Self Assembled Monolayers of Alkanethiols on Silver Surfaces

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Abstract | This short review compiles the studies on self assembled alkanethiol monolayers formed on silver surfaces with respect to their structure and stability. Alkanethiol-based assemblies on silver surfaces are poor cousins of thiol monolayers on gold. The formation of well-ordered monolayers on silver surfaces is relatively more difficult than the corresponding systems on gold since the inherent oxide film on silver interferes with the formation and stability of the assembly. There are contradictory reports on the nature and physicochemical characteristics of alkanethiol monolayers on silver surfaces. This review attempts to highlight various studies in the literature including our efforts in this area.

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1. Organic Thin Films

Organic thin film-based materials date back to the period 79 AD where the sailing of a ship was observed to be different when greasy material was smeared on water surface[1]. Subsequently, Benjamin Franklin performed experiments by spreading oil on water and observed that water waves got influenced by a drop of oil. He then wrote, "The experiment can be extended to estimate the sizes of molecules if one recognizes that oil forms a monolayer, no thicker than a molecule"[2]. Later, Lord Rayleigh conducted experiments in 1890 and calculated the thickness of the oil layer[3].

Organic thin films are based on molecular layers of surfactants or amphiphilic molecules on a substrate[4]. The constituent molecules in the film share a common orientation resulting in well-packed structures with compact arrangement[5]. The preparation of organic thin films are generally based on Langmuir method at the gas–liquid interface[6], Langmuir-Blodgett method (multilayers formed on solid substrates)[7], self-assembly (adsorption from either solution or vapour)[8] and organic molecular beam epitaxy (OMBE)[9]. Agnes Pockels[10] introduced a method to measure surface tension of surfactant films on water at the air–water interface and this developed in to a Langmuir trough later[11]. The technique of spreading surfactant at the air–water interface was introduced by Irwin Langmuir[11]. Since then, a variety of applications based on thin films, in areas such as medicine, engineering, biology and corrosion[7,12,13] had been demonstrated. Zisman prepared monomolecular layer of a surfactant by adsorption on metallic surfaces by a self-assembly process through spontaneous adsorption[14,15]. In recent times, Nuzzo and Allara at Bell Laboratories showed that monolayers of alkanethiolates on gold could be prepared by spontaneous adsorption of n-alkyl disulphides[16,17] from a volatile solvent. This finding revitalized the area of organic thin films and it has received considerable attention in the last two decades[18]. Self-assembly and Langmuir methods have been routinely used for the fabrication of monolayers of amphiphilic molecules on various substrates[19].

2. Self Assembled Monolayers

Spontaneous organization of amphiphilic molecules based on specific interactions between the substrate and the molecules[20] is a thermodynamically driven process resulting in stable structures under ambient conditions[16]. The stable assembly with monomolecular thickness (self assembled monolayers, SAMs) can be considered as fundamental building blocks with useful properties. The thickness of SAMs can vary from sub-nanometer to a few nm depending on the length of the adsorbate molecule. The adsorbates interact among themselves yielding rigidity to the molecular assembly. This process offers a simple and convenient method by which the interfacial properties of surfaces can be varied easily. The following figure shows a schematic representation of SAMs on a substrate[21].

The surfactant molecule should have a head group of definite chemical functionality and affinity towards the substrate. The molecule anchors on to the substrate through specific interactions between the substrate and the head group[22]. The interaction could be covalent as in the case of silane monolayers on oxide surfaces[23] or electrostatic as in the case of fatty acids on silver (24) or chemisorption as in the case of thiols on gold (20).

The SAMs are good models to correlate macroscopic properties (wetting, friction, adhesion) with microscopic molecular level organization[25]. The SAMs have also been used extensively to control the size, shape and the stability of nanometallic materials such as rods, spheres, tubes, clusters and particles in order to tune their size dependent behaviour[26]. Hence, they are essential elements in the upcoming area of nanoscience and nanotechnology.

Organosulphur compounds are known to have great affinity towards metallic surfaces (Au, Ag, Cu, Pt, Pd and Hg), particularly towards coinage metals, to form monomolecular assemblies and they are the most widely studied SAMs till date[27]. A variety of organosulphur compounds have been used to form SAMs that includes alkanethiols, dithiols, disulphides, sulphides, mercaptopyridines, thiophenes, cysteines, thio-carbamates, thioureas, thiophenols, and mercaptoanilines[20]. Gold is a natural choice for the substrate because of its inertness, relatively weak tendency to form an oxide and the favourable interaction of gold with sulphur[20]. Thiol monolayers on silver have been reported to a limited extent since the monolayer formation on silver is relatively difficult[28]. The presence of an oxide covering silver surface makes it difficult to prepare reproducible monolayers. Additionally, there are multiple sites of adsorption for thiols on silver (for example, three-fold hollow site, on-top site) as opposed to a single site (three-fold hollow site) on gold. There are several publications on the use of Ag surface modified with sulphur compounds (both aliphatic and aromatic) for surface enhanced Raman scattering (SERS) studies (28). The present attempt is to highlight the important aspects in the area of alkanethiol SAMs on silver surfaces with special emphasis to its structure and stability. As the literature on SAMs is very vast, we have limited the discussion to only alkanethiol SAMs on planar silver surfaces. The SAMs of aromatic molecules, monolayers on Ag nanoparticles, studies on sensing using SAMs on silver, multilayers on Ag etc. are not included.

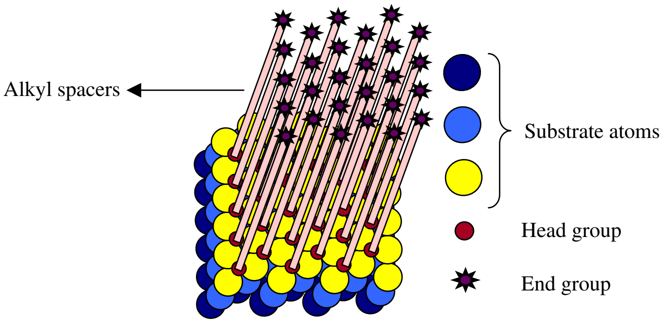
3. SAMs on Silver Surfaces

The monolayer characteristics and structure are found to be different on gold and silver surfaces and this is attributed to the difference in corrugation energy associated with silver–sulphur and gold-sulphur[29] interactions. In the case of gold, the formation of commensurate monolayer with $(\sqrt{3}\times\sqrt{3})R30^\circ$ lattice having an intermolecular spacing of 5.0 Å[20] has been reported while the SAM structure of thiols on silver is reported to exhibit dense packing with $(\sqrt{7}\times\sqrt{7})R19.1^\circ$ incommensurate lattice structure[28]. The sulphur group bonding are sp^3 and sp hybridization on Au (111) and Ag (111) surfaces respectively[30a, b, c]. The SAM of thiols on silver has been found to be tilted by 19 degrees from the surface normal[20] by various researchers while Bensebaa and co-workers have reported that thiol SAMs on silver closely resemble that of the SAMs on gold substrates[30d] with 30 degree tilt.

The oxidative adsorption of alkanethiolates on silver surface has been examined by White and co-workers[31] using voltammetry and surface enhanced Raman spectroscopy (SERS). The adsorption of short chain alkane thiols from aqueous alkaline media showed two energetically distinct steps in voltammetry, one corresponds to reversible and rapid adsorption of the thiolate leading to sub-monolayer coverage and the second corresponds to the complete coverage of the SAM. In-situ SERS has been used to follow the potential dependent adsorption isotherm on rough Ag surfaces. The total adsorption free energy is separated in to two components, one associated with the formation of silver–sulphur bond (–22 and –16 Kcal/mol for the low and high coverages respectively) and the second due to the hydrophobic and intermolecular forces based on the lateral interactions of methylene chains of the alkanethiols (1 Kcal/mol/CH_2). The second component reduced to 0.5 Kcal/mole/ CH_2 when the solvent is changed to methanol due to the solubility of thiol.

Pemberton and co-workers have reported the SAMs of butane-, dodecane- and octadecane-thiols on both mechanically roughened and electrochemically treated Ag surfaces[32]. Surprisingly, the two different surfaces showed similar spectral response revealing that the roughness does not

Figure 1: Schematic of a SAM on a substrate[21]



play a major role in determining the structure of the assembly. It is also observed that butane- and octadecane thiols formed ordered assemblies irrespective of chain lengths. This is in contrast to the observations that the thiol SAMs are generally well ordered only when the number of CH_2 unis exceeds ten. Around the same time, Fenter and coworkers reported the formation of incommensurate octadecyl thiol monolayer on silver and confirmed the stucture using low energy He diffraction and grazing x-ray diffraction studies[33a]. Several microscopic and spectroscopic techniques are used (STM, LEED, normal incidence X-ray standing waves) to understand the structure of short chain pentanethiol SAM on Ag (111) surfaces. The data revealed commensurate $\sqrt{7} \times \sqrt{7})R19^\circ$ phase which is different from the phases reported earlier for other alkanethiol SAMs[33d].

The difference in the structure of the monolayers reflects in their stability as well. The studies on the stability of the monolayers under ambient conditions in presence of air revealed a rapid oxidation of the thiolate moiety[33b]. Sum frequency generation (SFG) spectroscopy measurements revealed that the monolayer order is strongly affected by the alkyl chain length and the nature of the end group. Densely packed SAMs are observed when thiols of C_5SH and above are used but significant gauche defects are found when the number of methylene units are low[33c]. The order and stability of alkanethiol SAMs on silver could be improved by thermal treatment. The annealing of disorganized octadecanethiol- and hexanethiol SAMs on silver has been followed scanning tunneling microscopy (STM) under ambient as well as at different temperatures[34]. The adhesion and growth behaviour of alkanethiols on silver have been followed using STM[35]. Different phases of alkanethiol SAMs both under ambient temperature as well as function of temperature has also been reported using variable temperature infrared spectroscopy[30d] and the structure/stability is observed to depend on the chain length of the thiol. The effect of UV irradiation[36] as followed by SERS is found to proceed essentially by a two step mechanism. The exposure to UV caused the C–S bond scission and subsequently desorption of the hydrocarbon chain. The oxidation of sulphur occurred after significant time interval. The low chain length thiols (C_6SH and $C_{10}SH$) showed first order kinetics for the C–S bond scission. The long chain length ($C_{18}SH$) monolayer having ordered hydrocarbon chains behaved different. The initial oxidation led to the formation of sulfate and sulfite ions and subsequently the formation of complex products such as bisulfite ions is observed. The emission processes associated with molecule–metal cluster ions from SAMs of octanethiol on Ag based on the mass spectra and kinetic energy distributions are obtained using time-of-flight-SIMS under 15 keV Ga+ bombardment[37]. The cluster ions ejected from SAMs on silver are found to be less stable than those ejected from the SAMs on gold. X ray photoelectron spectroscopy has also been used to characterize dodecanethiol monolayers on Ag[38] to understand radiation induced damages and the results are similar to earlier studies where the oxidation of the sulphur species is observed.

Other substrates based on silver, for example, gold-silver alloy films have also been used to understand the structure and stability of ethanethiol and octanethiol SAMs[39]. The surface density of the monolayer is found to increase linearly with increasing Ag composition of the alloy. The STM studies revealed the lack of elemental periodicity on the alloy surface and consequently the absence of periodicity in the substrate–sulphur bonding. It should be pointed out that silver segregates on the surface due to low heat of sublimation and hence the alloy surface would be expected to behave similar to pure silver surface as opposed to gold.

Table 1: Heterogeneous electron transfer rate constants for $[Ru(NH_3)_6]^{2+/3+}$ couple on C_6SH SAM on Ag. The results within in the brackets are the ones observed at 25°C after heating the SAM to the corresponding high temperature.

Temperature (°C)	Rate constant for C_6SH SAM (10^{-3} cm s^{-1}) Prepared from neat thiol	Prepared from alchoholic solution
25	1.25	4.29
35	1.51	6.23
45	1.19	7.05
55	1.31	8.61
65	1.44 (0.56)	8.60 (5.23)
75	1.56 (0.89)	9.23 (6.6)

The SAMs of alkanethiols on metallic surfaces are generally formed by adsorption from solvents such as ethanol and n-hexane. During the adsorption process, there are possibilities of solvent molecules getting intercalated into the assembly and this might be a possible reason for the disorder observed in their structure. Hence, adsorption from neat thiol without any solvent has been proposed[21]. This might lead to the possibility of multilayer formation. Hence, one should take proper care in controlling the adsorption conditions. This is done by careful control of the adsorption time[21]. Subramanian formed SAMs of alkanethiols (chain lengths with varying $-CH_2-$ units from 3 to 16) based on adsorption from neat thiol[21]. Electrochemical quartz crystal microbalance (EQCM) studies that allow simultaneous measurements of electrochemical parameters (current, charge) and mass changes at electrode surfaces[40] are carried out to confirm the monolayer formation. The electrochemical desorption studies revealed the nature of desorption reaction to be,

$$AgS(CH_2)_nCH_3 + Ne^- Ag(0) + {}^-S(CH_2)_nCH_3$$

where N is the number of electrons involved in the redox reaction. Its value is determined to be '1' by Porter and co-workers for alkanethiol based SAMs on gold[41] and the desorption reaction on Ag and Au surfaces is found to be similar. Figure 2 shows the reflection absorption infrared spectra (RAIRS) spectra at 25°C obtained for C_6SH, $C_{12}SH$ and $C_{16}SH$ monolayers prepared from neat thiol. The spectra clearly reveal the ordered nature of monolayers based on methylene and methyl stretching modes. The observations are similar to the spectra observed on gold surfaces[20].

The tilt angle calculated based on methylene and methyl group bands[42,43] works out to be 19 ± 2° and 22 ± 2° for the SAMs prepared from neat thiol and ethanolic solutions. In general, alkanethiol monolayers on silver are reported to be almost perpendicular to the surface with a tilt angle of 9–15° from surface normal. Allara and co-workers have reported the structural rearrangements of n-alkanoate monolayers on silver surfaces, where the monolayer is found to be tilted to 19 degrees from the surface normal[44].

The thermal stability of thiol monolayers formed from neat thiols are found to be different as well. Figure 3 shows the temperature dependence of the RAIR spectra of C_6SH monolayer adsorbed from neat thiol. At 25°C, the methylene and methyl stretching modes are clearly observed and the SAM is found to be well-ordered and the end methyl groups are oriented. The deconvoluted spectrum (Fig. 4) revealed the components assigned to the individual vibrational modes.

The observed frequency shift for a temperature variation from 25°C to 150°C is only 4 cm^{-1} for the d^- mode. The d^- band showed two components in the deconvoluted spectrum (Fig. 4). The first one observed, below 2920 cm^{-1} is the result of ordered phase of the monolayer while the second component, observed above 2920 cm^{-1}, corresponds to the disordered phase of the monolayer. It is interesting to note that short chain thiol monolayers that are known to degrade at temperatures around 100°C[45] are stable even at 130°C. Similar trend is observed for the d^+ mode emphasizing the ability of the monolayer to sustain high thermal perturbations.

Cyclic voltammetry and impedance analysis have been used to scrutinize the packing and defects in the monolayer assembly. Figure 5 shows the cyclic voltammograms of the bare Ag electrode and hexanethiol SAM on silver surface[21].

Figure 2: RAIR spectra obtained for C_6SH, $C_{12}SH$ and C_{16} SH monolayers prepared from (A) neat and (B) ethanolic solutions of the thiols on polycrystalline silver surfaces.

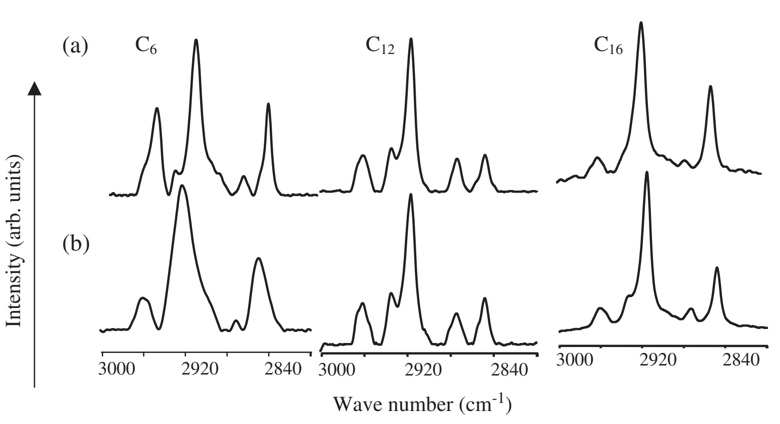


Figure 3: RAIR spectra recorded at various temperatures for C_6SH SAM on Ag(111). The adsorption is carried out from neat thiol.

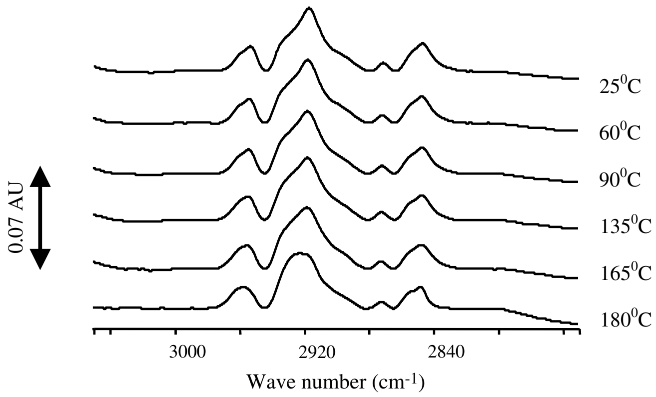
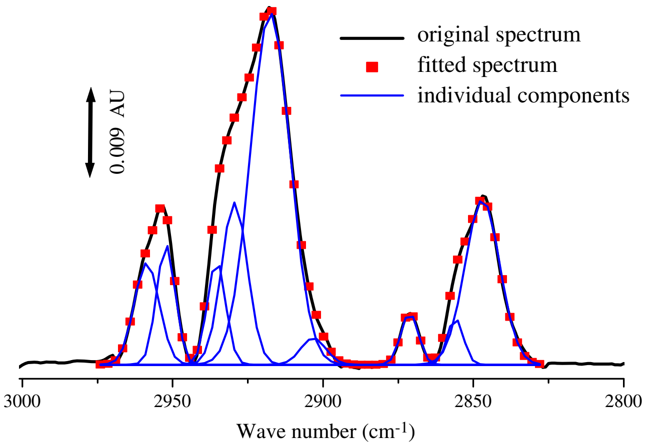


Figure 4: Deconvoluted spectrum of C_6SH SAM on Ag(111) surfaces.



A reversible redox response for the bare Ag electrode is clearly observed. The voltammograms for the hexanethiol monolayer modified electrodes showed excellent blocking behaviour as revealed by the observed low currents flowing in the cell (Fig. 5b&c). The heterogeneous rate constant values calculated from the voltammograms are shown in Table 1. It is clearly observed that the SAMs prepared from neat thiols are highly blocking as compared to the monolayers prepared from ethanolic solution.

The double layer capacitance associated with thiol monolayer–aqueous interface is determined using cyclic voltammetry and impedance measurements. The capacitance measured from the voltammogram is (1.02 ± 0.2) μF/cm^2 for the SAM prepared from neat thiol while the monolayer prepared from ethanolic solution showed a capacitance of 2.5 ± 0.25 μF/cm^2 clearly revealing the advantage of forming SAMs from neat thiol.

Topographical features of the C_6SH-SAMs on silver are shown in Fig. 6. The monolayer formed from ethanolic solution showed a smooth surface with roughness around 7.8 nm and is close to the roughness observed for the bare silver surface (5 nm). The domain size is about 100 nm. Presence of large domains with 300 nm size in the case of SAMs prepared from neat thiol revealed the relative order of the SAM.

Based on the above observations, it is clear that the SAMs of alkanethiols on Ag are not as well studied as that of the assemblies on Au. The silver surfaces are to be carefully handled in order to get

Figure 5: Cyclic voltammograms of 1mM $[Ru(NH_3)_6]^{2+/3+}$ in 0.1 M NaF supporting electrolyte on (a) bare silver and (b) C_6 SH modified Ag electrode where the monolayer is formed by adsorption from ethanolic solution of the thiol and (c) the SAM is formed from neat thiol.

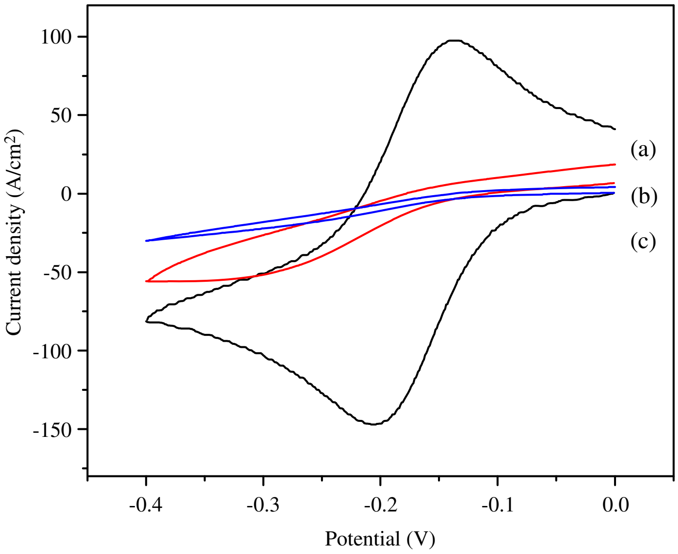
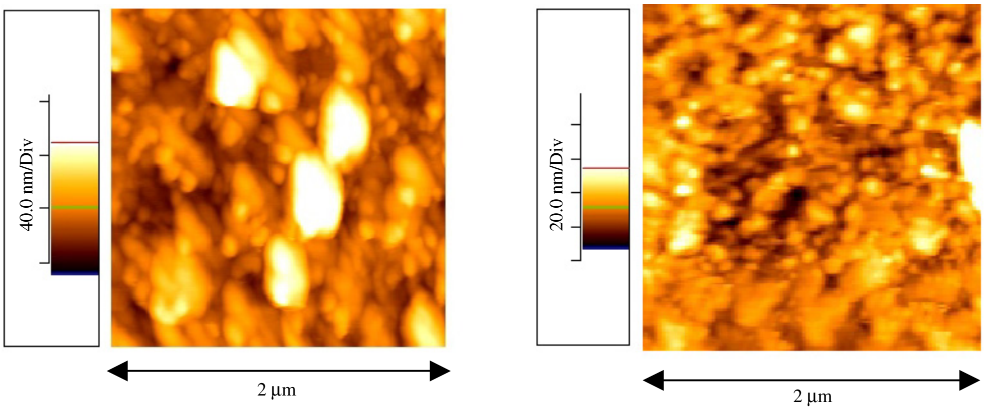


Figure 6: Contact mode AFM images of hexanethiol monolayer adsorbed from (A) neat thiol (b) ethanolic solution of the thiol on Ag(111) surface. Image size is 2 × 2 micron and the scan speed is 1 Hz.



reproducible monolayers. The recently proposed method of forming SAMs from neat thiols seem to yield more ordered structures than the ones formed by adsorption from a solvent. The stability and structural integrity improves considerably and this possibly would open up a way of getting very reproducible assemblies on Ag surface. Additional work needs to be carried out to understand the roughness of the adsorbent, thickness of the oxide layer present and other parameters in order to gain a full understanding of the SAMs on silver before it is used extensively for applications as in the case of SAMs based on gold.

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