

# A Brief History of Thiols: An Assembly of Self-assembly

D. Graham\*

\*Asemblon Inc, 15340 NE 92nd Street; Suite B,  
Redmond WA, USA, dgraham@asemblon.com

## ABSTRACT

For decades, thiols have been used to control surface chemistry and study surface interactions in a wide range of fields. The elegantly simple method of forming thiol self-assembled monolayers has enabled researchers to unleash their creative minds and begin to tap into true surface engineering designs. This brief overview will highlight the history of the use of thiols in self-assembly from simple solution deposition of homogeneous monolayers to the creation of patterned surfaces with UV photopatterning, stamps, and dip pen lithography. The versatility and simplicity of thiol self-assembly has kept the method in the forefront as one of the most common surface modification methods, and has led to new developments and opportunities in nanotechnology.

**Keywords:** self-assembly, surface chemistry, patterning, surface functionalization

## 1 EARLY THIOL HISTORY

The purpose of this document is not to provide a comprehensive summary of alkanethiols and their uses, but to give a sampling of the history of alkanethiol self-assembly and highlight some of the accomplishments and discoveries found from their use. Well written papers already exist in the literature that provide a comprehensive review of alkanethiols and their uses [1-3].

The history of self assembly is often started by discussing the early work of Zisman [4]. Zisman truly was a pioneer in the area of self-assembly and made very significant and important contributions to the literature. His earliest publication in 1946 on self-assembly introduced the assembly of a long chain alcohol, amine and carboxylic acid on glass and clean metal surfaces. From Zisman's work it is typical to jump to the 1980's when alkyltrichlorosilanes on silicon oxide were introduced [5] and then to the introduction of alkanethiols on gold by Nuzzo and Allara [6]. However it is interesting to note that alkanethiols were used for self-assembly long before Nuzzo and Allara published their first paper on the subject in 1983. The earliest mention of 'self-assembly' of thiols that I could find is U.S. patent 2,841,501 titled 'Silver Polish' published in 1958 [7]. While this patent is far from a scientific publication, the author had keen insight into the assembly mechanism of alkanethiols, in this case on silver. In the

patent the author describes, though excusing himself from presenting proof, the assembly mechanism, chemical reaction, stabilizing factors, and minimum chain length to form a stable self-assembled monolayer (SAM) on silver. It is interesting to note the accuracy of the author's hypotheses with regards to these ideas. The author describes the formation of a silver thiol bond (Ag-S-R) once the oxide has been removed by the abrasives in the polish. It is known that sulfur forms a semi-covalent bond with gold with a bonding energy around 45 kcal/mol [8]. The author then describes that after rinsing off the polish the resulting coating consists of thiol molecules that are aligned with their alkyl tails standing up away from the surface. This ordered arrangement of the thiol chains has been established by surface analytical methods such as infrared spectroscopy [9]. The author then gives insight into the factors that affect stability of the layers stating that straight chain alkanethiols work best since they can pack closer together. Finally the author states that alkanethiols with chains of 12 carbons or longer work best and form the most stable layers. Interestingly this corresponds well with current research that shows that in order to get an ordered monolayer one should use alkanethiols with a chain length of at least 10 carbons [10]. It is not known whether the author of the patent was aware of the work of Zisman, however he did show good insight into what was happening on the surface.

Though the use of alkanethiols on metals was potentially being used by silver owners around the country, their use in the scientific literature did not surface for many years after the 'Silver Polish' patent was issued. Fortunately the pioneering work of Nuzzo and Allara kick started a literal explosion of publications with their seminal work in 1983 demonstrating the assembly of disulfides onto gold substrates [6].

## 2 MODEL SURFACES AND CHARACTERIZATION

After the discovery of alkanethiol assembly on gold, there was a rush of papers characterizing the surfaces of alkanethiol monolayers. Due to the relative ease in controlling surface chemistry using alkanethiols, they have been used as controlled surfaces for studies using practically every surface analytical method imaginable. Alkanethiol SAMs have been characterized by RAIRS, Raman, XPS, FTIR, HREELS, NEXAFS, helium atom

scattering, X-ray diffraction, contact angle goniometry, ellipsometry, SPR, ToF-SIMS, AFM, STM, electron diffraction, SFG, and electrochemistry, just to name a few. Alkanethiols have been used to form monolayers on a wide variety of substrates including gold, silver, copper, nickel, platinum, palladium, mercury, zinc selenide, and cadmium selenide. This flexibility and wealth of surface analytical data has been a great advantage for users of alkanethiol SAMs as it provides a plethora of data and experimental details with which to compare one's own surfaces.

Most early studies of thiol SAMs focused on the structure and assembly mechanism of single and dual component monolayers on gold[10-14]. These and other studies led to the well recognized structure of alkanethiol SAMs shown in Figures 1 and 2 [15].

Understanding the structure of SAMs and discovering the ease and versatility of their use supplied researchers with a tool that could enable their creativity and has resulted in a rapid growth of unique applications of alkanethiol SAMs.

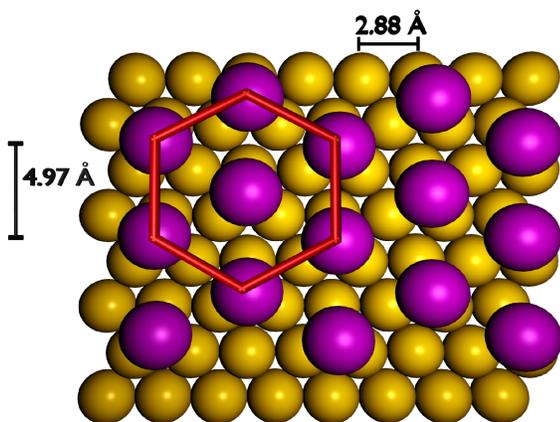


Figure 1. Schematic showing typical  $(\sqrt{3}\times\sqrt{3})R30^\circ$  hexagonal close pack arrangement of alkanethiols on gold.

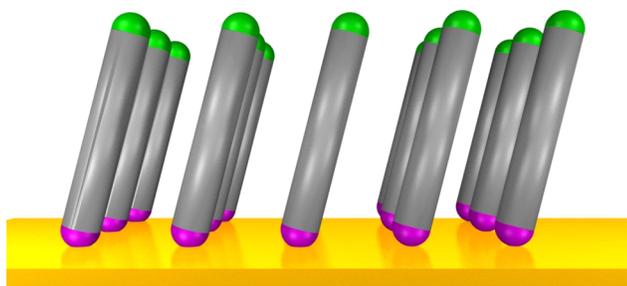


Figure 2. Schematic showing an ordered monolayer on gold.

### 3 PATTERNING SAMS

Though patterning SAMs is not the only expression of the creativity demonstrated with alkanethiols over the years, patterning has enabled and stimulated many unique applications and ideas about how to use alkanethiol SAMs.

One of the first patterning methods introduced was referred to as micromachining. This method involved forming a monolayer of one alkanethiol and then removing the thiol from designated regions by carefully removing the metal from those areas with a surgical scalpel blade or cut carbon fiber[16]. The sample was then introduced to a second thiol solution which allowed deposition of the second thiol in the areas of freshly exposed metal. Though this method was able to create micron sized patterns, it did not provide very precise control and resulted in the deformation of the metal surface in the local area of the pattern. However, within the same decade several more robust and flexible methods emerged that allowed controlled patterning of alkanethiols. These include, but are not limited to, UV photopatterning, microcontact printing, and dip pen lithography.

#### 3.1 UV Photopatterning

In 1993 Tarlov *et. al.* combined observations from two previous studies, one showing that alkanethiols on gold can be oxidized by exposure to UV light in air [17], and another showing that oxidized thiols can be displaced by fresh thiols by dipping the sample in a thiol solution [18], and showed that the combination of these two discoveries creates patterned surfaces [19].

UV Photopatterning enabled patterning of alkanethiols without touching the surface. It also used established technology in the fabrication of photomasks, and only required the use of a suitable UV light source in order to create the pattern.

Early examples of UV photopatterning showed feature replication down to around  $6\ \mu\text{m}$  [20]. Recently Sun *et. al.* have shown line widths below 50 nm using a UV laser with a near field scanning optical microscope [21].

#### 3.2 Microcontact Printing

In 1994 the Whitesides group introduced a new method of patterning that eliminated the need for expensive photolithography equipment and the use of clean rooms. This new method was microcontact printing and worked by the same simple process that is used to transfer ink onto paper using a rubber stamp [22]. The main process limitation of microcontact printing is creating the masters that are used to form the stamps. The masters are typically created using standard lithography processes on a silicon wafer. Features of desired sizes and shapes are created on the master. Then an elastomeric polymer, typically polydimethyl siloxane, is poured over the master and cured.

The stamp is then removed from the master, cut to size, and rinsed. The stamps can then be inked with an alkane thiol solution and placed on a gold substrate. All the areas of contact with the stamp get coated with a monolayer, while the unexposed areas remain uncoated. The sample can then be placed in a second thiol solution to fill in the uncoated regions. Features as small as 30 nm have been reported using microcontact printing [23]. It is interesting to note that though it has not received much attention in the literature, it is known that low molecular weight silicones are transferred along with the thiols during the stamping process [24, 25].

Microcontact printing has been used to create a wide range of surfaces with different feature sizes and shapes. The simplicity of the method and accessibility of the materials makes it an ideal platform for development and exploration of surface chemistry.

### 3.3 Dip-pen Lithography

In 1999 the Mirkin group developed a method for patterning that enabled precise control of the placement of alkanethiols on a surface by using an atomic force microscope tip to write using thiols as ink [26]. The discovery of dip pen lithography came out of an investigation of the capillary that forms between an AFM tip and the surface when working in air. The Mirkin group was able to use this meniscus of water that forms in air to pull thiols off the AFM tip and deposit them onto the surface. Initial work with dip-pen lithography was limited to writing small features over limited areas due to the write time limitations of a single AFM tip. However, recently NanoInk, a company specializing in dip-pen nanolithography, has introduced a system that is capable of writing with 55,000 tips simultaneously enabling parallel writing over large areas in short times.

## 4 ALKANETHIOLS AND NANOTECHNOLOGY

The vast knowledge of alkanethiol self assembly, their versatility in control of surface chemistry, and the wide range of methods that can be used to deposit them, has kept alkanethiols in the forefront of surface science over the last 30 years. This is still true today where alkanethiols are playing a critical role in the field of nanotechnology.

Nanomaterials are either created from the top down, by removing material until one gets nanoscale features, or from the bottom up, where nanoscale features are created using self-assembly. Alkanethiol SAMs are nanoscale surfaces themselves with typical layer thicknesses of 1 to 3 nm, and have been used successfully to create nanoscale patterns using various deposition methods. Alkanethiols are not only useful in the creation of nano-thick layers or nanoscale patterns, but they are also used extensively in the formation of nanoparticles and nanorods. Nanoparticles are often modified with alkanethiols containing specific

chemical functionalities that enable the researcher to tailor the surface properties of the particles and engineer them for specific applications.

It is only a matter of time until researchers devise ways to control alkanethiol chemistry on nanoscale features in the same way they pattern and manipulate the chemistry of larger scale substrates. The flexibility and control provided by alkanethiols is sure to inspire future scientists to develop new and innovative ways of engineering surface chemistry and solving important problems through scientific discovery.

## REFERENCES

- [1] Love, J.C., Estroff, L.A., Kriebel, J.K., Nuzzo, R.G., and Whitesides, G.M., *Chemical Reviews*, 105, 1103-1169, 2005
- [2] Schreiber, F., *Journal Of Physics: Confensed Mater*, 16, R881-R900, 2004
- [3] Ulman, A., *Chemical Reviews*, 96, 1533-1554, 1996
- [4] Bigelow, W.C., Pickett, D.L., and Zisman, W.A., *Journal Of Colloid and Interface Science*, 1, 513, 1946
- [5] Sagiv, J., *Journal of the American Chemical Society*, 102, 92, 1980
- [6] Nuzzo, R.G. and Allara, D.L., *Journal of the American Chemical Society*, 105, 4481-4483, 1983
- [7] Murphy, J.G., *Silver Polish*, U.S.P. Office, Editor. 1958, James G. Murphy: United States of America.
- [8] Dubois, L.H. and Nuzzo, R.G., *Annual Reviews in Physical Chemistry*, 43, 437-463, 1992
- [9] Nuzzo, R.G., Dubois, L.H., and Allara, D.L., *Journal Of The American Chemical Society*, 112, 558-569, 1990
- [10] Bain, C.D., Troughton, E.B., Tao, Y.-T., Evall, J., Whitesides, G.M., and Nuzzo, R.G., *Journal Of The American Chemical Society*, 111, 321-335, 1989
- [11] Nuzzo, R.G., Fusco, F.A., and Allara, D.L., *Journal Of The American Chemical Society*, 109, 2358-2368, 1987
- [12] Nuzzo, R.G., Zegarski, B.R., and Dubois, L.H., *Journal Of The American Chemical Society*, 109, 733-740, 1987
- [13] Bain, C.D., Evall, J., and Whitesides, G.M., *Journal Of The American Chemical Society*, 111, 7155-7164, 1989
- [14] Bain, C.D. and Whitesides, G.M., *Journal Of The American Chemical Society*, 111, 7164-7175, 1989

- [15] Poirier, G.E. and Tarlov, M.J., *Langmuir*, 10, 2859, 1994
- [16] Abbott, N.L., Folkers, J.P., and Whitesides, G.M., *Science* 257, 1380-1382, 1992
- [17] Huang, J. and Hemminger, J.C., *Journal Of The American Chemical Society*, 115, 3342-3343, 1993
- [18] Tarlov, M.J. and Newman, J.G., *Langmuir*, 8, 1398-1405, 1992
- [19] Tarlov, M.J., Donald R. F. Burgess, J., and Gillen, G., *Journal Of The American Chemical Society*, 115, 5305-5306, 1993
- [20] Huang, J., Dahlgren, D.A., and Hemminger, J.C., *Langmuir*, 10, 626-628, 1994
- [21] Sun, S., Chong, K.S.L., and Leggett, G.J., *Nanotechnology*, 16, 1798-1808, 2005
- [22] Kumar, A. and Whitesides, G.M., *Applied Physics Letters*, 63, 2002-2004, 1993
- [23] Odom, T.W., Thalladi, V.R., Love, J.C., and Whitesides, G.M., *Journal of the American Chemical Society*, 124, 12112-12113, 2002
- [24] Graham, D.J., Price, D.D., and Ratner, B.D., *Langmuir*, 18, 1518-1527, 2002
- [25] Glasmaster, K., Gold, J., Andersson, A.-S., Sutherland, D.S., and Kasemo, B., *Langmuir*, 19, 5475-5483, 2003
- [26] Piner, R.D., Zhu, J., Xu, F., Hong, S., and Mirkin, C.A., *Science* 283, 661-663, 1999