Ordered Monolayers of Organosulfur Compounds on Gold Substrates

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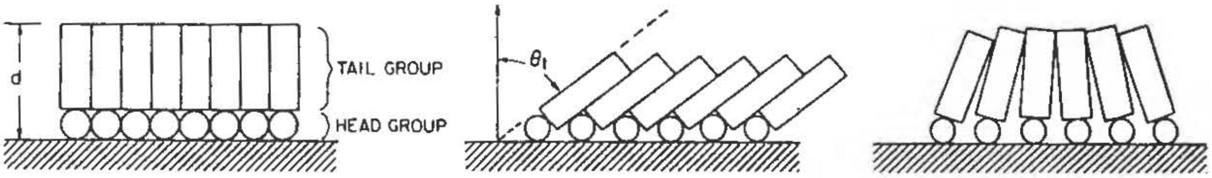
Langmuir and Blodgett first devised an approach to building ordered monolayers in the 1930's [1]. Although a great deal of research has been done on polymer thin films and adsorbed Langmuir-Blodgett lamellar structures, the use of covalent bonds in preparing ordered films is far less advanced [2]. Covalently bound substrates have found utility in the construction of chemically modified electrodes [3], as well as giving insight into such processes as quantum mechanical tunneling during intramolecular electron transfer [4].

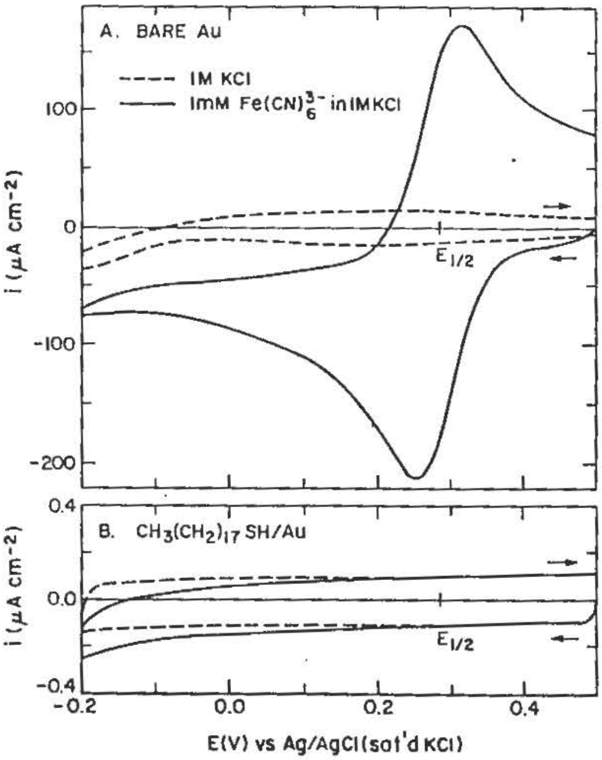
In 1983, Sagiv set forth explicitly the synthetic scheme of covalently adsorbing amphiphiles onto a substrate from the liquid phase to produce monolayers or multilayers [5]. Finklea and Allara attempted the synthesis of an ordered monolayer on gold using this methodology, employing octadecyltrichlorosilane as the adsorbing agent [6]. However, the films thus prepared were unsatisfactory, due to incomplete polymerization at the gold surface and the presence of point defects in the monolayer.



Turning to an adsorbing species which would have strong interaction with the gold substrate, Finklea exposed clean gold surfaces to solutions of alkyl mercaptans with long hydrocarbon chains (C_{12}, C_{14}, C_{16}, and C_{18}) [7]. Monolayers of the mercaptans formed spontaneously, and were found to be electrochemically stable over a wide range of potentials. The monolayers were found to passivate the gold surface, reducing the electrochemical oxidation of the substrate by 3-5 orders of magnitude. Tafel plots of electroactive metal ions using mercaptan covered gold electrodes showed somewhat anomalous Faradaic currents, which support electron transfer through point defects in the film as well as electron tunneling.

Similar studies were performed using a variety of organic disulfides [8]. Utilizing ellipsometric analyses, it was shown that the ellipsometric thickness of the monolayer varied regularly with n, the number of methylene units in the hydrocarbon chain extending from the disulfide head. Infrared reflectance spectroscopy of several disulfide films show that the molecular units comprising the monolayer are intact, that is, the films are not a result of decomposition. Further analyses of the IR spectra allowed a conformational assignment for the alkyl chains to be made; that of a tilted (35-65° from surface normal) all-trans backbone. X-ray photoelectron spectroscopy supports the assigned composition of the monolayers. XPS and variable temperature IR spectroscopy indicate that the hydrocarbon films are thermally stable until they desorb from the substrate without decomposition (180-200° C).

Further examination of alkyl mercaptan monolayers was performed on the series $CH_3(CH_2)_n$ SH were n = 1, 3, 5, 7, 9, 11, 15, 17, and 21 [9]. Ellipsometric data shows a correlation between chain length and film thickness, with some variation at short alkyl chain lengths suggesting that short chain thiol monolayers are more disordered than long chain films. In addition, infrared spectroscopy verifies the integrity of the film, but shows that frequencies for the asymmetric methylene stretch transition approach values recorded for the bulk crystalline mercaptan as n increases. Both ellipsometry and IR spectroscopy support a trend of increasing order in the monolayer lattice as n increases. Additional electrochemical characterization was performed with aqueous Fe^{3+} ion, showing the blocking ability of ordered monolayers. The electrode response as a function of thickness of monolayer also confirmed the assertion that faradaic processes occured as a result of tunneling through disordered, or defect, regions in the film.



Docosyl mercaptan, didocosyl sulfide and didocosyl disulfide (RSH, RSR, and RSSR, where R = $CH_3(CH_2)_{21}$) were adsorbed onto single crystal gold foils, and examined by electron diffraction to determine the packing arrangement of such monolayers [10]. Docosyl mercaptan and didocosyl disulfide adsorbed on gold (111) in a hexagonal lattice, with a c(7x7) overlayer. These lattices show the greatest chain tilt, at 25-35°, and the largest interchain distance, 4.97 A. The same compounds adsorbed on gold (100) show a more closely packed structure, in a c(10x10) lattice with an interchain distance of 4.54 A, and a chain tilt angle of 6-12°. Didocosyl disulfide exhibits additional phases on gold (100), with smaller interchain distances and smaller tilt angles. Didocosyl sulfide exhibits diffraction data exactly analogous to the disulfide, raising questions of disulfide impurities. However, these measurements verify the highly ordered nature of the monolayer packing.

Attempts to manipulate the character of the monolayer film began with simultaneous adsorption of two alkyl mercaptans onto the gold substrate [11]. The two mercaptans used were a long chain hydrocarbon thiol ($CH_3(CH_2)_{21}SH$) and a shorter chain thiol with a terminal hydroxy functional group ($HO(CH_2)_{11}SH$). Contact angle measurements, ellipsometric data, and X-ray photoelectron spectroscopy reveal that the monolayer resists a gradual change in surface character. A monolayer exhibiting predominantly long-chain thiol character or predominantly short-chain hydroxy-capped thiol character is preferred over a mixed monolayer. These studies show not only the sensitivity of wetting measurements to changes in surface structure, but also the ability to manipulate the composition of the monolayer films.

This manipulation of the nature of the monolayer was then attempted using symmetrical and unsymmetrical dialkyl sulfides [12] to insure a homogeneous surface character. Films were prepared using symmetrical hydrocarbon disulfides, symmetrical, carboxylic acid capped disulfides, and mixed disulfides. In addition, the effect of variable chain length on surface character was examined. The effect of polar carboxylic acid groups upon wettability was substantial, even when the carboxylic group was embedded within the monolayer. Contact angles of water upon long-chain hydrocarbon films, however, were found to be very high. The kinetics of formation of the monolayer films was examined using wetting measurements and ellipsometry, showing complete film formation from solution in approximately 60 minutes. The stability of the films in aqueous solution of various pH was examined, as was the composition of the films themselves (using infra red and X-ray photoelectron spectroscopies).

The detailed examination of organosulfur monolayers reveals a structure similar to a thin liquid crystal, the degree of order of which is determined by the length of the alkyl chain, and the type of sulfur compound used (alkanethiols produce higher ordered lattices than sulfides). The monolayer films themselves can be manipulated to a high degree, both to reach a preferred film thickness and to customize the degree of liquid-substrate interaction desired. These attributes indicate immediate relevance to electron-transfer studies, modelling of biological systems, and show a potential utility to surface science methods.

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