requires hours at similar alkanethiol concentrations.⁴

It has been proposed that this accelerated assembly is a result of a ‘confinement effect’ in the gap between the tip and the SAM that is trailing the tip:^{4,8,9} during nanografting, the incoming thiol molecules are forced into an upright, oriented and compact structure, bypassing the time-consuming ‘lying-down’ phase of SAM growth from solution. To ensure that the gap is small enough to restrict the molecular orientation, the new thiol molecules must be incorporated within a few milliseconds at a typical tip writing speed of hundreds of nm s⁻¹. Despite the studies that rely on the effect to regulate the molecular scale structures of nanografted patterns,^{8,10} a detailed understanding of local interactions responsible for the many orders of magnitude acceleration remains to be achieved.

In this letter, we seek to elucidate the mechanistic details by performing nanografting under controlled electrode potentials, so that we can modulate the interactions between the head-group of the adsorbate (negatively charged sodium dodecyl sulfate, SDS) and the gold substrate. In contrast to past studies that rely on thiols, the sulfate groups used allow us to gain new insights into the roles of the head-group/surface interactions in tip directed self-assembly. We were able to nanograft ordered, long-lived structures of SDS that are laterally stabilized within an alkanethiol matrix. These ordered patterns are only formed during nanoshaving under positive applied potentials (Fig. 1), enabling dynamic control of the molecular patterns with time-varying applied potentials. However, in sharp contrast with alkanethiols, we are also able to ‘nanograft’ SDS patterns *that are entirely unconnected* to the matrix SAM. The results presented here suggest important mechanistic details about the role of the matrix SAM—beyond confining and orienting incoming molecules—as well as the structure of the underlying gold surface during nanografting ordered chemical patterns. Further, dynamic control of head-group/surface interactions during tip-directed assembly can potentially permit the facile generation of other higher-resolution chemical structures or nanoscale chemical gradients.

SDS was selected as a model molecule for nanografting because it only differs from a regular alkanethiol by the sulfate head-group (Fig. 1), whose interactions with the gold surface can be modulated by applying potentials to the electrode surface.^{11–13} SDS can form a number of ordered structures at the gold–water interface,^{12,14} such as hemispherical domes, half-cylinders, or condensed bilayers (*i.e.* interdigitated bilayers films of SDS molecules with melted alkane chains)¹⁵ depending on the electrode potential applied – even if the concentration is below the critical micelle concentration (cmc). As the solubility of alkanethiols in pure water is too low to allow tip-induced desorption of the SAM, 1 : 1 mixture of ethanol : water was used instead to improve the solubility.⁵ At the SDS concentrations in the patterning solution we use, 5 mM to 10 mM SDS in 1 : 1 ethanol : water, no formation of ordered structures on bare gold was observed *via* AFM (Fig. S1†) over the course of ~1 hour. The concentrations are higher than the micromolar concentrations of alkanethiols generally used for nanografting, but below the cmc of SDS.^{16,17}

Figure 1. Schematic of potential-controlled nanografting of sodium dodecyl sulfate (SDS) (inset), which has a negatively charged head-group attached to the alkyl chain. (A) A selected nanoscale region of a preformed alkanethiol self-assembled monolayer (SAM) is mechanically desorbed (nanoshaved) by the AFM probe in the presence of a SDS. (B) If the SAM is nanoshaved while the surface is held at 800 mV (vs. Ag/AgCl), an ordered bilayer of SDS forms. However, if the SAM is nanoshaved at 0 mV, no ordered SDS layer forms, even if the surface potential is later raised to 800 mV.

Figure 2. Nanoshaving a matrix C18 SAM in the presence of a SDS solution. (A) (left) Contact mode AFM image of regions nanoshaved when the surface was at open-circuit potential (OCP), no ordered chemical patterns are formed. (right) Height profiles show that the nanoshaved regions are not as deep as expected given the thickness of a C18 SAM, suggesting that there is a disordered layer of SDS. (B) At 800 mV (vs. Ag/AgCl), regions nanoshaved at OCP appear the same (top) while regions nanoshaved at 800 mV appear occupied with ordered layers of SDS molecules (bottom), whose height relative to the C18 SAM corresponds to that of a SDS bilayer. (C) These SDS patterns are stable even when a negative potential (−400 mV) is applied to the surface.

Under the open-circuit potential (OCP, ~ 280 mV vs. Ag/AgCl), a pre-formed monolayer of C18 was nanoshaved at a tip velocity of 800 nm s^{-1} . We observed features that are 1.2 nm lower than the surrounding monolayer (Fig. 2A). The depth is smaller than 2.2 nm , which one would expect for bare gold, but notably larger than the depth of an area with an ordered SDS monolayer, which should be only $0.5\text{--}0.6 \text{ nm}$. Therefore, we assume that the shaved areas are covered with a disordered layer of SDS.

As the electrode potential was raised to 800 mV , no change in the height of the regions that were shaved at OCP was observed (Fig. 2B) – the SDS did not spontaneously form ordered structures within nanoshaved pits even at positive potentials. However when we then nanoshaved nearby regions at 800 mV , these regions were 0.4 nm taller than the matrix C18 SAM (Fig. 2B and S2†). That these features are resolvable *via* contact-mode AFM suggests a significant measure of mechanical stability and orientational order. Condensed bilayers of SDS have previously been observed to form at gold–water interfaces when the electrode potential is higher than 450 mV .¹² These bilayers have recorded heights of 2.05 nm in water,^{11,12,15} but the thickness of surfactant bilayers has been found to be highly sensitive to solvent and it would be unsurprising for SDS bilayers to appear thicker within a C18. No qualitative differences were observed with a higher tip writing velocity (up to several $\mu\text{m s}^{-1}$, Fig. S3†), suggesting that the assembly is not diffusion limited, unlike the nanografting of thiols, which is carried out at lower concentrations.⁴ While we could mechanically desorb the molecules in the region by re-shaving over them at lower potentials (Fig. S4†), no change was observed in the SDS patterns as the potential was brought to -400 mV (Fig. 2C). By contrast, SDS on bare gold is completely desorbed at potentials as negative as -200 to -300 mV .¹¹ The remarkable stability indicates the degree to which alkane–alkane interactions stabilize the patterns in the matrix. The potential-induced desorption process likely requires structural defects in which the sulfate groups are exposed to water and high electric fields. Therefore unlike SDS layer on unpatterned gold, the SDS layer trapped in C18 is significantly more ordered and its desorption incurs a high kinetic barrier.

To determine the onset potential at which ordered SDS patterns could form, we nanoshaved a large square region while cyclically modulating the electrode potential between 0 mV and 800 mV (Fig. 3A and B). Initially sweeping the potential downwards from 800 mV to 0 mV at 25 mV s^{-1} , we observed a very sharp, discrete transition between ordered SDS pattern formation and disordered SDS at approximately 600 mV , close to the onset potential observed during step-wise tests of potential-dependent SDS patterning (Fig. S3†). Similar sharp potential-induced phase transitions in SDS layers on bare gold have been reported.¹⁴ The potentials of both the order $\rightarrow$ disorder transition ($V_{\text{o}\rightarrow\text{d}}$) and that of the disorder $\rightarrow$ order transition ($V_{\text{d}\rightarrow\text{o}}$) appear to be the same. Moreover the ordered patterns remained even while the potential was lowered below that threshold, which implied that the SDS structures were stabilized even when not confined on all sides by the ordered matrix. The heights of the ordered SDS patterns appeared smaller in these experiments (approximately the same height the C18 layer) than those embedded within the C18 matrix. When not completely surrounded by an ordered alkanethiol matrix, the bilayer patches may deform in response to pressure from the AFM tip during imaging or compress slightly to minimize the exposed area of the hydrophobic alkane chains.

Figure 3. (A) Nanografted patterns of SDS obtained by cyclically varying the potential between 0 mV and 800 mV during shaving (below). (B) Potential applied during nanoshaving for the respective patterns.

The previous experiment suggested that total confinement might not be necessary for ordered SDS patterns to nucleate on the surface during tip-directed assembly; that is, as the applied potential was swept above the $V_{d \rightarrow o}$ during the nanoshaving process, SDS still formed well-ordered structures even though no vertically aligned thiol or SDS molecules were present along the trailing side of the pattern to orient the incoming SDS. To test the extent of confinement by the (oriented) matrix SAM necessary for AFM-directed assembly of the bilayer SDS, we attempted to nanograft a ‘free-standing’, ordered SDS pattern that did not have any contact with the C18 matrix (Fig. 4A): first by nanoshaving a $300 \text{ nm} \times 300 \text{ nm}$ region at 0 mV to create a region that contains a disordered SDS layer, then nanoshaving a $100 \text{ nm} \times 100 \text{ nm}$ area within that pattern at 800 mV. Within the $300 \text{ nm} \times 300 \text{ nm}$ region, we observed an ordered pattern ($100 \text{ nm} \times 100 \text{ nm}$) that was disconnected from the matrix C18 SAM (Fig. 4B, left and S5†). The pattern appeared stable over several frames, did not grow in lateral dimensions, and did not spread out or diffuse.¹⁸ To our knowledge, such free-standing structures have not been reported in nanografting literature. The SDS pattern desorbed from the surface as the potential was lowered to 0 mV (Fig. 4B, right). The ordered structures did not form if, instead, the $100 \text{ nm} \times 100 \text{ nm}$ region was also nanoshaved at 0 mV (Fig. S6†). However, when we attempted to shave under the SDS solution on a bare gold surface with no pre-formed SAM at 800 mV (Fig. S7†) only local surface roughening was observed ($\sim 0.3 \text{ nm}$) in the nanoshaved regions and ordered SDS patterns were not formed. In addition, we also applied high local pressure under a dodecanethiol–ethanol solution on an area that had been nanoshaved (Fig. S8†). No features that were indicative of a nanografted SAM could be observed, confirming that in sharp contrast to the nanografting of SDS, confinement between the tip and an ordered SAM is necessary to form ordered nanostructures of alkanethiol. The results above raise the questions of (1) how the ordered SDS patterns are able to first form or nucleate on the surface without confinement, and (2) why the formation of the patterns requires both an applied potential and simultaneous nanoshaving (implying there are time-sensitive effects), and reveal unique roles for each of the following elements of nanografting under potential control: the electrode potential, the AFM tip, and the matrix SAM. Understanding their interplay and respective contributions can shed light on the molecular mechanism for nanografting without the ‘confinement effect’.

Figure 4. (A) Schematic of ‘nanografting’ ordered, free-standing (un-confined) SDS structures. (left) A large region (300 nm × 300 nm) is nanoshaved at 0 mV then (right) a 100 nm × 100 nm region inside that area is nanoshaved at 800 mV (disordered SDS not shown). (B) An ordered, nanografted SDS pattern that does not contact the C18 monolayer (left) imaged at 800 mV. (right) Imaged afterward at 0 mV.

The electrode potential modulates the interaction between the surface and the sulfate head-group, and in this case also helps to reduce repulsion between the charged sulfate head-groups and allows them to pack closer together.¹¹ While alkanethiols form a commensurate structure of which the lattice constant closely matches the van der Waals radius of the alkane chain,^{19,20} these potentials may be necessary to achieve surface densities needed to promote chain–chain interactions that stabilize the SDS pattern. The positive potential may help to orient the sulfate groups toward the surface during nanoshaving. In addition, the potential allows water to displace physisorbed alkane chains.^{21–23} Hence, compared to alkanethiol molecules that undergo slow transition from the lying down phase to the ordered stand-up phase, SDS molecules in lying down phase can more readily adopt an upright orientation that is needed to form a compact molecular layer. Therefore, nanoscale confinement by the tip and an ordered SAM may not be needed for nanografting SDS. Nanografting of SDS with control over the rate of potential cycling during nanoshaving as well as the concentration of SDS (or similar molecules) may help to further elucidate the kinetics of the assembly process and the respective contribution of each aspect to the accelerated assembly during nanografting.

The tip remains critical in nucleating and directing self-assembly of ordered SDS layers, as ordered SDS layers do not appear without tip writing even after the potential is raised to +800 mV. Primarily, the tip can mechanically remove transiently adsorbed, disordered SDS layers to enable the access of new molecules to bare surface. We have considered another possible role for the tip in nucleating ordered SDS structures: during nanoshaving, the flux of incoming molecules towards the nanoshaved regions may be augmented by a dip pen-like transfer of SDS molecules adsorbed on the AFM probe to the gold.² However, the coverage of SDS on the AFM probe

under liquid is much lower than the coverages of ink molecules in dip-pen nanolithography, and the concentration of SDS in the solution ensures a sufficient flux to the nanografted area. Therefore, transfer of the molecules through the tip surface is unlikely to be significant.

The need for a pre-formed alkanethiol matrix for the nanografting SDS structures, even when the matrix was not connected to the SDS structure, is surprising and remains to be understood. One possible reason is that residual thiol molecules may remain in the nanoshaved regions and serve as ‘seeds’ for nucleating ordered SDS growth. This scenario appears unlikely, as we could pattern bilayer SDS into regions that had been shaved three consecutive times at 0 mV to remove as many C18 molecules as possible (Fig. S5†). Another plausible explanation for the need of a nearby SAM is that the exposed gold within the nanoshaved regions possesses a different surface structure than bare gold that entirely lacks a C18 matrix. The formation of an ordered alkanethiol SAM from solution requires significant restructuring of the gold surface in the process: reconstruction of the bare gold surface is lifted, and as the surface density of alkanethiols increases—two thiol molecules bind to a single gold adatom in a compact alkanethiol monolayer—the gold surface is ‘etched’ as additional gold adatoms are ejected to the surface.²⁴ As a result, a gold surface with an alkanethiol SAM which has been nanoshaved may possess a different structure than a gold surface where the reconstruction has been lifted electrochemically. A more favorable surface structure within the nanoshaved regions may be required for other molecules such as SDS, which does not bind to gold strongly enough to lift reconstruction on its own, to form ordered patterns at the gold–solution interface in the first place. Kolb and Petri¹³ found that the electrochemically induced adsorption of SDS was highly sensitive to the state of the unpatterned gold surface. While SDS would form ordered structures at potentials above 230 mV when the electrode surface was unreconstructed, on a reconstructed gold surface ordered SDS structures would not form until the (SDS-stabilized) reconstruction lifted at ~410 mV. Hence a unique structure of the gold surface within the nanoshaved regions of the matrix SAM, and not necessarily confinement by the SAM, could be a necessary component for the (accelerated) tip-directed assembly of bilayer SDS during nanografting. Scanning tunneling microscopy of the gold within the nanoshaved regions may be required to determine the atomic scale structure of the surface in the nanoshaved regions. Potential controlled nanografting using other unthiolated molecules may help determine how the surface structure may accelerate the assembly of SDS and whether this phenomenon is unique to SDS.

Conclusions

While in traditional nanografting experiment, the interactions between gold and the thiol headgroups are not easily varied, the electrostatic control of the interactions between a charged headgroup and the surface provides a convenient handle to differentiate the relative contributions of the inter-chain (or inter-molecular) interactions and head-group/surface interactions. Future studies that vary the molecular structure, the concentration of the nanografting solution and the applied potential can provide additional insights into the mechanistic details of the nanografting process as well as the stability of the nanografted structures. Moreover, the results raised new questions concerning the role of the Au–S interface during nanografting. Future high resolution studies that provide an atomic-scale understanding of the nanoshaved gold surface may reveal new roles of unusual surface structures, adatoms, or residual alkanethiols in the tip-directed assembly.

Our ability to nanograft ordered, kinetically trapped structures using unthiolated molecules may also allow the generation of more complex molecular nanosystems. While here we have focused on SDS, the ease at which these structures were patterned suggests that nanografting is a promising method to pattern other molecules bearing a charged headgroup, such as phospholipids. Additionally, dynamic control of the surface potential during nanoshaving provides a convenient second handle for controlling surface order. With nanografting solutions containing mixtures of molecules that respond differently to surface charges, the dynamic modulation of the potential during patterning may provide a facile route towards generating precise nanoscale chemical gradients that remain difficult to generate with current techniques.²⁵

Note

† Electronic supplementary information (ESI) available: Materials and methods; additional AFM images of nanografted SDS; control experiments. See <http://dx.doi.org/10.1039/C3NR00771E>.

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