

Self-assembled monolayers (SAMs) of carboxylic acids: an overview

Review Article

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Abstract: The field of self-assembled monolayers (SAMs) of organic compounds on different substrates is of importance because it provides a suitable and efficient method of surface modification. The formation of robust, stable monolayers from carboxylic acids on two and three dimensional surfaces of different substrates have been reported. Carboxylic acids are promising class of organic compounds for monolayer formations where traditional alkanethiols or alkoxysilanes show limitations.

Keywords: Organic thin films • Self-assembled monolayers (SAMs) • Carboxylic acid terminated SAMs

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1. Introduction

Self-assembled monolayers (SAMs) are ordered molecular assemblies formed by the chemisorptions of organic molecules (adsorbates) onto the substrate surface [1]. SAMs became an interesting topic of research in past few years as the applications of these molecular assemblies on metallic surfaces range from important technological areas such as lubrication, corrosion, catalysis and optics to biomedicine and artificial enzymes. Their well-ordered arrays and ease of functionalization make them ideal for applicability in many fields. A great interest in monolayer chemistry and SAMs observed after their successful utilization for construction of monolayers on metallic or metal oxide nanostructures, *i.e.*, the formation of three dimensional SAMs; which has led to probe the applications of these systems into sensoristic and biomedicine fields [2a-c]. However majority of the studies until now have been focused on the interactions of alkoxy/chlorosilanes with -OH terminated oxide surfaces and on the adsorption of thiols on gold or other metallic surfaces.

Figs. 1 and 2 represent graphically the number of articles/reports published in the fields of SAMs including all types of SAMs over the years and publications of carboxylic acid based SAMs respectively (data shown till November 2010). It can be said that alkanethiols have been used extensively in coating films of metals, metal

oxides, and ceramic materials by using both Langmuir-Blodgett (LB) and self-assembly methods. Alkanethiols usually form SAMs with a higher degree of perfection on nanostructure of gold [3-16]. The use of gold as a substrate however, may pose a problem in applications where optical transparency is an issue. Furthermore, gold is not a suitable material for silicon processing in microelectronics. Other amphiphiles such as carboxylic acids, phosphonic acids *etc.* have not attracted the same attention and have been studied less than thiols. *n*-alkanoic acid as an amphiphile has been used for coating of various surfaces, but only a small number of reports have been documented. The reason for the interest in carboxylic acids as surfactants is related to their use as lubricants, corrosion-resistant materials, and catalysts [17-19].

Another class of organic compounds utilized for construction of monolayers is trichlorosilanes or trialkoxysilanes. SAMs constructed on different substrates by use of silane compounds also cover wide range of applications [20-23]. But potential applications of alkyltrichlorosilane SAMs in the engineering of surface properties are somewhat limited due to the polymeric nature of these assemblies. A very small number of studies employ alternative chemistries, such as use of phosphoric acid [24] and phosphonic acids [25] for construction of monolayers. When we think of switching over to another metallic (or non metallic)

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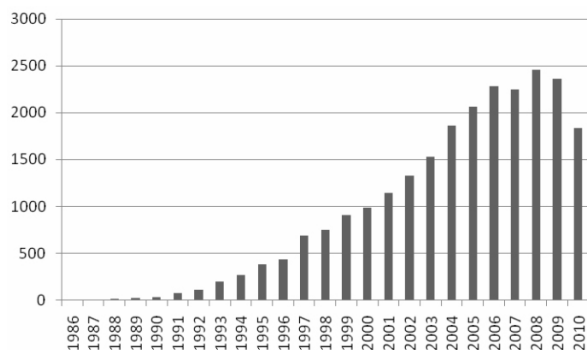


Figure 1. No. of publications on SAMs over the years

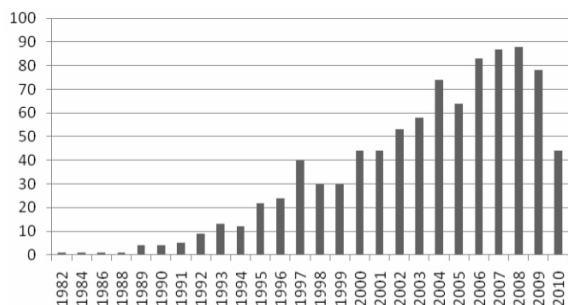


Figure 2. No. of publications on carboxylic acid based SAMs

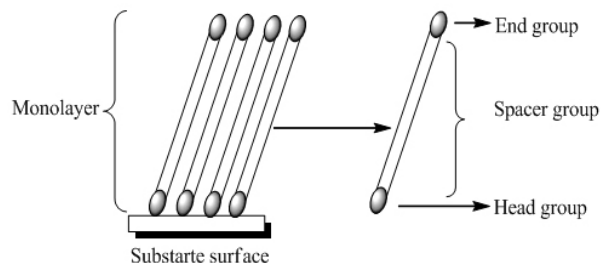


Figure 3. Essential parts of organic building-block for SAMs

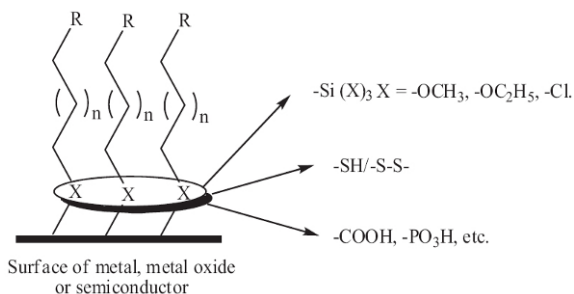


Figure 4. Types of organic compounds used for construction of SAMs

surfaces other than gold (for instance the surfaces in electronic applications); the chemistry of metal with the anchoring group of the adsorbate organic molecules plays an important role. Use of other metals other than the costly noble metals will require other systems than organosulfur compounds in order to get well ordered robust monolayers and in this case carboxylic acids are

useful building-blocks for the formation of stable SAMs on various metallic surfaces.

Provided below is collective information on the SAMs constructed from use of different carboxylic acids and on carboxylic acid terminated SAMs on different substrates (e.g. noble-metals, alloys, metal oxides etc.).

2. Self Assembled Monolayers (SAMs) in Chemistry

The building-block of SAMs is generally an organic compound (adsorbate) possessing a chemical functionality called head-group with a specific affinity for the metal (or metal oxide) surface. The other two important parts of the organic compound forming the monolayer are the spacer chain and the end-group (see Fig. 3).

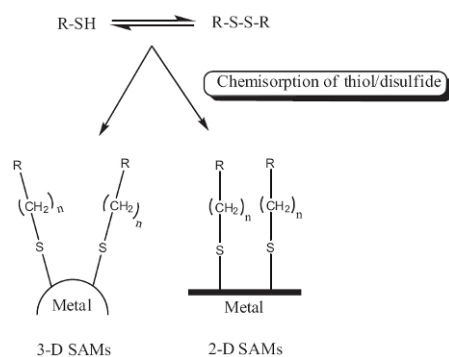
SAMs are well suited for studies in nanoscience and nanotechnology because they are easy to prepare as they do not require any specialized equipment for their preparation and can be constructed on objects of different size and shape such as thin films, nanoparticles, nanowires, nanocages in colloids. Mercaptans, organosilanes and carboxylic acids are extensively used as building blocks for the preparation of molecular self-assemblies on metallic surfaces through chemisorption. The first gold-alkanethiolate monolayer was produced by Allara and Nuzzo at Bell laboratories in 1983 [9]. The two researchers realized the utility of combining a relatively inert gold surface with a bifunctional organic molecule in a well-ordered, regularly oriented array. At the same time these scientists reported formation of monolayers from alkanolic acids. SAMs offer a unique combination of physical properties that allow fundamental studies of interfacial chemistry, solvent-molecule interactions and self-organization.

Table 1 shows a list of organic compounds with various functional head-groups which are suitable building-blocks for the formation of self-assembled monolayers, together with their specific substrates: the R moiety (spacer and/or end-group) can be modulated according to the required applications. It can be seen that organic compounds containing thiol, disulfide and carboxylic acid groups are major classes used for this purpose, covering a wide range of metal, semiconductor and oxide surfaces. It should be stressed the very fact that well-ordered SAMs can be formed also on a variety of substrates other than noble-metal nanostructures makes them attractive and versatile tool of surface modification.

Table 1. List of adsorbates for specific substrates.

Surface	Substrate	Adsorbate(s)
Metal	Au	R-SH, R-S-S-R, R-S-R
	Ag	R-NH ₂ , R-NC, R-COOH
	Pt	R-NC, R-SH
	Pd	R-SH
	Cu	R-SH
	Hg	R-SH
Semiconductor	GaAs (III-V)	R-SH
	InP (III-V)	R-SH
	CdSe (II-VI)	R-SH
	ZnSe (II-VI)	R-SH
Oxide	Al ₂ O ₃	R-COOH
	TiO ₂	R-COOH, R-PO ₃ H
	YBa ₂ Cu ₃ O ₇	R-NH ₂
	ITO ^a	R-COOH, R-SH, R-SiX ₃
	SiO ₂	R-SiX ₃

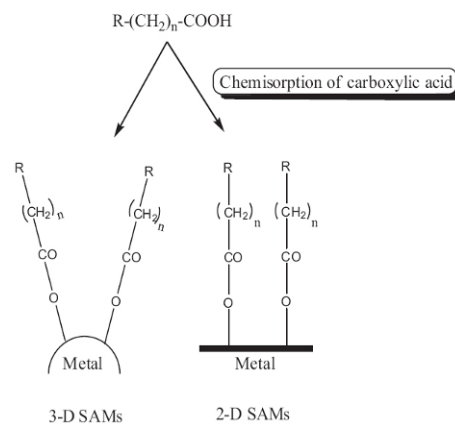
^a Indium titanium oxide [tin-doped indium oxide: solid solution of indium(III) oxide (In₂O₃) and tin(IV) oxide (SnO₂)].

**Figure 5.** Chemisorption of alkanethiols or disulfides on surface

2.1 Organosulfur based SAMs

As explained before, the construction of SAMs requires that the organic component be provided with a chemical functionality, or “head-group”, possessing a specific affinity for the surface. Alkanethiols are most utilized compounds for this purpose, essentially due to the observation that sulfur presents, in its reduced state, high affinity towards metals, particularly silver or gold while the carboxy group shows affinity towards other metals such as copper, palladium, platinum, and mercury. Such affinities also favours the displacement of adventitious organic materials whose absorption usually fulfils the requirement for lowering the free energy of the interface between the metal or metal oxide and the environment. Fig. 5 shows the formation of 2-D and 3-D SAMs from chemisorption of alkane thiols.

After absorption, the properties of the resulting two- (2-D) or three-dimensional (3-D) metallic nanostructures can be adjusted by modifying the chemical nature of the terminal (end) group R of the carbon chain: accordingly, these classes of organic compounds can be used to prepare highly ordered monolayers for their use in modern micro-nano fabrication, in biomaterials, biosensors,

**Figure 6.** Chemisorption of carboxylic acid on surface

molecular electronics, as well as for applications in analysis or in the study of interfacial phenomena, corrosion protection and electrode modification. The most extensively studied class of SAMs is derived from the adsorption of alkanethiols on gold, silver, copper, palladium, platinum, and mercury [2c]. Although the stability of these (alkane thiol monolayers) especially on gold remains a matter of debate as thiol chemisorption reaction is well known as kinetically favored and thermodynamically unstable. This is the reason that desorption of the thiol monolayer from the substrate is observed in certain cases.

2.2 Carboxylic acid based SAMs

Although thiol- and silane-based systems represent the bulk of the SAM literature, there are a number of reports of monolayers based on organic acids or ions (Fig. 6). For example, alkanolic, sulfonic, and phosphonic acids have been demonstrated to form organized monolayers on several metal or metal oxide surfaces. Also, organic ions, such as quaternary ammonium salt detergents, form stable-monolayer films on substrates like mica that have a nonzero net charge at accessible pH values. Aside from the practical significance of expanding the range of substrates that may be coated with SAMs, these systems (carboxylic acids) offer the opportunity to explore how the adsorbate-substrate interaction affects the assembly process and it should be stressed that the mechanism of formation of SAMs in this case involves different interactions than those in thiol or silane based SAMs. For surfaces made up of a metal other than gold; the chemistry of the metal and the anchoring group of the adsorbate organic molecules play an important role. Use of metals other than the costly noble metals will require other systems than organosulfur compounds; in this case carboxylic acids are useful building blocks for the formation of stable SAMs on metal surfaces whose oxidation potential is less than gold.

2.3 Alkoxysilane or chlorosilane based SAMs

The growth of trichlorosilane (similarly trimethoxy- or triethoxysilane)-based SAMs (Fig. 7) is unique among SAM systems in that it involves an irreversible covalent cross-linking step which is the formation of Si-O bonds not only with the surface hydroxyl groups but also with the silicon atom in the neighboring chain [26-41]. This is critical to the desirable properties of this class of SAMs, including their chemical and mechanical robustness on a variety of substrates. There is also the potential for hydrolytic bond formation to -OH surface groups that would immobilize adsorbate molecules. Again, this is critical to the stability of the final monolayer.

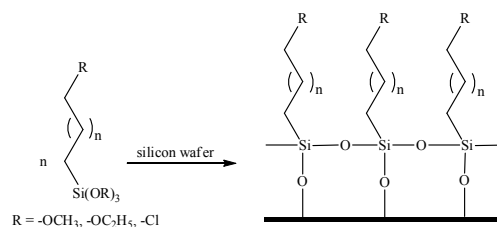


Figure 7. Alkoxysilane based SAMs

3. SAMs from Chemisorption of Carboxylic Acids

3.1 Important carboxylic acid based SAMs

Spontaneous adsorption of long-chain *n*-alkanoic acids has been studied in the past few years. Chemisorption in this case is an acid-base reaction, and the driving force is the formation of a surface salt between the carboxylate anion and a surface metal cation. Allara and Nuzzo [17,18] and Ogawa *et al.* [42] studied the adsorption of *n*-alkanoic acids on aluminum oxide. Schlotter *et al.* [43] studied the spontaneous adsorption of such acids on silver. Tao and coworkers showed that the chemisorption of alkanolic acids on amorphous metal oxide surfaces is not unique [44a,b]. It was found that on AgO surfaces, the carboxylate two oxygen atoms bind to the surface nearly symmetrically, while on surfaces of CuO and Al₂O₃, the carboxylate binds asymmetrically to the surface displaying tilt angles close to zero (Fig. 8). Recent Raman studies suggest that a monolayer of stearic acid adsorbed to a smooth Ag surface is less ordered than the stearic acid layer on Al₂O₃ [45] and that the chains in SAMs on Al₂O₃ are oriented along the surface normal. Table 2 summarizes the important reports from literature on carboxylic acids based SAMs.

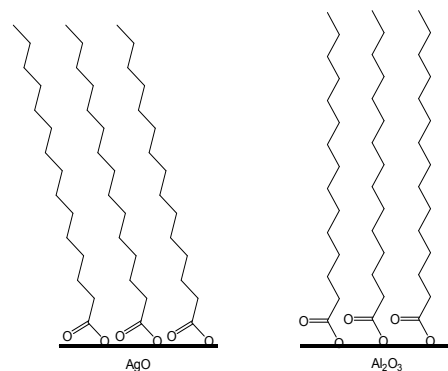


Figure 8. Monolayers of fatty acids on Ag and Al oxide surfaces.

3.2 Behavior of bifunctional molecules

In previous section we have seen the reports made on utilization of carboxylic acid functionalized molecules for monolayers preparation. However interesting observations were made for bifunctional molecules; organic compounds containing a thiol and a carboxylate functionality in the same molecules behaves differently in orientation of the monolayers with respect to the surface used. For example Muraly Sastry *et al.* [47a] in their experiments have reported on construction of monolayers from 4-carboxythiophenol (CTP) molecule on gold and aluminium surfaces. During the monolayer

formation from this aromatic molecule it has been found that thiol gets chemisorbed on gold giving rise to carboxy terminated SAMs and carboxylic group gets chemisorbed on aluminium oxide giving thiol terminated SAMs (Fig. 9). The same observation was reported by Alivisatos *et al.* [47b] back in 1992. These reports are of importance for construction of SAMs with desired terminal groups.

This aspect of selective chemisorptions has been used to self-assemble Ag colloidal particles from solution by forming a covalent linkage with the terminal thiol groups of CTP molecule. SAMs formed on Au surfaces with carboxylic acid surface functionality appear to be inefficient in coordinating to Ag clusters from solution. Interesting observations were reported by the research group of Zharnikov on chemisorptions of 16-mercaptohexadecanoic acid on Indium tin oxide (ITO) surface well documented with X-ray photoelectron studies [57]. Which shows binding of the bifunctional acids to ITO surface *via* carboxylic group resulting in thiol terminated SAMs. The immersion of ITO into a mixture of thiols and carboxylic acid results in a preferred adsorption of the acid. Accordingly, COOH(CH₂)₁₅SH adsorbs *via* the acid functionality, leading to a thiol terminated SAM that may be utilized to couple gold particles to ITO a similar approach as explained before where thiols groups at the periphery of the monolayers used to chemisorb silver nanoparticles. So there are conditions where carboxylic acids preferentially adsorb over thiols from the solution.

Table 2. Important observations about SAMs of carboxylic acids from literature

Substrate	Adsorbent	Observations	Ref. no.
Stainless steel	Alkanoic acids, functionalized alkanoic acids	Closely packed and well ordered self-assembled monolayers of various long-chain organic acids were formed on steel surface.	46
Gold, Aluminium, Silver	4-Carboxythiophenol	A comparative study of the formation of monolayers using a bifunctional molecule on two different substrates has been demonstrated. The nature of coordination of the molecules to the two metal surfaces is different, leading to different terminal functionality of the monolayer surface.	47
Gold	Fatty acids	DFT calculations are carried out to study fatty (carboxylic) acid molecules adsorbed on Au(111) via their COOH functional group. Focusing on model systems consisting of monolayers of COOHC ₆ H ₁₂ X molecules with different terminal groups X such as -COOH, -SH, and -CH ₃ .	48
Iron nanoparticles	Alkanoic acids	Nanophased amorphous iron particles were coated by various carboxylic acids and their physical properties were studied by differential scanning calorimetry (DSC), thermogravimetric (TGA) analysis, temperature-programmed desorption, infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy, and magnetism).	49
Gold	Hexanoic acid	Adsorption of carboxylic acids from liquid solutions on gold was investigated by electrochemical experiments including voltammetric measurements and quartz crystal microgravimetry.	50
Zirconium oxide	Long-chain alkanoic acid, ω-hydroxy alkanoic acids	Formation of conformationally ordered monolayers of long-chain alkanoic acids on zirconium oxide powder via a chelating bidentate zirconium carboxylate surface bond. -Hydroxyalkanoic acids and their NMR studies.	51
Stainless steel	Decanoic, Myristic, Palmitic, and Stearic acid	Electrochemical formation and characterization of decanoic, myristic, palmitic, and stearic acid self-assembled monolayers on a native oxide surface of 316L stainless steel have been studied. This study describes a new approach to surface modification of stainless steel in which the self-assembly of n-alkanoic acids is facilitated by applying a potential to the stainless steel in an organic electrolyte solution.	52
Aluminium oxide	Alkanoic acids	This work reports the observations on comparative study of the formation of self-assembled monolayers of alkanoic acids on bare aluminium oxide surface and aluminium oxide surface treated with zirconium oxide.	53
Hafnium oxide	Stearic acid	Self-assembled monolayers (SAMs) of four long aliphatic molecules with binding groups of phosphonic acid, carboxylic acid, and catechol were formed and characterized.	54
Aluminium oxide	Stearic acid	This work presents of the stability and bonding mechanism of stearic acid monolayers on aluminium oxide surface.	55
Silver	n-alkanoic acids, 4-alkoxybenzoic acid, 4-alkoxybiphenyl-4-carboxylic acid	Formation of stable self-assembled monolayers of carboxylic acids on a silver surface and their reversible reorganization to form discrete clusters of hydrogen-bonded free acids upon exposing the monolayer assembly to H ₂ S vapors.	56
Indium tin oxide	Alkane thiol, carboxylic acids and carboxy terminated thiols	Self-assembly of amphiphilic molecules, alkanethiols, carboxylic acids and bifunctional SH(CH ₂) ₁₅ COOH on indium tin oxide (ITO) and their characterization by X-ray photoelectron and near edge X-ray absorption fine structure spectroscopies, contact angle measurements, and atomic force microscopy.	57
Gold, silver and iron oxide nanoparticles	10,12-pentacosadiynoic acid (PCDA)	Gold and silver nanoparticles of different size, decorated by the chemisorption of diacetylenic monomers having a -COOH anchoring group, were prepared in aqueous dispersions. The topochemical photo polymerization of the colloidal suspensions was carried out by UV irradiation and studied by means of spectroscopic techniques.	58, 60
Gold and silver nanocages	10,12-pentacosadiynoic acid (PCDA)	The noble metal nanocages were functionalized with PCDA chains and then irradiated with UV light to induce polymerization of diacetylene groups present in the chemisorbed carboxylic acid monolayers.	59
Gold and Indium tin oxide electrodes	12-Ferrocenyldodecanoic acid	Orthogonal self-assembly (OSA) of carboxylic acids and thiols. The selectivity of the thiols for Au and the carboxylic or phosphonic acids for ITO is determined by a combination of cyclic voltammetry experiments using ferrocene-tagged molecules, scanning Auger microscopy, and imaging secondary ion mass spectrometry (SIMS) to map the distribution of thiols, carboxylic acids, and phosphonic acids on derivatized Au and ITO microstructures.	61

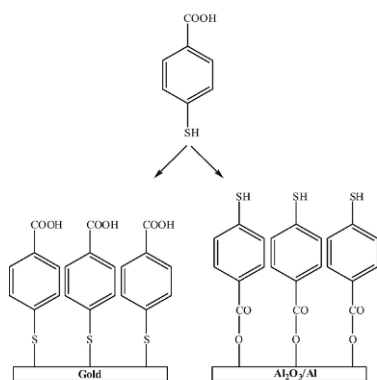


Figure 9. Chemisorption of (4-carboxythiophenol) on two different surfaces

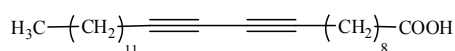


Figure 10. PCDA monomer

3.3 Carboxylic acid based polymerizable SAMs

Construction of SAMs from long-chain carboxylic acids containing functional group along the atom chain such as the polymerizable diacetylene groups has been a part of recent studies, where monolayers from functionalized thiols, carboxylic acids containing diacetylenic units have been constructed [60,61]. Later topochemical photopolymerization of the diacetylenes chemisorbed on various metallic nanostructured surfaces (such as nanoparticles, nanocages etc.) have been carried out. The resulting polymeric monolayer structures were then characterized by various instrumental techniques such as scanning electron microscopy (SEM), infrared spectroscopy (IR) and Raman spectroscopy. The photopolymerization of 10,12-pentacosadiynoic acid (PCDA, Fig. 10) was carried out successfully after fabrication of SAMs on metallic nanostructures where the carboxylic group anchors the monomer onto the surface (Fig. 11).

The same (PCDA) amphiphilic diacetylene compound was deposited on the surface of nano sized magnetite particles (Fe_3O_4) using a self-assembly method [62]. The diacetylene molecular assembly formed on the surface of nanoparticle was subjected to photopolymerization. This resulted in the formation of a polymeric assembly on the surface of the nanoparticles in which the adjacent diacetylene molecules were connected through conjugated covalent networks. The presence of immobilized polymer species on the surface of nanoparticles is expected to protect them from agglomeration thereby stabilizing their physical properties.

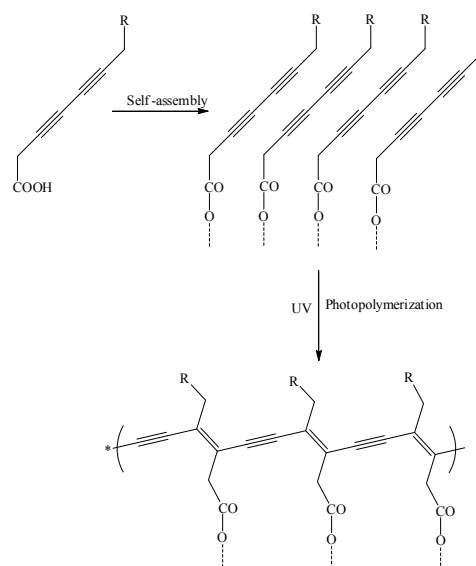


Figure 11. Photopolymerization of diacetylene compounds in monolayers

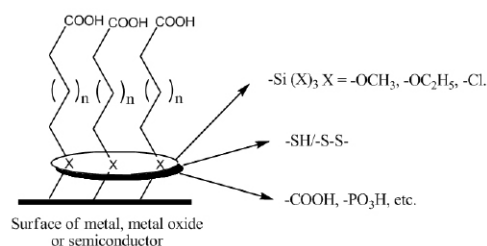


Figure 12. Carboxylic acid terminated SAMs

3.4 Carboxylic acid terminated SAMs

Monolayers of organic compounds on various substrates constructed from bifunctional organic compounds out of which one is carboxylic acid may be constructed in such a way that the carboxylic groups orient at the periphery of the monolayers (Fig. 12). Such carboxylic acid terminated monolayers have shown their importance in protein immobilization [62-66], electrochemistry [67-73], crystal growth [74], chemical analysis [75,76], and in surface modifications or surface reactions [77-80].

The reactive carboxylic functional group can be used to carry out reactions as that of a normal carboxylic acid in organic chemistry. These type of reactions carried out on the surface of the substrate are called as surface reactions. Reactions carried out on functional groups of monolayers in certain cases found to be faster than in solutions. Furthermore in case of three dimensional SAMs constructed on metallic nanostructures containing carboxylic groups add hydrophilic character to the system hence help to improve its solubility and also to selectively bind to biomolecules [89].

Table 3. Important carboxylic acid terminated SAMs

Substrate	Adsorbent	Observations	Ref. no.
Polycrystalline gold	11-mercaptoundecanoic acid	Horse heart cytochrome c (cyt c) has been covalently immobilized onto self-assembled monolayers (SAMs) from 11-mercaptoundecanoic acid (MUDA) developed on single-crystal or polycrystalline gold substrate surfaces. The cyt c immobilized substrates were characterized by atomic force microscopy (AFM).	81
Gold	11-mercaptoundecanoic acid	Reports the preparation of aluminum oxide films on gold substrates by means of using boehmite ^a where 11-mercaptoundecanoic acid (MUDA) self-assembled monolayers are used as sacrificial binders by means of carboxylic groups present in the monolayer that keep boehmite particles on a gold surface.	82
Crystalline silicon, silicon nitride	11-bromoundecanoic acid	Carboxylic acid terminated monolayers have been covalently anchored on the surface of crystalline silicon and silicon nitride (Si ₃ N ₄) using wet-chemistry methods. Their concentration has been determined by adopting a stepwise procedure with a fluorescent probe in solution.	83
Platinum nanoparticles	Thioglycolic acid	A facile one-step synthetic methodology to obtain ~1 nm, water-soluble carboxylate-terminated, platinum nanoparticles is reported. The methodology involves visible light as a reaction trigger and platinum acetylacetonate and thioglycolic acid as chemical reactants. These carboxy terminated nanoparticles are stable for weeks and can be easily transferred into organic solvents such as toluene, chloroform or dichloromethane using the cationic surfactant.	84
Silicon wafers	Undecylenic acid	Direct photochemical reaction of undecylenic acid on the hydrogenated Si(111) surface gives rise to monolayers terminated with intact carboxylic acid end groups. The IR studies proved that no reaction occurs between the carboxyl group and the silicon surface showing selective chemisorptions of alkene over carboxylic group.	85
Nitinol and nickel oxide	(12-Carboxydodecyl) phosphonic acid	Carboxylic acid terminated phosphonic acid monolayers as covalent linkers between the polymer and oxide surfaces. This was achieved through surface-initiated free radical polymerization using an azo-initiator. The modifications on the surfaces were characterized by IR, MALDI, AFM and contact angle measurements.	86
Gold	16-mercaptohexadecanoic acid	Interchain reaction between two carboxyl terminated chains giving rise to surface anhydrides using fluoro-N,N,N',N'-tetramethylformamidinium hexafluoro phosphate (TFFH) reagent has reported. This is an excellent example of a surface reaction.	87
Silicon	Ethyl undecylate and n-alkenes	The structure, reactivity, and acid-base properties of mixed monolayers prepared by photochemical reaction of hydrogen-terminated silicon with mixtures of ethyl undecylate and n-alkenes were studied by ATR-FTIR spectroscopy and contact-angle measurements. Later the ester terminated molecules were hydrolyzed to corresponding acids to generate carboxylic acid terminated mixed monolayers.	88

^a A boehmite particle, also known as pseudoboehmite (or aluminum oxyhydroxide), is a poor crystalline form of mineral boehmite, which has an infinite arrangement of the Al-O-Al core structure with the aluminum atom octahedrally coordinated by five oxide and one hydroxide anions

3.5 Applications

As per their counterparts (alkanethiols and alkoxy silane based SAMs) monolayers based on carboxylic acid have also shown their applicability in various fields such as lubricants, corrosion resistant materials and stabilization of nanostructures where various metal or metal oxide surfaces were coated with them. Carboxylic group terminated monolayers are important members in carrying out surface reactions where the terminal carboxylic acid groups are used to carry out various organic reactions or for covalent immobilization of biomolecules. Bifunctional molecules on certain metal

oxide surfaces tend to absorb *via* carboxylic group this phenomenon is useful to generate thiol terminated SAMs, which later can be utilized for further chemisorption of other metallic nanostructures to create nanoarrays. Effective coating of carboxylic amphiphiles prevent agglomeration of nanoparticles and result in modification of physical properties, carboxylic groups add hydrophilic nature to the nanostructure where solubility is an issue. Systems such as energy conversion devices where metals (or metallic oxides) other than costly noble metals needed to be utilized; conjugated carboxylic acids are useful building blocks for the monolayer construction.

4. Conclusions and Outlook

Because SAMs are being used as a route for suitable modification of surfaces involving a greater variety of substrates and adsorbate chemical functionality, this route of surface modification is becoming increasingly important. Although the mechanism of chemisorptions of carboxylic acids and orientations of the molecules in monolayer have been less studied, These amphiphiles represent a class of materials that retains its importance in specific applications and posses potential applications in various fields. However the challenge of constructing stable SAMs from carboxylic acids on wide variety of

substrates and synthesis of newer long-chain carboxylic acid derivatives designed keeping in mind structure property relationship as building blocks of SAMs remains wide open.

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