Regulation of Local Structure of Ternary Self-Assembled Monolayers Using Nanografting

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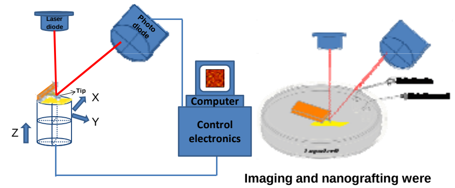
Introduction

- Multi-component self-assembled monolayers (SAMs) of alkanethiols on noble metal surfaces are of great interest due to their rich domain structures, and their application of fine tuning surface functionalities.
- Nanografting is used to provide an *in-situ* standard for surface characterization and to regulate self-assembly reaction pathways and outcome.
- This work will reveal the structural characterization of ternary SAMs, and the regulation of their local structures using nanografting.

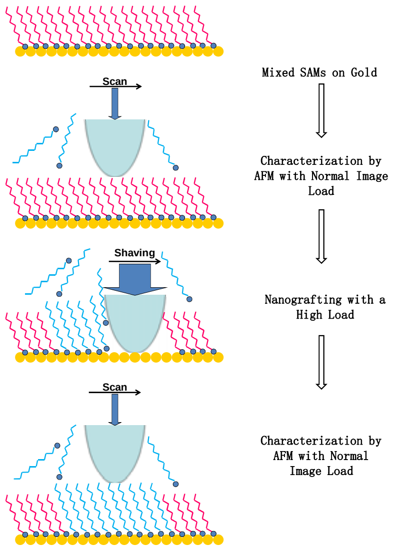
Atomic Force Microscopy



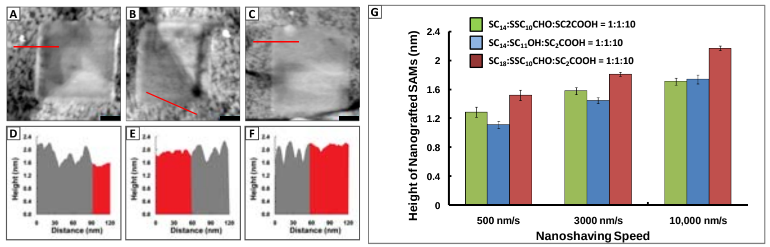
AFM is used to visualize surface morphology and domain structure.

Imaging and nanografting were carried out in liquid medium, containing the desired reactants.

AFM-based Nanografting

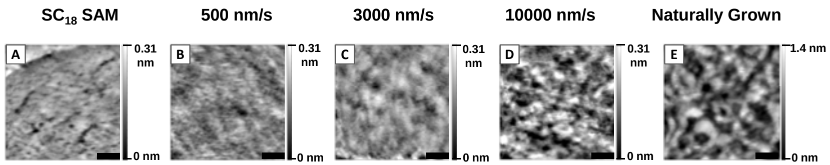


Nanografting Enables the Regulation of the Surface Composition and Phase Segregations of Ternary SAMs



As shaving speed increases, the height of nanografted ternary SAMs increases. This phenomenon is observed in SC_{18}:SC_{10}CHO:SC_2COOH, SC_{14}:SC_{10}CHO:SC_2COOH, and SC_{14}:SC_{11}OH:SC_2COOH ternary systems. This indicates that more SC_{18} molecules are adsorbed onto the surface as speed increases.

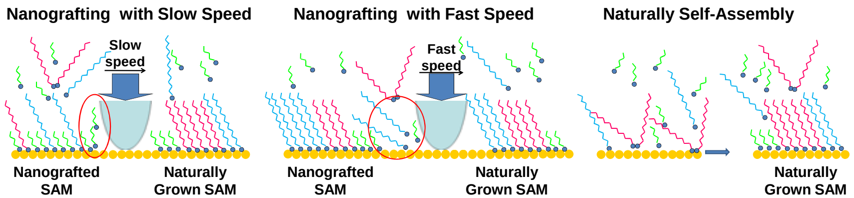
Comparison of nanografted patterns' heights produced at different shaving speeds. Topographic images show the overall review of the naturally grown and nanografted patterns of SC_{18}:SSC_{10}CHO:SC_2COOH ternary SAMs produced at speeds of [A] 500 nm/s, [B] 3,000 nm/s and [C] 10,000 nm/s, respectively. [D], [E] and [F] are corresponding cursor profiles indicated in [A], [B] and [C], respectively. [G] Height of nanografted ternary SAMs of SC_{14}:SSC_{10}CHO:SC_2COOH (green bars), SC_{14}:SSC_{11}OH:SC_2COOH (blue bars) and SC_{18}:SSC_{10}CHO:SC_2COOH (red bars), respectively. Scale bars = 50 nm.



By varying nanoshaving speed, the surface phases can be regulated from one type of phase with molecular-level mixing to a near-naturally grown surface structure with segregated phases.

Comparison of local surface phases of nanografted and naturally grown SC_{18}:SSC_{10}CHO:SC_2COOH ternary SAMs. High resolution AFM images reveal the local structure of [A] a single-component of SC_{18} SAM, nanografted ternary SAMs produced at [B] 500 nm/s, [C] 3,000 nm/s and [D] 10,000 nm/s and [E] naturally ternary grown SAMs, respectively. Scale bars = 20 nm

Spatial Confinement Is Responsible for the Observed Nanografted SAMs' Height and Surface Phase Differences

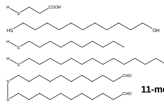


- **Due to the spatial confinement during slow shaving, the adsorption of smallest molecules (SC_2COOH) is kinetically favored over bulkier molecules (SC_{18} and SSC_{10}CHO). By increasing the shaving speed, the spatial confinement is decreased. The surface coverage of SC_{18} increases, which leads to the increase of nanografted patterns' height. The adsorption of SC_{18} peaks when the speed is optimized and prohibits SSC_{10}CHO self-assembly. Therefore, the surface coverage of SC_{18} in the nanografted SAMs produced at high speed is higher than naturally grown SAMs.**
- **The adsorption is dictated by collisions due to the spatial confinement (at slow speed). Therefore, one type of phase with molecular level mixing is formed. Since spatial confinement is not sufficient at the fast shaving speed, the self-assembly pathway is close to that of naturally grown SAMs. Therefore, phase segregations take place.**

Ternary Systems Presented in This Work

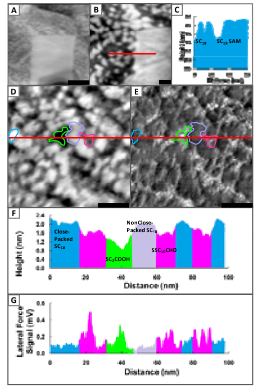
SC_{18}:SC_{10}CHO:SC_2COOH (0.02 mM, 1:1:10)
SC_{14}:SC_{10}CHO:SC_2COOH (0.04 mM, 1:1:10)
SC_{14}:SC_{11}OH:SC_2COOH (0.04 mM, 1:1:10)

Molecular structure of alkanethiols and disulfide



3-mercaptopropionic acid (SC_2COOH)
11-mercaptoundecanol (SC_{11}OH)
tetradecanethiol (SC_{14})
octadecanethiol (SC_{18})
11-mercapto-1-undecanal disulfide (SSC_{10}CHO)

Assignment of Surface Phases Using High-Resolution Image and Nanografting



Four types of domains are formed on the ternary SAMs. The brightest regions exhibit similar height to that of the nanografted SC_{18} SAM, which is mostly composed by close-packed SC_{18}. The bright regions are nonclose-packed SC_{18}. The major component of grey regions is SSC_{10}CHO, which forms shadow-like structures surrounding the SC_{18} regions. The dark regions are SC_2COOH dominated phases.

Simultaneous high-resolution AFM of SC_{18}:SSC_{10}CHO:SC_2COOH ternary SAMs (0.02 mM, 1:1:10) [A] AFM topograph reveals the overall morphology of a nanografted SC_{18} SAM on the naturally grown ternary SAM. [B] is zoom-in scan of [A]. [D] topographic image and [E] lateral force image demonstrates the 2D phases in a naturally grown ternary SAM. [C], [F] and [G] are corresponding cursor profiles as indicated in [B], [D] and [E], respectively. Scale bar of [A] = 100 nm. Scale bars of [B], [D] and [E] = 100 nm.

Conclusion

- By nanografting SC_{18} into SC_{18}:SSC_{10}CHO:SC_2COOH ternary systems, the height of four types of surface phases can be accurately determined, 2.18 ± 0.04 nm, 1.93 ± 0.11 nm, 1.47 ± 0.08 nm and 1.03 ± 0.15 nm.
- The heights are consistent with close-packed SC_{18}, nonclose-packed SC_{18}, SSC_{10}CHO dominated, and SC_2COOH dominated phases. The theoretical heights of SC_{18}, SSC_{10}CHO and SC_2COOH are 2.23 nm, 1.55 nm, and 0.78 nm, respectively.
- The overall heights of nanografted SAMs increase with increased shaving speed. This indicates that more SC_{18} molecules adsorb onto the surface as speed increases. In addition, the coverage of SC_{18} peaks when the speed is optimized, at which point SC_{18} adsorption prohibits SSC_{10}CHO self-assembly. Therefore, the coverage of SC_{18} is more than that of naturally grown SAMs.

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