Investigations of the Structural Dependence of Gold-Bound Alkanethiolate Monolayers on Chain Length and the Evolution of Barrier Strength to Electron Transfer

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Organized monomolecular assemblies formed by the chemisorption of alkanethiols on gold have been extensively examined the past several years in a wide range of areas in the electrochemical arena. One of the long-standing questions deals with how the length of alkyl chain affects the barrier strength of the adlayer with respect to heterogeneous electron transfer. It is generally viewed that the decrease in the barrier strength of the adlayer as the chain length decreases arises from a lowering in the packing density of the adlayer. However, there are still issues related to how the structure evolves as the length of the chain decreases. This presentation examines the results from a wide range of characterizations, especially that using scanning tunneling and atomic force microscopy, in an effort to further define the nature of the structural evolution. It is concluded that while the packing density may undergo a decrease as the length of the chains decrease, the extent of the decrease is much smaller than generally viewed. Results supporting this conclusion will be presented and critically examined.

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