Inorganic Monolayers On Electrode Surfaces

Andrew Gewirth,¹ Lien Lee,¹ Jongwon Kim¹ and Craig Teague¹ ¹University of Illinois Department of Chemistry 600 S. Mathews Avenue Urbana, IL 61801 USA

In this talk we discuss ways in which the reactivity of metal electrode surfaces is modified by inorganic complexes. We explore a result wherein a-dodecatungstosilicate (a-SiW12O404-) and related polyoxometalates spontaneously form adherent, ordered monolayer arrays on Ag and other oxophilic surfaces, the structure of which is controlled by the shape of the anion in order to maximize the number of Ag-O bonds between anion and surface and to preserve van-der-Waals contacts between adsorbed molecules. The covalent attachment of these molecules to the Ag electrode surface is confirmed by detailed x-ray reflectivity measurements. These surface anions also passivate the Ag electrode surface and evince interesting electron transfer properties. Through application of sufficiently negative potentials, formation of multilayer structures comprised of layers of the polyoxometalate and Ag cations can be formed. By changing the chemical composition of the polyoxometalate, surfaces exhibiting desirable properties such as increased efficacy in forming ordered monolayers can be synthesized.