

Title: Quantifying lateral interactions in gold self-assembled monolayers: The effect of topography and surface concentration

Abstract Body: Chemically modified (photo)electrodes are an incredibly versatile material for sensing and synthetic chemistry applications. Hybrid photoelectrodes, which convert solar energy and small molecule feedstocks into liquid fuel are chemically complex interfaces that rely on the covalent attachment of molecular catalysts to a semiconductor surface. A fundamental understanding of the non-covalent interactions between molecular layers on these surfaces is needed to rationally design interfaces that maintain the selectivity of the molecular catalysts and favor electron transport into or out of the electrode. My research focuses on quantifying lateral interactions between electroactive molecules attached to gold surfaces of increasing roughness. Self-assembled monolayers (SAMs) on gold are a well-characterized model system for structure-function studies, particularly involving questions about molecular packing and interactions. The roughness of the underlying electrode material plays an important role in molecular packing and has significant impacts on bulk properties such as surface wetting. To determine if roughness (nanometers to tens of nanometers scale) increases lateral interactions on chemically modified electrodes, I measured the electrochemical reversibility and electron transport kinetics in 6-(ferrocenyl)hexanethiol SAMs. Gold electrodes were prepared with a template stripping method where the template topographies were changed with metal-assisted chemical etching. The electrodes were then immersed in mixtures containing different ratios of 6-(ferrocenyl)hexanethiol and 1-hexanethiol, resulting in monolayers of different surface concentrations of ferrocene. Surface roughness was determined with AFM. Surface concentration of ferrocene and lateral interactions that result from these concentrations were determined with voltammetry. Future studies will incorporate carbon dioxide catalysts into the mixed monolayer SAMs, and structure-function hypotheses tested against our understanding of ferrocene.