Supporting Information

Nanografting Sodium Dodecyl Sulfate under Potential Control: New Insights into Tip-directed Molecular Assembly

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EXPERIMENTAL METHODS.

Materials. Gold wire (99.99%, 1 mm diameter) was purchased from Scientific Instrument Services, Inc. Sodium dodecyl sulfate (SDS) (molecular biology grade) was purchased from Fisher Scientific, Inc. Octadecanethiol (C18) was purchased from Asemblon, Inc. Only ultrapure water (>18 MΩ·cm) generated from a Barnstead Diamond Nanopure water purification system was used.

Preparation of the Gold Surface. A gold bead containing single-crystal Au(111) facets was made by melting a gold wire in the manner of Clavilier et al.[S1], mounted on a platinum foil, and subsequently cleaned in hot nitric acid and via a hydrogen flame annealing. To prepare a C18 SAM, the gold bead was immersed in a 1-2 mM solution of ethanolic C18 overnight, then rinsed with ethanol and used immediately.

Nanografting of SDS under potential control. 5 or 10 mM solutions of SDS were prepared by dissolving solid SDS in ultra-pure water to 10 or 20 mM, respectively, sonicated and mixed with equal volume of ethanol. An Agilent 5500 AFM was used for all in situ electrochemical AFM experiments with contact mode imaging under SDS solutions using a custom built fluid cell containing a Pt/Ir wire (counter electrode) and a small Ag/AgCl reference electrode, which has a low leakage junction formed by the gap between a Pt wire and glass. Fluid cell and electrodes were cleaned in piranha solution (1 : 3

H_2O_2 : H_2SO_4) prior to use and copiously rinsed with water. (CAUTION: Piranha solution can react violently with organic materials, and should be handled with personal protective equipment. Piranha solution should not be stored in tightly sealed containers.) SNL-10 (Bruker) probes with spring constants of approximately 0.2-0.4 N/m and had been cleaned in aqua regia (3 : 1 HCl : HNO_3) [S2, S 3] were used for all experiments. During the experiments, surface potential was controlled using an integrated potentiostat in the AFM or with a BAS Electrochemical Workstation (Epsilon, Bioanalytical Systems). Nanoshaving protocol was performed as previously described:[S4] briefly, selected regions of the C18 self-assembled monolayer were removed by applying high forces using the AFM probe using the PicoLith module of PicoView at the lowest force to achieve high-quality patterns into C18 (generally, between 100 and 200 nN). No differences were observed whether nanografting was performed under a nitrogen environment (not shown).

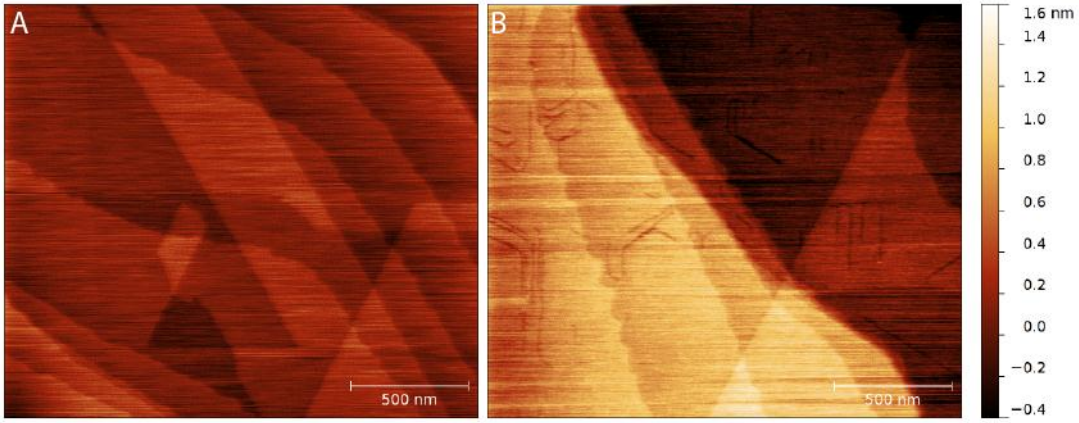

Figure S1. A) Contact-mode AFM images of a bare gold surface (with no pre-formed C18 SAM) at open-circuit potential under a 10 mM SDS solution in 1:1 ethanol:water. No strongly adsorbed SDS is apparent. B) After ~1 hour, the surface still appears free of SDS structures. The structure of the gold Au(111) surface, with sparse, depressed strips that are ~0.2 nm below the rest of the surface and angled at 60° relative to each other, is consistent with a metastable phase where the $(23x(3)^{1/2})$ reconstruction is partially lifted to the (1x1) phase;[S5] the depressed strips are likely the remaining reconstructed areas, where ejected adatoms make the rest of the surface appear 0.2 nm taller. A 100 x 100 nm region was nanoshaved at high forces to no effect, further indicating a lack of strongly adsorbed SDS.

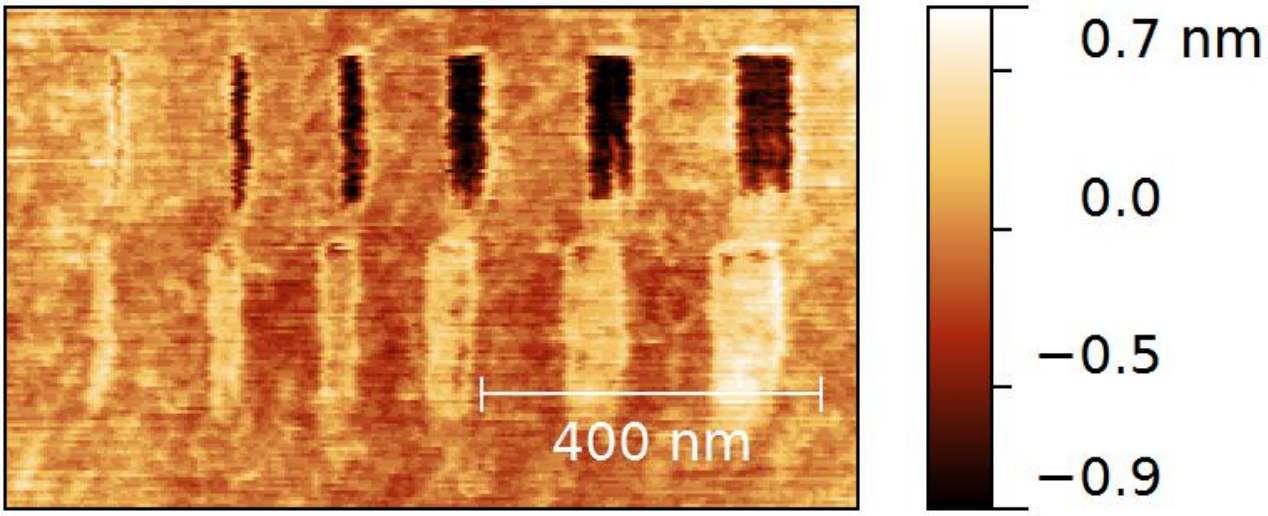

Figure S2. Nanografting of SDS into C18 SAM. The features in the top row were nanoshaved at 0 mV. The features in the bottom row were generated at 800 mV. Imaged at 0 mV.

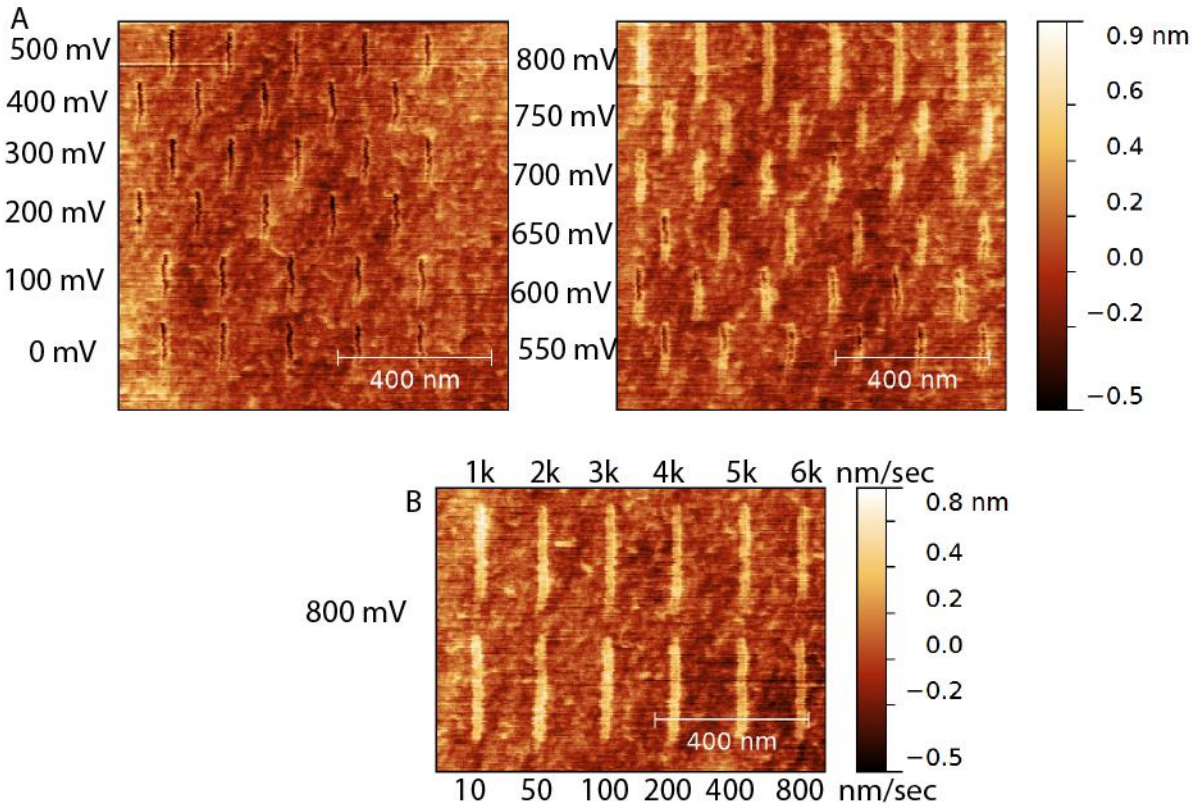

Figure S3. Effect of A) applied potential and B) tip writing speed (in nm/sec) on nanografting of SDS. During tests of different applied potentials, tip speeds for each potential were (from left to right): 10 nm/sec, 50 nm/sec, 100 nm/sec, 200 nm/sec, 400 nm/sec, (800 nm/sec).

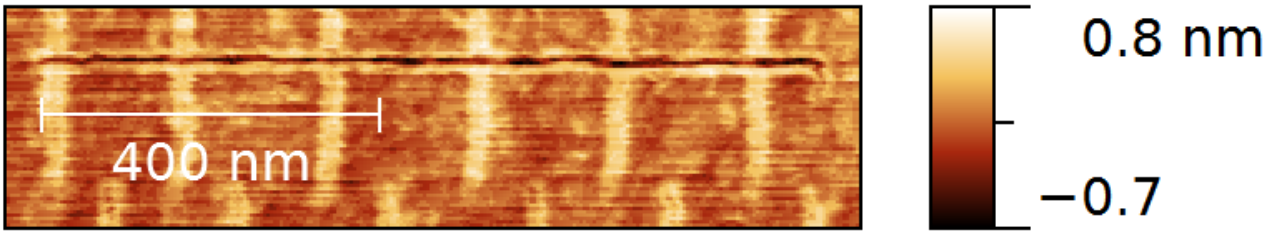

Figure S4. Mechanical desorption of SDS patterns (from Figure S3A), by nanoshaving across the patterns with the surface potential held at 0 mV.

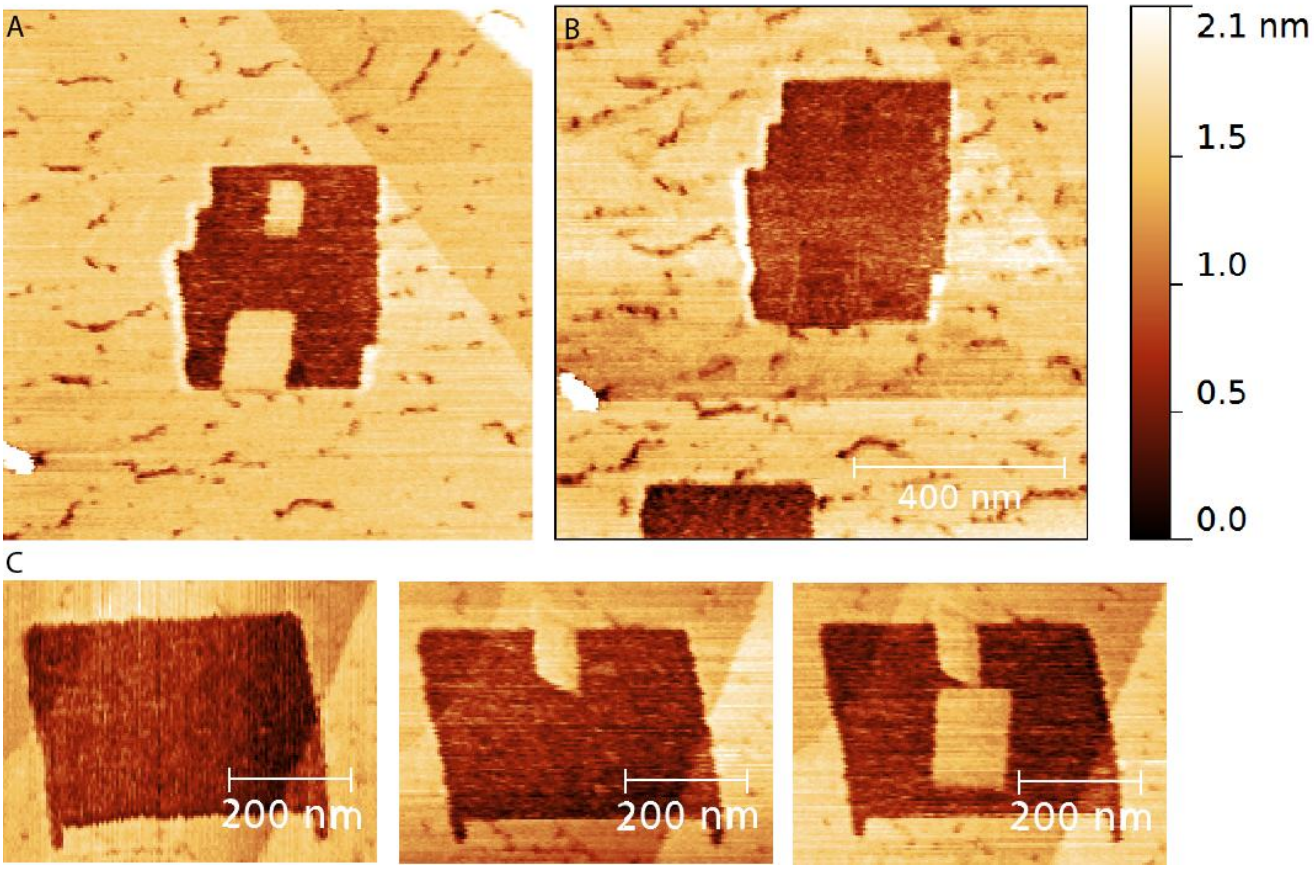

Figure S5. Additional examples of un-confined electrostatic nanografting of SDS. A) A large region of C18 was nanoshaved three consecutive times at 0 mV in an attempt to remove as many alkanethiols as possible. Then smaller regions were nanoshaved with the surface at 800 mV, and imaged at 800 mV. B) The same region imaged at 0 mV. Both the SDS patterns desorb from the larger nanoshaved region, even the pattern of SDS which appears close to the edge. C) Sequential assembly of un-confined SDS patterns by first nanoshaving a large region with the surface at 0 mV (left), then nanoshaving again at 800 mV (middle- pattern exposed on three sides, and right- pattern exposed on four sides).

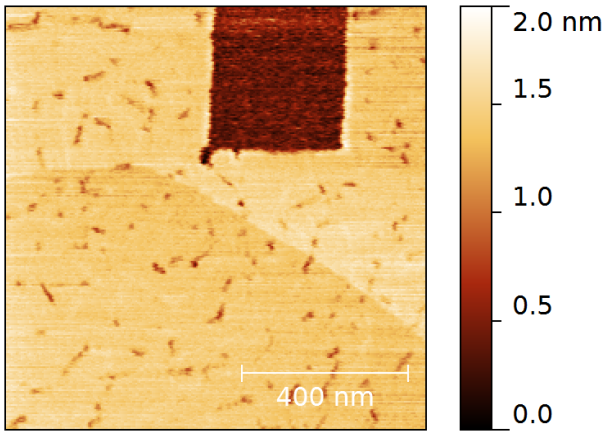

Figure S6. Simultaneous nanoshaving and applied potential (though not contact with the pre-formed SAM) are required for the nanografting of a well-formed SDS pattern. A large region of C18 was nanoshaved at 0 mV. Then smaller regions were nanoshaved with the surface at 0 mV, and imaged at 800 mV. No ordered SDS structures can be resolved by AFM.

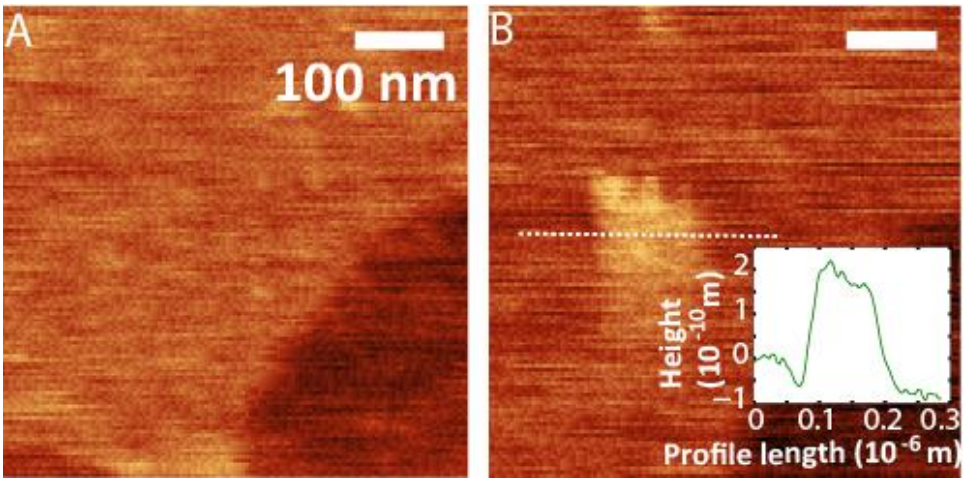

Figure S7. A) Bare gold (with no C18 SAM) held at 800 mV. No strongly adsorbed SDS is visible. B) After nanoshaving the surface at 800 mV, no patterning of ordered SDS occurs. The increased height (~ 0.25 nm) of the surface is consistent with roughening of gold atoms at the nanoshaved regions.

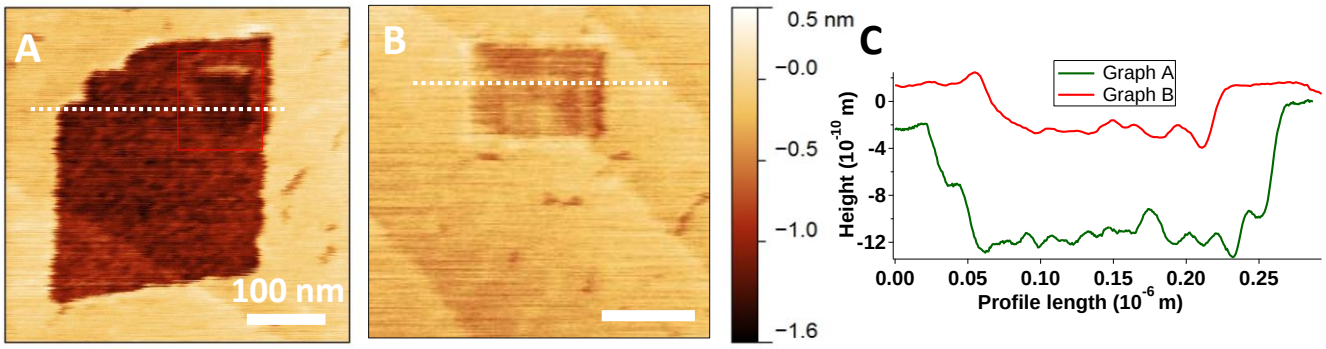

Figure S8. Control experiment of unconfined nanografting of dodecanethiol (C12). A) A large region of C18 was nanoshaved three consecutive times in ethanol, and exposed to 2 μM C12 ethanol solution. Then smaller region inside the red square were shaved again in the presence of C12. In contrast to the case of SDS, no new monolayer structure was formed. B) Nanografting in the same C12 solution generates an ordered C12 monolayer inside the C18 matrix. C) Cross section profiles showed that the nanografted pattern was 0.5nm deep, consistent with the formation of an ordered layer of C12. On the other hand, the large region in figure A was 1.2nm deep, indicating a disordered layer of C12 is within the pattern. The smaller region that was nanoshaved again was 0.2nm deeper, which is possibly due to removal of gold adatoms during nanoshaving.

REFERENCES.

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S5. He, Y.; Borguet, E. *Journal of Physical Chemistry C* **2011**, *13*, 5726.