Molecular Mechanisms of Genetically Engineered Peptides for Inorganics on Gold and Graphite Surfaces

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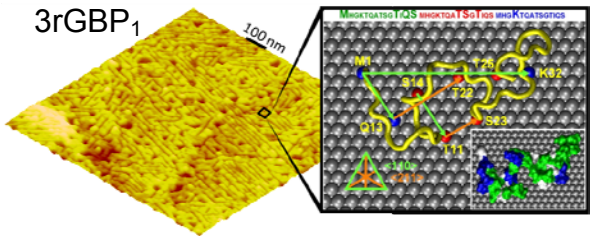
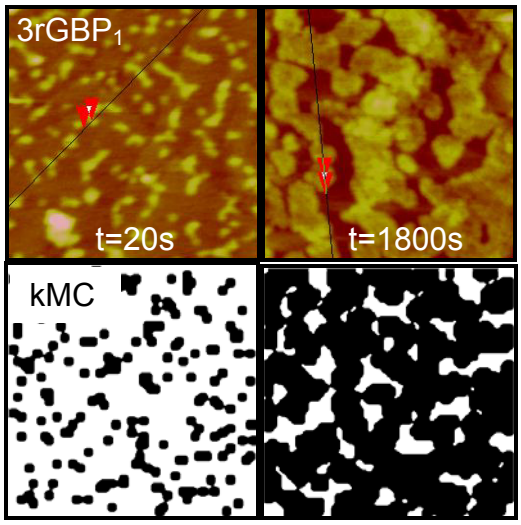
Statement of Purpose: Gold and graphitic carbon represent two biocompatible and conductive materials used in current and future diagnostic device building as well as biocompatible surfaces for implant applications. Recently, Genetically Engineered Peptides for Inorganics (GEPIs) have demonstrated the ability to enhance enzymatic activity of GEPI-inserted surface bound proteins, control the formation and assembly of nanoscale materials, as well as target between material surfaces of similar nature. Though shown to be effective in these applications, little is understood about the molecular mechanisms which these peptides undergo to achieve their advanced functionality. Here, we utilize a combinatorial approach involving both atomistic and molecular-scale techniques to understand and explain the adsorption, clustering and film formation of selected gold-binding peptides (3rGBP1) and graphite binding peptides (GrBP5) to their respective material surfaces.

Methods: To gain a continuum understanding of peptide adsorption, we first combine the atomistic details of Molecular Dynamic (MD) calculations built upon existing Nuclear Magnetic Resonance (NMR) derived constraints[1]. The structural observations are then correlated to high resolution *ex situ* AFM as well as geometric lattice docking analysis[1]. To study the adsorption process on the molecular level, we use long timescale (seconds, hours) Atomic Force Microscopy (AFM) studies supported by novel kinetic Monte Carlo (kMC) simulation[2]. Au(111) surfaces were flame annealed prior to use and HOPG (SPI-1 Grade, SPI supplies) surfaces were used as cleaved. Peptide solutions were prepared in Phosphate buffer and DI H_2O. For AFM time-lapse studies, samples are exposed to peptide solution for various periods of time while mounted facing down onto a 150 µL solution well. Deposition, diffusion, and aggregation (DDA) coarse-grained kMC modeling is applied with calibrations from existing analytical SPR data for sticking coefficient and collision frequency with the Au(111) surface. The deposition of monomers, their coalescence as well as the mobility of clusters are modeled by a cluster size dependant diffusion equation.





Results: As seen by AFM, both $3rGBP_1$ as well as $GrBP_5$ GEPI sequences form 6-fold symmetric supramolecular assemblies on their respective surfaces at equilibrium corresponding to the gold and carbon lattices. Further, a putative gold docking site is identified on the $3rGBP_1$ molecule to be a planar loop region contained in the second repeat of the molecule by geometric docking analysis. kMC results show the dynamic evolution of both monomers and clusters of peptides on the Au(111) surface, and the requirement of cluster mobility to be accounted for to accurately model the process.

Conclusions: Both $3rGBP_1$- as well as $GrBP_5$-formed peptide films are characterized both by time-lapsed and equilibrium high resolution AFM.[1,2] The supramolecular order found in $3rGBP_1$ is further explained by atomistic lattice correlation analysis, identifying a putative gold-docking surface containing a planar arrangement of heteroatoms from the second repeat of the peptide found to align with the <110> and <211> Miller indices of the Au lattice. The observed dynamic adsorption process is further explained by kMC simulation and only accurate when peptide cluster mobility is taken into account. From the time-lapsed imaging, we find the average mobility of single peptides on gold surfaces to be ~1 x 10^{-12} cm^2s^{-1} by a simple rate equation approach. Molecular recognition of the symmetry from both gold and graphite surfaces is observed and explained for both $3rGBP_1$ and $GrBP_5$ peptides, respectively. This research is supported by NSF-MRSEC and -IRES programs at the University of Washington.

References:

[1]So CR. ACS Nano 2009;3:1606-1615.

[2]So CR. Angew. Chem. Int. Ed. 2009;48:5174-5177.