

Nanostructured Organic and Inorganic Thin Films with Novel Molecular Recognition Properties

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An important theme of research in surface and interface science is one directed towards the development of molecular level understandings of interactions and processes occurring at solid-liquid interfaces.¹ Interfacial interactions play a crucial role in such phenomena as adhesion,² wetting,^{3,4} electrochemistry,⁵ catalysis,^{6,7} and critically underpin the functioning of numerous sensor technologies⁸ and the biological systems that support life.^{9,10} Self-assembled monolayers of alkanethiols (SAMs)^{11,12} are a valuable tool for modeling such phenomena because of their ease of preparation, stability, highly ordered structure, and the diversity of the compatible chemistries that can be utilized to covalently incorporate a wide range of functionalities into them. The study of molecular recognition, which concerns the selective interaction or non-covalent binding of a probe molecule to a receptor, is well suited for modeling with SAMs.

For optimal molecular recognition studies, the SAM must be highly ordered and essentially be free of pinhole defects. Towards this end, a chemical treatment of the gold substrate was developed. The substrate was sequentially treated with piranha solution (3:1 conc. H_2SO_4 :30% H_2O_2), followed by immersion in 3:1:16 $\text{HCl}:\text{HNO}_3:\text{H}_2\text{O}$. We found that the SAMs assembled on these treated substrates had exceptional barrier properties, being extremely impermeable to aqueous redox moieties as measured by cyclic voltammetry (CV). Atomic Force Microscopy (AFM) revealed that this treatment results in a coalescence of the finescale metal grains into larger often irregular shaped domains. Commercially acquired films grown by thermal evaporation behaved in a similar manner but displayed more extensive grain growth. X-ray diffraction (XRD) rocking angle measurements made of the Au(222) peak show a reduction in the FWHM of approx. 50-80% in the treated Au films, indicating that the oxidative treatment induces a significant bulk recrystallization of the metal. The dynamics suggest that the recrystallization is related to the preferential dissolution of Au and/or impurities present at grain boundaries. This dissolution leads to their unpinning and subsequent merger into larger grains. This hypothesis was tested by cosputtering copper with the Au to form a dilute Cu/Au thin film. AFM data confirmed that the inclusion of this diluent significantly enhances grain growth and decreases surface RMS roughness.

Supported lipid layers were formed via the fusion of large unilamellar vesicles of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) to mixed self-assembled monolayers (SAMs) on gold comprised of ferrocene-functionalized hexadecanethiol chains ($\text{FcCO}_2\text{C}_{16}\text{SH}$) diluted in either hexadecanethiol (C_{16}SH) or 1-hydroxyl-hexadecanethiol (HOC_{16}SH). For the former case, the DMPC adsorbs predominantly as a single layer to form a hybrid bilayer membrane (HBM). The structures obtained in this way were characterized by a variety of methods, ones that include electrochemical measurements, ellipsometry and surface plasmon resonance (SPR). Cyclic voltammetry (CV) reveals that the electrochemistry of the ferrocene groups present in the SAM are strongly perturbed by the adlayer structure. The voltammograms for this system are complex, exhibiting significant potential shifts for the redox behavior of the ferrocene groups, and suggest an important role for irreversible electrode processes. The electrochemical behaviors of the ferrocene groups incorporated into a mixed SAM

prepared using the more polar hydroxyl terminated thiol are quite different. The adsorption of DMPC via vesicle fusion in this case leads to the adsorption of bilayer assemblies of the lipid on top of the SAM. The coverages of the DMPC suggested by the SPR data lie between the values expected for fusion processes depositing either one or two bilayers of the lipid on top of the SAM. In this instance, we believe that the DMPC adsorbs in the form of a multilayer structure presenting multiple bilayer sheaths as well as some lesser quantities of unruptured vesicles. This assertion is supported by both SPR data and non contact mode atomic force microscopy (AFM). The electrochemical properties of the ferrocene moieties present in the structure are largely unperturbed following DMPC adsorption in this case. Subsequent studies revealed that the adsorbed DMPC strongly influences the interactions of the tethered ferrocene groups with secondary aqueous molecular redox probes present in the electrolyte solution. Permselective properties are seen in this adlayer structure. The electrochemical rectification seen in CV surveys demonstrated that probes such as $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{C}_5\text{H}_5\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_3)\text{PF}_6$, and $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ are able to penetrate the DMPC layer while species such as $\text{C}_5\text{H}_5\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{N}^+\text{H}(\text{CH}_3)_2)$, $\text{C}_5\text{H}_5\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{OH})$, and $\text{C}_5\text{H}_5\text{Fe}(\text{C}_5\text{H}_4\text{COO}^-)$ are not. The presence of the ferrocene moiety in the supporting SAM is not a direct cause of the selective permeability noted: pure hydroxyl-terminated SAMs modified with DMPC also show selective permeation in CV studies. The discrimination imparted by the DMPC does not appear to be one based solely on the charge type of the redox probe. The cationic metal centers of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ permeate the DMPC adlayers, for example, while the more sterically demanding probe, tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate, does not. We believe that molecular scale defect structures present in the adsorbed DMPC layer confer the molecular discrimination properties seen.

Unilamellar vesicles of 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and varying quantities of either 1,2-dimyristoyl-sn-glycero-3-[phospho-rac-(1-glycerol)] (sodium salt) (DMPG) or 1,2-dimyristoyl-3-trimethylammonium-propane (chloride salt) (DMTAP) were used to deposit lipid bilayer assemblies on self-assembled monolayers (SAMs) on gold. The supporting SAMs in turn were composed of $\text{FcCO}_2\text{C}_{16}\text{SH}$ diluted to low coverage in HOC_{16}SH or a single-component monolayer phase of the latter. The mass coverages of the DMPC/DMPG layers deposited in this way were measured with SPR and found to decrease with an increasing content of DMPG in the vesicles. The SPR data show that the lipid assembly, while stable with respect to gentle rinsing in aqueous buffer, is reversible and the lipid adlayer removable by immersion in a solvent such as ethanol. The effects of the adsorbed lipid layer on the electrochemical interactions of the hybrid lipid/SAM with several redox probes [eg. $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$, and $\text{C}_5\text{H}_5\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{N}^+\text{H}(\text{CH}_3)_2)$] were characterized using CV. At a composition of 5% DMPG in DMPC, the permeabilities of the probes through the lipid layer were affected significantly relative to that observed with a pure DMPC layer. These effects include a striking observation of an enhanced, ionic-charge-specific molecular discrimination of the electrochemical probes. At higher concentrations of the DMPG, significant permeation of the lipid adlayer was seen for all the probes. These latter changes are also attended by a significant increase in the capacitive currents measured in CV experiments as compared to those observed for either a pure SAM or one modified by only DMPC. This effect likely results from the influence of the charged lipid on the diffuse Gouy-Chapman electrolyte layer at the SAM interface. In contrast to the behaviors seen with DMPG, the incorporation of DMTAP into the adsorbed DMPC had no impact on the permeation of the adlayer by soluble redox probes as judged by the

observed electrochemistry, a result that appears to correlate with a less ideal mixing of lipids in the DMPC/DMTAP system relative to that of a DMPC/DMPG mixture.

Taken together, the results suggest that the assembly of secondary adsorbate layers of phospholipids provide an interesting method for modifying the electrochemical properties of thiolate SAMs on gold. Such adlayers can exhibit perm-selection towards species in solution, as evidenced in the electrochemical properties seen with soluble redox probe molecules. These species therefore do affect the character of the structure/property correlations seen in electrochemical measurements in ways that are both complex and surprising. Our current understandings suggest that the phase behaviors of the lipid are strongly implicated in the perm-selection noted and can be used to modify it by design through the assembly of lipid adlayers of mixed composition.

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