

Active Control of Surface Transport with Electrochemically Generated Chemical Potential Gradients

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Methods which can produce ultrathin film surface coatings with lateral variations on the nm- μ m length scale, which can subsequently be used to control the interaction of the solid with its environment, are of particular relevance to advanced technologies. Recent work from this laboratory has demonstrated electrochemically generated gradients that are dynamically controllable, *i.e.*, spatial composition patterns may be created then altered at any time by changing the potential program applied to a thin metal film electrode, thereby allowing the chemical and physical properties of a surface to be manipulated *in situ* in both space and time.

Self-assembled monolayers (SAMs) of alkanethiols on Au constitute a powerful chemical system in which to investigate the active control of surface properties, because the resulting properties are dominated by the ω -substituent, *i.e.*, the substituent farthest from the S headgroup. Thus, two-component mixed monolayers - those containing two types of molecules with differing ω -substitution - can be tailored in composition to engineer surfaces capable of controlling a wide variety of phenomena at solid-liquid interfaces. Furthermore, using electrochemical potential gradients to vary the composition profile of two-component SAMs laterally opens the way to controlling interfacial properties by melding compositional tailoring with surface patterning. These monolayer composition patterns can vary continuously, *e.g.* linearly, as a function of lateral position across a surface, or discontinuously, as in isolated domains, depending on the fabrication method.

Gradients in alkanethiol surface composition on thin ($20 \text{ nm} \leq d \leq 50 \text{ nm}$) Au electrodes have been fabricated by taking advantage of their electrosorption properties. Injecting milliamp currents yields significant in-plane voltage gradients so that, rather than assuming a single value of potential, an in-plane potential distribution, $V(x)$, is imposed on the electrode surface, according to,

$$V(x) = V_0 + \int \frac{i\rho(l)}{A} dl$$

where i is the magnitude of the injected current, $\rho(l)$ is the film resistivity, and A is the cross-sectional area. The extent and position of the gradient can be tuned by adjusting the magnitude of the injected current and the voltage offset, respectively. Furthermore, the in-plane electric potential gradient means that, relative to a solution reference couple, electrochemical reactions occur at defined spatial positions corresponding to the standard potential, $V(x) \sim E^0$. The spatial gradient in electrochemical potential can then produce spatially dependent electrochemistry. Surface-chemical potential

gradients can be prepared by arranging the spread of potentials to span an electrochemical wave mediating redox-associated adsorption or desorption. For example, reductive desorption of alkanethiols into alkaline solutions occurs at $E^0 \sim -0.8 \text{ V vs. Ag/AgCl}$, varying only modestly with chain length and terminal group. Thus, by arranging the electrochemical potential drop to span the region of E^0_{des} for the alkanethiol of interest a gradient in alkanethiol surface coverage, $\Gamma(RSH)$, can be created. Fortuitously, the reductive desorption process can be followed *in situ*, even though it is in the presence of a 10^3 -fold larger background, because current injection into thin films produces in-plane voltages with inherently high signal-to-noise ratios, $S/N > 10^4$. Of particular interest are schemes in which the thiols are terminated with ligands which can direct cellular adhesion or the assembly of multilayer architectures.