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# **Self Assembled Monolayers - A Review**

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**Abstract:** Self assembly provides a simple route to organise suitable organic molecules on noble metal surface by using long chain organic molecules with various functionalities like -SH,-COOH, $-NH_2$ , Silanes etc. These surfaces can be used to build up interesting nano level architectures. Self assembly is an interesting process for biological relevance because it provides a novel approach to complex structure having nanometre scale dimensions. The self assembled monolayers (SAMs) can be characterized by the number of techniques such as Contact angle goniometry, X-ray photoelectron spectroscopy, Infra red and scanning probe microscopy which provides the valuable information about the SAMs.

Keywords: SAMs, monolayer, characterization, SAM formation.

## **Introduction**

Self assembled monolayers (SAMs) are highly ordered molecular assemblies formed spontaneously by chemisorptions and self organization of long chain molecules on the surface of appropriate substrates. This is an interesting process for its biological relevance because it provides a novel approach to complex structure having nanoscale dimensions. These types of structures are difficult to prepare by traditional methods<sup>1</sup>. Alkanthiols self assembly onto gold is the most studied example of SAMs which determine the strong gold sulphur and chain- chain interactions. SAMs have been applied in the sensors<sup>2-3</sup>, interfaces<sup>4</sup> development of and microfabrication <sup>5-9</sup>. One of the most important class of SAMs is based on the strong adsorption of sulphurbased compounds- thiols, diulphides, sulphide, and related moieties on coinage metals, particularly Au, Ag, Cu as well as Pt, Hg, Ga, As {100} and InP {100} surfaces<sup>10-16</sup>. During the formation of self assembled monolayers adsorption is generally carried out by placing the substrate in dilute solution of thiols. Any solvent which is capable of dissolving the thiol can be used. Adsorption can be also carried out under

potential control or from the vapour phase <sup>12</sup>. A wide range of fundamentals groups can be merged into the SAM without any destabilisation <sup>10-16</sup>. The nature of the terminal groups plays an important role in determining the properties of the monolayers such as wettability and ionisation <sup>14</sup>. The field of self assembled monolyers has fascinated tremendous growth in synthetic sophistication and depth of characterization over the past few years <sup>17</sup>.

In 1946 Zisman has studied the preparation of mono molecular layers by adsorption (self assembly) of a surfactant onto a clean metal surface. Nuzzo and Alara also showed that SAMs of alkanethiols on gold can be prepared by adsorption of di-n-alkyl sulphides from dilute solutions. Formation of monolyers by self assembly of surfactant molecules at surface are the examples of the general phenomenon of self assembly. Self assembly process provides a chance to increase fundamental understanding of self organization, structure property, relationships and interfacial phenomenon. Excellency of SAMs depends upon the tailoring of both head and tail groups of the constituient molecules. It is useful for understanding of phenomenon affected by coupling, intermolecular, molecular substrates and molecule-solvent interaction like ordering and growth, wetting, adhesion, lubrication and corrosion <sup>18</sup>.

Self assembly is a term of superamolecular chemistry <sup>19</sup> and is generally used to define the superamolecular interaction among molecules in solution or solid state to give special arrangement or architectures. This is also used for formation of micelles and other systems formed by the surfactants. In this review we will elaborate the term SAM on the metal surface or adsorption of molecules on the solid surface.

# Formation of self assembled mono and multilayers on a metal surface

Till date gold has been the most well studied surface for the self assembly process by using alkanethiols. In the literature formation of SAMs of alkanethiols on gold can be summarised as in which, Au (111) surface present the best characteristics for the formation of SAMs. The thiolate groups (formed by deprotonation as a result on the interaction) are associated with the three Au atoms on the surface. Interaction between Au-Sulfur is reversible which permits the alkanethiols anions to interact among themselves in order achieve formation of highly compact monolayers. the Alkanethiolates with about 10-20 carbon atoms achieve highest organised monolayers and assemble on a gold surface with an angle  $30^{\circ}$  from the normal to the surface.

One of the simplest ways to form the self assembled monolayers is to dip an extremely clean oxidized gold sheet surface into an ethanol solution of corresponding alkanethiols. Other types of organic solvents can also be used. The conc. of the thiol may vary between 1mM and 1 $\mu$ M. There is a complete formation of SAM occur within a time limit of 12-18 hr at room temperature because self assembly of molecules occur

within first few seconds but more time is required for the organised and compact monolayers <sup>18</sup>. A systematic representation for the formation of SAM is described in the Fig. (1).

SAM has been built on Silver, Copper, Nickel, Palladium and Platinum<sup>20</sup> metal surfaces. But Silver, Nickel and Copper are due to their less interaction can easily oxidize. Copper can oxidize extremely so it is difficult to obtain the organised and compact SAM on this metal. A very stable SAM on the Platinum surface has been obtained by using isocynide <sup>21</sup>. Many metal complexes such as  $Ru(bpy)_3 \stackrel{22}{}; (C_2H_5)_2Fe \stackrel{23}{}$  and porphyrin<sup>24-26</sup> can be self assembled by thiol or disulphide anchor groups on an gold or indium tin oxide (ITO) electrode, in this not only the basic electron transfer kinetics but also photocurrent generation of sensing properties have been explored. Except gold other organic groups such as carboxylate, phosphonate and isocynide also urged to act as surface immobalised groups <sup>27</sup>. These organic groups have different reactivity towards Gold, Platinum and metal oxide. It is also termed as orthogonal self assembly which is reported earlier i.e. thiol and disulphide groups bound to Gold substrate <sup>28</sup>.

On the other hand cyanide and pyridine groups are bound to a platinum surface and phosphonate and silanol groups to indium tin oxide and metal oxide surface <sup>29</sup>. Thiol -Au self assembled chemistry has been extensively studied but till date phosphonate metal oxide self assembled chemistry is not so mature. In phosphonate –metal oxide self assembled chemistry the growth mechanism of long chain phosphonic acid on mica or sapphire has been investigated earlier by many researchers <sup>30-31</sup>.



Fig. 1 Self-assembled monolayers are formed by simply immersing a substrate into a solution of the surfaceactive material.

#### Self Assembled Monolayers of Fatty acids

There is a continuous absorption of long chain nalkanoic acids (C<sub>n</sub>H<sub>2n+1</sub>COOH) in the earlier years. In this acid base reaction and the driving force which is responsible for formation of a surface salt between the carboxylate anion and surface metal cation. Scholltter and his co-workers also reported the spontaneous adsorption of such acids on silver surface <sup>32</sup>. Chemisorption of alkanoic acids on amorphous metal oxide surface is not unique which was shown by Tao and he observed that on the AgO surfaces the carboxylate two oxygen atoms bind to the surface in a symmetrical way while on the CuO and Al<sub>2</sub>O<sub>3</sub> surface. Carboxylate binds asymmetrically to the surface and show tilt angle zero. From the current Raman studies it was observed that monolayers of steric acids on a smooth Ag surface are less ordered than the layer formed on Al<sub>2</sub>O<sub>3</sub> surface<sup>33</sup>. It has been also observed that the chains in SAMs on AgO are lying along normal to the surface and he has also observed through the IR studies that monolayers on AgO are well arranged than their counterparts on Al<sub>2</sub>O<sub>3</sub>.

## **Monolayers of organosilicon Derivatives**

For the formation of self assembled monolayers of alkylchlorosilanes, alkylalkoxysilanes, and alkylaminosilanes require hydroxylated surfaces as substrates for their formation. The driving force for this self-assembly is the in situ formation of polysiloxane, which is connected to surface silanol groups (-SiOH) via Si-O-Si bonds. Substrates on which these monolayers have been successfully prepared include silicon oxide <sup>34-39</sup>, aluminum oxide <sup>40-41</sup>, quartz <sup>42-43</sup>, glass <sup>39</sup>, mica <sup>44-46</sup>, zinc selenide <sup>39-40</sup>, germanium oxide <sup>47</sup>, and gold <sup>48-50</sup>. Recently Allara and his coworkers have compared OTS monolayers on silicon oxide and on gold activated by UV-ozone exposure. IR spectroscopy, ellipsometry, and wetting

measurements showed identical average film structures <sup>51</sup>.

# Organosilane self assembled monolayers on SiO<sub>2</sub>

Organosilanes generally consist of a silicon atom tetrahedrally bound to three similar functional groups (short chain alkoxy group or chlorines) then to a functional group. In case of S-Au ineraction the bond is mostly charged transfer in nature but head groupsubstrate interaction of the Silane and SiO<sub>2</sub> surface is quite different<sup>52</sup>. In this silane molecule condense with native hydroxyl group adorning the SiO<sub>2</sub> surface, forming a thin layer of covalently polysiloxane at the interface. Organosilane SAMs on SiO<sub>2</sub> have a great importance in the photo resist industry because of their patterening by energetic beams which affords structures that can direct the substrates topographical etching.

#### Alkanthiolates on the noble metal surfaces

Lot of the work have been reported in the field of structure as well as placement of alkanethiolate films on the surfaces other than the gold such as Platinum <sup>53</sup>, Palladium <sup>54-56</sup>, Silver <sup>57-58</sup> and Copper <sup>56, 58</sup>. This area has not been spread extensively but no doubt it will be extremely useful in balancing order and placement of molecules with an ability to create stable and functional nanostructures.

### Amino terminated SAMs

Amidation is one of the most widely used surface reactions on self assembled monolayers. Surface amino groups can be easily converted to amides by coupling with a carboxylic acid. An aminotrithiol has been used for SAM formation <sup>59</sup> and cystammine absorbs spontaneously onto gold surfaces forming a uniform and active amino terminated monolayer. Amidation of cystammine SAMs with azobenzene is shown in Fig. (2).







Fig. 3 The reaction scheme of 2, 3-dichloro-1, 4-naphtoquinone to the aminoalkanethiol SAMs on gold surface<sup>62</sup>

#### Self assembly of alkanethiols on a gold surface

Aminoalkane thiols are utilized for the modifications of Au surface and to introduce amino group on it. Amino group is usually modified with amine reactive materials such as protein molecule or biomaterials to functionalize the Gold surface. 11-amino-1undecanethiol monolayers on a gold electrode were formed and studied the effect of the terminal groups on the redox reponswes of ferrocene derivatives by voltmetric techniques <sup>61</sup>. They have also reported the relationship between the alkyl chain length of aminoalkanethiols and the redox behaviour of 2, 3dichloro-1,4-napthoquinone attached to the terminal amino group shown in Fig. (3).

Carboxyalkanethiols are also used for the modification of gold surface to introduce the carboxylic group on it. Glenn and co-workers used carboxyalkanethiol and poly L-lysine to create cytochrome b<sub>5</sub>-immoblized multilayer <sup>63</sup>. Hydroxylalkanethiols are utilized as dilution reagents or blocking reagents on a gold surface or to present the nonspecific binding of analytes on the surface.

Mixed SAMs of thiol derivatized single-stranded DNA (HS-ss-DNA) and 6-hydroxy-1-hexanethiol on a gold surface. They prevented non specific adsorption of HS-ss-DNA<sup>64</sup>. Dubrovsky and his co-workers controlled the nonspecific adsorption of protein on the surface of a gold coated silicagel for the preparation of well defined and surface-functionalized supports for biological assay<sup>65</sup>.

#### **Characterization of SAMs**

Self assembled monolayers (SAMs) can be characterized by number of experimental methods which includes physical measurements like contact angle and wetability, spectroscopic techniques such as ellipsometery <sup>66</sup>, X-ray photon spectroscopy (XPS) <sup>67</sup>,

infrared spectroscopy (IR) <sup>68</sup>, quartz crystal membrane (QCM) <sup>69</sup>, surface enhanced Raman spectroscopy <sup>70</sup>, (AFM) <sup>71</sup>, scanning tunnelling microscopy <sup>72</sup>, fluorescence spectroscopy, surface Plasmon resonance (SPR) etc. which provide valuable information about the structure and dynamics of SAMs. Due to their biological importance several biomolecules like enzymes or whole cells can be immobilized on SAM surface and their lipid like microenvironment can be characterized specially for electrochemical sensing or biomolecular electronics. Few of the methods are discussed in this paper.

#### **Contact angle goniometry**

To determine the hydrophobicity and hydrophilcity of a surface, this technique is commonly used; it has been also applied to the surface of SAM. In this method a drop of H<sub>2</sub>O (or any other liquid) is put into contact with the surface, then angle between the film and liquid droplet is measured. It determines the degree of surface order as well as indicate the incorporation of functional groups, contact angle also changes with varying film composition. Water droplet will make a smaller contact angle for the hydrophilic surface such as (-OH,-COOH, -CO<sub>2</sub>CH<sub>3</sub> terminated surfaces) on the water will more effectively wet the hydrophilic surfaces. Many research groups have used contact angle goniometry to analyze and to estimate the relative mole fractions of the adsorbates composing mixed SAMs, as the contact angle will change with varying film composition. The resolution of the techniques is occur within the tens of microrange, so as a result submicron pattern are not readily observed.

#### X-Ray Photon Spectroscopy

This method is employed to probe the chemical nature of SAM, it determine that a covalent bond exist between the sulphur head group and the gold substrate, it also defined the chemical species, oxidation states of constituent atoms in the SAM, also demonstrated that the thickness of single monolayer film.

In this technique incident X-rays bombarded the sample and the electrons are ejected from the core shells of the atoms within the SAM. These electrons are collected and dispersed in an analyzer and binding energy are calculated by measuring the kinetic energies of the electron when enter the analyzer. It is specific to each element and gives indications of the oxidation state of the elements. The thickness of the SAM depends upon the ratio of the substrate signal before and after the presence of the SAM. It is capable of identifying the oxidation state as well as elements present in the SAMs. This technique is considered as a powerful diagnostic tool to analyze SAMs when they have been chemically modified.

### FT-IR

FT-IR has been widely used to measure the vibrational frequencies of bonds within molecules. This technique has been used to characterize the vibrational modes of SAMs (for both SAMs of n-alkanethiols on gold substrate as well as for SAMs of alkanoic acids on alumina supports); it is most recognized for characterizing the general order within the alkyl matrix of the molecular backbone.

The alkyl tails vibrate at characteristic frequency range of 2800-3000 cm<sup>-1</sup>. Both the breadth of these peaks as well as the frequencies of the vibrations themselves

## **References**

- Isaacs L., Chin D. N., Bowden N., Xia Y. and Whitesides G. M., Perspectives in Supramolecular Chemistry, Wiley & Sons, Chichester, 4, 1 (1999).
- Huisman B.H., Kooyman R. P. H., van Veggel F. C. J. M. and Reinhoudt D. N., Molecular recognition by self-assembled monolayers detected with surface plasmon resonance. Adv. Mater., 8, 561-564 (1996).
- Schierbaum K. D., Weiss T., Thoden van Velzen E. U., Engbersen J. F. J., Reinhoudt D. N. and Gopel W., Molecular Recognition by Self-Assembled Monolayers of Cavitand Receptors. Sci., 265, 1413-1415 (1994).
- Shon Y. S., Lee S., Colorado R., Perry S. S. and Lee T. R., Spiroalkanedithiol-Based SAMs Reveal Unique Insight into the Wettabilities and Frictional Properties of Organic Thin Films. J. Am. Chem. Soc., 122, 7556-7563 (2000).

gives a picture with a relative order and fraction of chain defects within the SAM. FT-IR can also identify the presence of functional groups by identifying their particular vibrational frequencies such as (amides, carboxylates and hydroxyls). Thus the progress of reaction at SAM surface can be determined using FT-IR.

### Scanning probe microscope

Scanning probe microscope played an important role and they assist in the patterening of SAMs because it analyzes the spatial distribution of adsorbates across a surface. Stability of SAM structure is critical and they will give rise to final patterned structures. Mobility of the n-alkanethiolates once absorbed to the surface, their thermal stability and their resistance to variety of solvents and other environmental factor will ultimately determine the fate of the applications of the SAMs.

### <u>Conclusion</u>

Self assembled monolayers (SAMs) are crystalline chemisorbed organic single layer formed on solid state substrates by spontaneous organization of molecules. Self assembly of thiols on gold has stimulated and facilitated numerous surface chemical studies and oppournities. SAMs are an ideal model that can be used to study phenomenon such as wetting, friction, adhesion and biological interaction.

- Diaz D. J., Hudson J. E., Storrier G. D., Abruna H. D., Saudararajan N. and Ober C. K., Lithographic Applications of Redox Probe Microscopy. Langmuir, 17, 5932-5938 (2001).
- Alain C., Geissler M., Schmid H., Michel B. and Delamarche E., Self-Assembled Monolayers of Eicosanethiol on Palladium and Their Use in Microcontact Printing. Langmuir, 18, 2406-2412(2002).
- Lopez G. P., Biebuyck H. A., Frisbie C. D. and Whitesides G. M., Imaging of features on surfaces by condensation figures. Sci., 260, 647-652 (1993).
- 8. Xu S., Miller S., Laibinis P. E. and Liu G. Y., Fabrication of Nanometer Scale Patterns within Self-Assembled Monolayers by Nanografting. Langmuir, 15,7244-7251(1999).
- Liu G.Y., Xu S. and Qian Y., Nanofabrication of Self-Assembled Monolayers Using Scanning Probe Lithography. Acc. Chem. Res., 33, 457-466 (1999).

- 10. Ulman A., Academic Press: New York, 1991.
- Ulman A., Formation and Structure of Self-Assembled Monolayers. Chem. Rev., 96, 1533-1554 (1996).
- Finklea H. O., Electroanalytical Chemistry, Eds. A. J. Bard, I. Rubinstein, Marcel Dekker: New York, 19,109- 335(1996).
- Dubois L. H. and Nuzzo R. G., Synthesis, Structure, and Properties of Model Organic Surfaces. Annu. Rev. Phys. Chem., 43, 437-463 (1992).
- Finklea H. O., Encyclopedia of Analytical Chemistry, Ed. R. A. Meyers, Wiley: Weinheim, 10, 10090-10115 (2000).
- Nuzzo R. G. and Allara D. L., Adsorption of bifunctional organic disulfides on gold surfaces. J. Am. Chem. Soc., 105, 4481-4483 (1983).
- Strong L. and Whitesides G. M., Structures of selfassembled monolayer films of organosulfur compounds adsorbed on gold single crystals: electron diffraction studies. Langmuir, 4, 546-558 (1988).
- 17. Ulman A., Academic Press: Boston, 1991.
- Ulman A., Formation and Structure of Self-Assembled Monolayers. Chem. Rev., 96, 1533-1554 (1996).
- 19. Lehn J.M., Supramolecular Chemistry, VCH, Weinheim, 1995.
- Whitesides G.M., Williams J.A. and Gorman C.B., Alkanethiol Reductive Desorption from Self-Assembled Monolayers on Gold, Platinum, and Palladium Substrates. J. Phys. Chem. C 111, 12804-12810 (2007).
- Hickman J.J., Laibinis P.E., Auerbach D.I., Zou C., Gardner T.J., Whitesides G.M. and Wrighton M.S., Toward orthogonal self-assembly of redox active molecules on platinum and gold: selective reaction of disulfide with gold and isocyanide with platinum. Langmuir, 8, 357-361 (1992).
- 22. Sato Y. and Uosaki K., Performance of a prototype of the CMS central detector. J. Electroanal. Chem., 384, 57-58 (1995).
- Sikes H.D., Smalley J.F., Dudek S.P., Cook A.R., Newton M.D., Chidsey C.E.D. and Feldberg S.W., Rapid Electron Tunneling Through Oligo phenylenevinylene Bridges. Sci., 291, 1519-1521 (2001).
- 24. Offord D.A., Sachs S.B., Ennis M.S., Eberspacher T.A., Griffin J.H., Chidsey C.E.D. and Collman J.P., Synthesis and Properties of Metalloporphyrin Monolayers and Stacked Multilayers Bound to an

Electrode via Site Specific Axial Ligation to a Self-Assembled Monolayer. J. Am. Chem. Soc., 120, 4478-4487 (1998).

- 25. Li D., Moore L.W. and Swanson B.I., Formation of Metal Clusters on the Surfaces of Covalently Bound Self-Assembled Ligand Monolayers. Langmuir, 10, 1177-1185 (1994).
- 26. Finklea H.O. and Hanshew D.D., Electron-transfer kinetics in organized thiol monolayers with attached pentaammine(pyridine)ruthenium redox centers.J.Am. Chem. Soc., 114, 3173-3181 (1992).
- 27. Hickman J.J., Zou C., Ofer D., Harvey P.D., Wrighton M.S., Laibinis P.E., Bain C.D. and Whitesides G.M., Combining spontaneous molecular assembly with microfabrication to pattern surfaces: selective binding of isonitriles to platinum microwires and characterization by electrochemistry and surface spectroscopy. J. Am. Chem. Soc. 111, 7271-7272 (1989).
- Hatzor A., Moav T., Cohen H., Matlis S., Libman J., Vaskevich A., Shanzer A. and Rubinstein I., Coordination-Controlled Self-Assembled Multilayers on Gold. J. Am. Chem. Soc., 120, 13469-13477 (1998).
- 29. Cao G., Hong H.G. and Mallouk T.E., Layered metal phosphates and phosphonates: from crystals to monolayers. Acc. Chem. Res., 25, 420-427 (1992).
- Woodward J.T., Ulman A. and Schwartz D.K., Self-Assembled Monolayer Growth of Octa decylphosphonic Acid on Mica. Langmuir, 12, 3626-3629 (1996).
- Messerschmidt C.and Schwartz D.K., Growth Mechanisms of Octadecylphosphonic Acid Self-Assembled Monolayers on Sapphire (Corundum): Evidence for a Quasi-equilibrium Triple Point. Langmuir, 17, 462-468 (2001).
- 32. Allara D.L. and Nuzzo R.G., Spontaneously organized molecular assemblies. 1. Formation, dynamics, and physical properties of n-alkanoic acids adsorbed from solution on an oxidized aluminum surface. Langmuir, 1, 45-52 (1985).
- 33. Allara D.L. and Nuzzo R.G., Spontaneously organized molecular assemblies. 2. Quantitative infrared spectroscopic determination of equilibrium structures of solution-adsorbed nalkanoic acids on an oxidized aluminum surface. Langmuir, 1, 52-61 (1985).
- Sagiv J., Organized monolayers by adsorption; Formation and structure of oleophobic mixed monolayers on solid surfaces. J. Am. Chem. Soc., 102, 92 (1980).

- Silberzan P., Leger L., Ausserre D. and Benattar J.J., Silanation of silica surfaces. A new method of constructing pure or mixed monolayers. Langmuir, 7, 1647-1651 (1991).
- 36. Wasserman S.R., Tao Y.T. and Whitesides J.M., Structure and reactivity of alkylsiloxane monolayers formed by reaction of alkyltrichlorosilanes on silicon substrates. Langmuir, 5, 1074-1087 (1989).
- Le Grange J. D., Markham J. L. and Kurjian C. R., Effects of surface hydration on the deposition of silane monolayers on silica. Langmuir, 9, 1749-1753 (1993).
- Maoz R. and Sagiv J., Modification of polymer latex. J. Colloid Interface Sci., 100, 465-475-483 (1984).
- 39. Gun J., and Sagiv J., On the formation and structure of self-assembling monolayers : III. Time of formation, solvent retention, and release. J. Colloid Interface Sci., 112, 457-472 (1986).
- 40. Gun J., Iscovici R. and Sagiv J., On the formation and structure of self-assembling monolayers: II. A comparative study of Langmuir—Blodgett and adsorbed films using ellipsometry and IR reflection—absorption spectroscopy. J. Colloid Interface Sci., 101, 201-212 (1984).
- Tillman N., Ulman A., Schildkraut J.S. and Penner T.L., Incorporation of phenoxy groups in selfassembled monolayers of trichlorosilane derivatives; Effects on film thickness, wettability and molecular orientation. J. Am. Chem. Soc., 110, 6136-6144 (1988).
- 42. Brandriss S. and Margel S., Synthesis and characterization of self-assembled hydrophobic monolayer coatings on silica colloids. Langmuir, 9, 1232-1234 (1993).
- 43. Mathauser K. and Frank C.W., Naphthalene chromophore tethered in the constrained environment of a self-assembled monolayer. Langmuir, 9, 3002-3007 (1993).
- 44. Mathauser K. and Frank C.W., Analysis of electric properties of chemically adsorbed multilayers on solid substrates. Langmuir, 9, 3446-3451 (1993).
- Carson G. and Granick S., Self-assembly of octadecyltrichlorosilane films on mica. J. Appl. Polym. Sci., 37, 2767-2772 (1989).
- 46. Kessel C.R. and Granick S., Formation and characterization of a highly ordered and wellanchored alkylsilane monolayer on mica by selfassembly. Langmuir, 7, 532-538 (1991).

- 47. Schwartz D.K., Steinberg S., Israelachvili J.and Zasadzinski Z.A.N., Growth of a self-assembled monolayer by fractal aggregation. Phys. Rev. Lett., 69, 3354-3357 (1992).
- Finklea H.O., Robinson L.R., Blackburn A., Richter B., Allara D.L. and Bright T., Formation of an organized monolayer by solution adsorption of octadecyltrichlorosilane on gold: electro chemical properties and structural characterization. Langmuir, 2, 239-244 (1986).
- 49. Rubinstein I., Sabatani E., Maoz R. and Sagiv J., Theory of energy loss in scanning transmission electron microscopy of supported small particles. Proc. Electrochem. Soc., 86, 175-179 (1986).
- 50. Rubinstein I., Sabatani E., Maoz R. and Sagiv J., Stand-alone cosmic muon reconstruction before installation of the CMS silicon strip tracker. Electroanal. Chem., 219, 365-369 (1987).
- 51. Allara D.L., Parikh A.N. and Rondelez F., Evidence for a Unique Chain Organization in Long Chain Silane Monolayers Deposited on Two Widely Different Solid Substrates. Langmuir, 11, 2357-2361 (1995).
- 52. Rachel K. S., Penelope A. L. and Weiss S. P., Patterning self-assembled monolayers. Prog. Surface Sci., 75, 1–68 (2004).
- 53. Schlenoff J.B., Li M. and Ly H. Stability and Self-Exchange in Alkanethiol Monolayers. J. Am. Chem. Soc., 117, 12528-12536 (1995).
- 54. Love J.C., Wolfe D.B., Chabinyc M.L., Paul K.E. and Whitesides G.M., Self-Assembled Monolayers of Alkanethiolates on Palladium Are Good Etch Resists. J. Am. Chem. Soc., 124, 1576-1577 (2002).
- 55. Carvalho A., Geissler M., Schmid H., Michel B. and Delamarche E., Self-Assembled Monolayers of Eicosanethiol on Palladium and Their Use in Microcontact Printing. Langmuir, 18, 2406-2412 (2002).
- 56. Laibinis P.E., Whitesides G.M., Allara D.L., Tao Y.T., Parikh A.N. and Nuzzo R.G., Comparison of the structures and wetting properties of self-assembled monolayers of n-alkanethiols on the coinage metal surfaces, copper, silver, and gold. J. Am. Chem. Soc., 113, 7152-7167 (1991).
- 57. Xia Y., Kim E. and Whitesides G.M., Template self assembly over patterned electrodes by an applied field . J. Electrochem. Soc., 143, 1070-1076 (1996).
- 58. Xia Y.N., Kim E., Mrksich M. and Whitesides G.M., Syntheses of copper nanoparticles in

gelified microemulsion and in reverse micelles . Chem. Mater., 8, 601-611 (1996).

- 59. Whitesell J. K. and Chang H. K., Directionally Aligned Helical Peptides on Surfaces. Sci., 261, 73-76 (1993).
- 60. Yu H. Z., Zhao J. W., Wang Y. Q., Cai S. M. and Liu Z. F., Amidation of cysteamine SAMs with azobenzene . J. Electroanal. Chem., 438, 221 (1997).
- 61. Takehara K., Takemura H. and Ide Y., Electrochemical studies of the terminally substituted alkanethiol monolayers formed on a gold electrode: Effects of the terminal group on the redox responses of  $Fe(CN)^{3-}_{6}$ ,  $Ru(NH_3)^{3+}_{6}$  and ferrocenedimethanol. Electrochim. Acta, 39, 817-822 (1994).
- 62. Mukae F., Takehara K. and Takemura H., Electrochemical Behavior of the Naphtoquinone Anchored onto a Gold Electrode through the Self-Assembled Monolayers of Aminoalkanethiol. Bull. Chem. Soc. Jpn., 69, 2461-2467 (1996).
- Glenn J. D. H. and Bowden E. F., Diffusionless Electrochemistry of Cytochrome b<sub>5</sub> Adsorbed on a Multilayer Film Electrode. Chem. Lett., 25, 399 (1996).
- Herne T. H. and Tarlov M. J., Characterization of DNA Probes Immobilized on Gold Surfaces. J. Am. Chem. Soc., 119, 8916-8921 (1997).
- 65. Dubrovsky T. B., Hou Z., Stroeve P. and Abbott N. L., Self-Assembled Monolayers Formed on Electroless Gold Deposited on Silica Gel: A Potential Stationary Phase for Biological Assays Anal. Chem., 71, 327-332 (1999).
- 66. Porter M.D., Bright T.B., Allara D.L. and Chidsey C.E.D., Structural characterization of n-alkyl thiol monolayers on gold by optical ellipsometry, infrared spectroscopy, and electrochemistry. J. Am. Chem. Soc., 109, 3559-3568 (1987).

- Bourg M.C., Badia A. and Lennox R.B., Gold–Sulfur Bonding in 2D and 3D Self-Assembled Monolayers: XPS Characterization J. Phys. Chem. B104, 6562-6567 (2000).
- Nuzzo R.G., Dubios L.H. and Allara D.L., Formation and structural characterization of a selfconsistent series of polyfunctional organic monolayers. J. Am. Chem. Soc., 112, 558-569 (1990).
- Aslam M., Bandyopadhyay K., Lakshminarayanan V. and Vijayamohanan K., Comparative Behavior of Aromatic Disulfide and Diselenide Monolayers on Polycrystalline Gold Films Using Cyclic Voltammetry, STM, and Quartz Crystal Microbalance. J. Colloid. Interface Sci., 234, 410-417 (2001).
- 70. Bandyopadhyay Vijayamohanan К., K., Venkataramanan M. and Pradeep T., Self-Assembled Monolayers of Small Aromatic Disulfide and Diselenide Molecules on Polycrystalline Gold Films: A Comparative Study of the Geometrical Constraint Using Temperature-Dependent Surface-Enhanced Raman Spectroscopy, X-ray Photoelectron Spectroscopy, and Electrochemistry. Langmuir, 15, 5314-5322 (1999).
- Finklea H.O., Snider D.A., Fedyk J., Sabatani E., Gafni Y. and Rubenstein I., Characterization of octadecanethiol-coated gold electrodes as microarray electrodes by cyclic voltammetry and ac impedance spectroscopy. Langmuir, 9, 3660-3667 (1993).
- Poirier G.E., Characterization of Organosulfur Molecular Monolayers on Au(111) using Scanning Tunneling Microscopy. Chem. Rev., 97, 1117-1128 (1997).

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