



## Review

# Stability: A key issue for self-assembled monolayers on gold as thin-film coatings and nanoparticle protectants

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## ABSTRACT

This review examines the use of self-assembled monolayers (SAMs) on gold as nanoscale protective coatings for both nominally flat substrates and for nanoparticles. The thermal and chemical stabilities of the SAMs are discussed, and the various strategies used by researchers to generate thin films with enhanced resistance to corrosion and/or decomposition are described. The use of multidentate adsorbates to achieve the desired objectives is emphasized.

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## 1. Introduction

The extraordinary stability of gold has been the focus of study since ancient times. Gold's resistance to oxidation and corrosion has led to its use in such diverse applications as the decorative gold leaf found on the exteriors of temples in Asia, the reflective coatings used in sun visors for astronaut spacesuits [1], the caps and crowns in common use for dental work, the coinage and jewelry that have become a store of wealth in most cultures, and the metal of choice for a wide range of nanoparticle studies where biocompatibility is a concern. Gold nanoparticles also have become the focus of increasing interest in part due to their potential optical, electronic, and catalytic applications. The discovery of the relative ease of generating self-assembled monolayers (SAMs) via the adsorption of a variety of surfactants onto two-dimensional or "flat" gold substrates has dramatically increased the number of applications that utilize gold surfaces. SAMs have also been developed for a broad array of surfaces other than gold due to the many potential applications for these protective coatings in nanotechnology; however, gold is the predominant surface used in fundamental research. Details of the formation, characterization, properties, and/or applications of protected flat surfaces and gold nanoparticles have been reviewed [2,3]. Owing to the intense interest in the potential of such nanoscale coatings, one of the topics that has been widely studied is the need to enhance the stability of SAMs. Although several review articles have described the study and use of SAMs on flat gold and/or gold nanoparticles [2–8], none of these reviews has focused specifically on the issue of monolayer stability, save for a brief summary in the article by Salvarezza and co-workers [5].

This review provides a brief history of SAMs and emphasizes their use as nanoscale protective coatings for nominally flat substrates and for nanoparticles. The study examines both the thermal stability and the chemical stability of the films, and highlights the various strategies used by researchers to generate thin films with enhanced resistance to corrosion and/or decomposition. Particular focus is given to the use of multidentate adsorbates to achieve the desired objectives.

## 2. Background

### 2.1. A brief history of monolayer films

Issues of thin-film stability have played a dominant role in monolayer studies ever since the publication of the groundbreaking work of Irving Langmuir in 1917 [9]. In this seminal article, Langmuir not only detailed his argument that the fatty acid films formed at the air/water interface were composed of a single layer (a monolayer) of molecules, but also described his design of a tray that could be used to provide a sensitive differential method to measure surface tension. This innovation was particularly important for working with films of room-temperature solids, since these films have a tendency to "crumple up" during the experimental procedure. Langmuir's ensuing collaboration with Katherine Blodgett led to further development of methods to manipulate monolayers,

where the resulting films once transferred to a substrate eventually became referred to as "Langmuir–Blodgett" films (LB films). But several complications are involved in the successful deposition of well-formed LB films on a solid substrate; in particular, the applied horizontal pressure on the film during deposition must be balanced with a variety of factors that influence the monolayer's formation, such as the content of the water (e.g., ions or buffering agents), the temperature, and the rate of deposition [10].

In 1946, Zisman published the initial results of his work on thin films, advancing the study of monolayers through the formation of films on metal surfaces [11]. Using a substantially different approach than the Langmuir–Blodgett technique, he noted that particular amphiphilic compounds (including long chain carboxylic acids) could be used to form well-ordered monolayers directly from solution. The resulting films were autophobic, lending themselves to a number of potential applications in surface science [12]. His continuing research during the next 30 years provided additional insight into key aspects of the current study of self-assembled monolayers, including the observed impact on surface energetics and film formation upon modifying the terminus of the adsorbate's alkyl chain [13,14].

A number of surfactant systems have been examined to determine which synthetic routes lead to stable monolayer films. In 1978, Haller with IBM reported upon his work on thin films in which alkylsilane monolayers were formed on silicon and gallium arsenide semiconductor surfaces [15]. This work was soon followed by that of Sagiv in which mixed-monolayers were the targeted products, but the formation of stable alkylsilane films were the key innovations [16]. Such films have the advantage of van der Waals stabilization for the extended alkyl chains, bonding to the substrate through surface hydroxyl groups and cross-linking between the individual headgroups for added resistance to displacement. For these reasons, extensive research has been conducted on a large variety of alkylsilane systems [17]. However, issues related to the challenges involved in the preparation of these films, questions about the role that surface hydration plays in the film development, and the degree to which the adsorbates are influenced by such hydration, along with stability problems for the monomer prior to its use, represent ongoing challenges for this technology.

In 1983, Nuzzo and Allara published the results of their work with dialkyl disulfides on gold and the resulting well-organized monolayer films [18]. Soon afterward, additional research revealed that alkanethiols would form films as effectively as disulfides, producing SAMs that mirrored those formed from disulfides [19]. These types of monolayers exhibit many useful characteristics for scientific study, mostly owing to key factors that allow for the formation of an easily reproducible and moderately stable film. First of all, gold surfaces are relatively inert to oxidation and provide a substrate, when freshly deposited, that is free of oxides and competing adsorbates [3,20]. Second, the bond between sulfur and gold is strong, with a bond enthalpy of ~40–45 kcal per mole [4,21]. Third, the sulfur–gold bond forms preferentially in the presence of other competing chemical functionalities, providing the ability to modify the terminus of the alkanethioladsorbate with a variety of functional

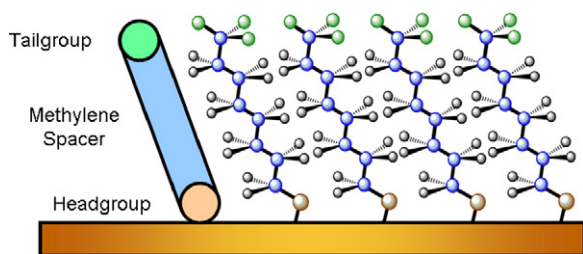


Fig. 1. Illustration of the three components of an ordinary thiol-based self-assembled monolayer adsorbate in comparison to a representative film formed from  $\text{CF}_3(\text{CH}_2)_7\text{SH}$ .

groups, including  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{CN}$ , and  $-\text{COOH}$  [18]. Fourth, the all *trans*-extended conformation of the alkyl chains that are characteristic of most alkanethiolate SAMs are stabilized by van der Waals forces that play a key role in film integrity for densely-packed monolayer films. And fifth, thiol-based monolayers on gold are easily formed from dilute solution under ambient conditions [20]. Because these adsorbates exhibit dependably reproducible assembly characteristics, analysis of the role that key structural components for a typical adsorbate molecule play is possible, and the insight gained from such research is useful in the development of an understanding of what characteristics contribute to stable monolayer films.

The content of this review reflects the predominance of thiol-based SAMs on gold in the literature and relies largely on research performed on these systems. Unless otherwise specified, the information given below relates to these types of SAMs. For brevity, thiols and thiol-based SAMs will be identified according to the number of carbons in their chains (e.g., C12SH for  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ ).

## 2.2. Fundamentals of self-assembled monolayers

The overall stability of a self-assembled monolayer film is closely tied to the key structural components of the individual adsorbates: the headgroup, which attaches the adsorbate to the substrate, the methylene spacer, which stabilizes the adsorbate once a fully formed film has developed, and the tailgroup, which contacts the outside world and provides a point of incorporation for surface functional groups [22]. An illustration of these structural components is provided in Fig. 1.

The first contribution to a stable thin film formed at an air/solid or liquid/solid interface comes from the attachment of the headgroup to the surface. The anchoring of the individual adsorbates at one end of the surfactant chain creates a significantly improved stability for these surface-bound systems when compared to monolayer films at an air/liquid interface. While a broad variety of headgroups have been utilized in SAM research, the dominant system in the literature has been that of thiol-based SAMs formed on  $\text{Au}(111)$ ; however, other gold surfaces have also been examined. In a study published in 1993, Camillone et al. compared the SAM structures formed on  $\text{Au}(111)$ ,  $\text{Au}(110)$ , and  $\text{Au}(100)$  [23]. These authors concluded that the nature of the domain structures that formed for C22SH adjusted to adapt to the underlying substrate lattice (e.g., the periodicity and packing density for the adsorbate is different for each surface). Such variances in surface structure can influence the stability of the resulting SAM, particularly at domain boundaries and defect sites. Additional information regarding other headgroups and substrates can be found in recent review articles [5,6].

The key role that the methylene spacer plays in the creation of a well-organized self-assembled monolayer film can be found in the work of Porter et al. [24]. For their study, the authors prepared a series of normal alkanethiols that extended from the short chain

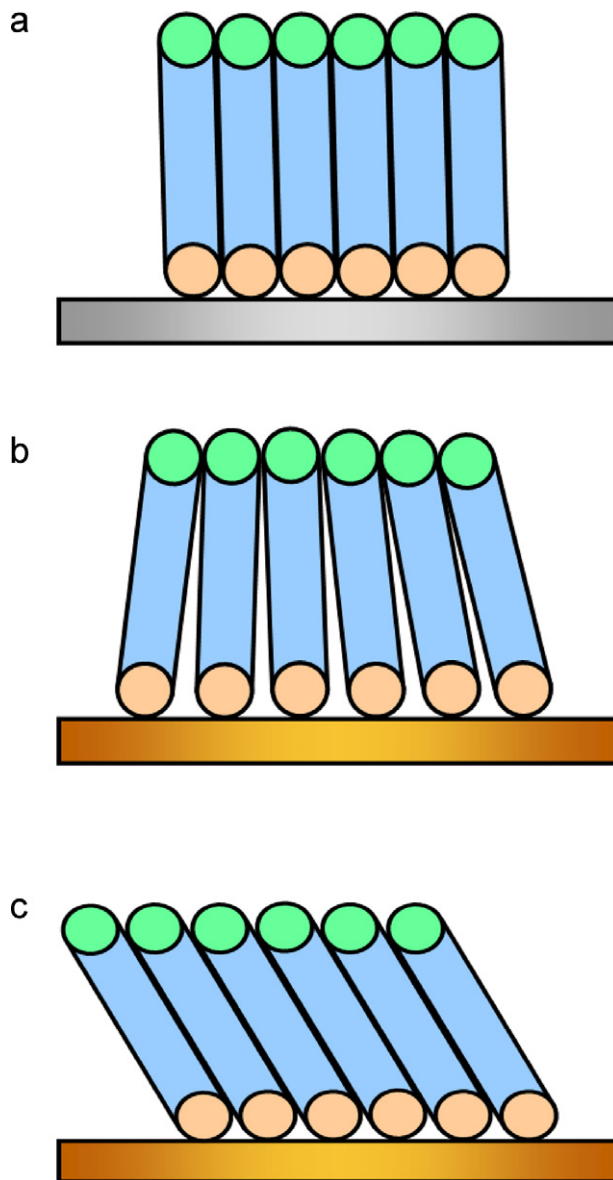


Fig. 2. Comparison of possible adsorbate packing patterns of self-assembled monolayers. (a) A well-packed SAM on a hypothetical metal where the distance between interfacial metal attachment sites is equivalent to the van der Waals radii of the adsorbate chains. (b) A poorly organized adsorbate on gold where the SAM fails to achieve a packing order that adjusts for the variance between the surface attachment distances and the adsorbate chain van der Waals radii. (c) A well-ordered SAM where the chains tilt to adapt to the variance between the surface attachment distances and the adsorbate chain van der Waals radii.

Adapted from Ref. [24].

C2SH to the long chain C22SH. The authors concluded that the long chain thiols formed densely packed, crystalline-like monolayers, where the fully extended alkyl chains were tilted from the surface normal by  $20\text{--}30^\circ$ . However, as the chain length for each SAM was decreased, the thin films that were formed exhibited greater disorder and a reduction in density. The relative uniformity of the observed tilt for the adsorbates was attributed to the mismatch between the spacing of the headgroups bound to the substrate at specific lattice points as compared to the van der Waals radii of the alkyl chains and the resulting chain spacing for a densely-packed array (see Fig. 2). The fully-formed assembly tilts from the surface normal to maximize the van der Waals attractive forces between adjacent chains.

In a 1990 study of a series of SAMs having a variety of tailgroups, Nuzzo et al. determined that the terminal functional groups were not buried in the film but were exposed at the interface [25]. Subsequent research has focused in part on the manipulation of ideal surfaces formed through the exposure of an interfacial array of adsorbate tailgroups. Yet these tightly packed surfaces exposing the tailgroups of the individual adsorbates can also contribute to a reduction in monolayer stability. Unlike the headgroup, the tailgroup is not bound to a surface or, in most cases, to each other and, depending upon the size and reactivity of the tailgroup, its presence can diminish the interchain attractive forces between the methylene spacers of neighboring chains by pushing these alkyl chains apart. An example of how this phenomenon can influence a thin film can be found in the work of Chidsey and Loiacono, where a series of alkanethiol adsorbates with varying tailgroups were examined to determine how different termini impact the barrier properties of the SAMs produced from such adsorbates [26]. The authors concluded that the terminal groups that were the most disruptive of the monolayer packing density created films that had the poorest barrier properties.

A study by Bensebaa et al. determined the key factors that influence the structure and stability of SAMs on flat surfaces are: substrate quality, deposition solvent, time of monolayer incubation, thiol concentration, and deposition temperature [27]. Individual studies related to these parameters have aimed at optimizing SAM systems through research that analyzed such factors as the adsorption solvent [20], the adsorption kinetics of film growth as measured by surface plasmon resonance spectroscopy for films in solution [28], the outcome of changes in concentration for the adsorbate solution [29], the role of gold surface defects and how such defects are influenced by heat as evaluated by scanning tunneling microscopy (STM) [30]. While analysis of the fundamental parameters involved in the development of a well-ordered alkanethiol SAM on flat gold has been an important approach to maximizing the possibility of utilizing these thin films in a wide range of applications, the need to understand the complications involved in applying this technology to non-uniform or curved surfaces is also required.

### 2.3. Charge-stabilized and SAM-stabilized metal nanoparticles

Monolayer-protected nanoparticles (MPNs), also known as SAM-coated nanoparticles or, in some instances, monolayer-protected clusters, have been the focus of a large number of research studies owing to their enhanced stability. In general, many methods have been used to stabilize gold nanoparticles, and they can be classified into four categories: (i) electrostatic stabilization, (ii) phosphine ligation, (iii) thiol ligation, and (iv) ligand exchange. A description of how these methods of nanoparticle stabilization strategies were developed is summarized in the following paragraphs. Details of the preparation, characterization, optical properties, and/or applications of MPNs in general and gold nanoparticles specifically, can be found in both a thorough review article [2] and an excellent book [31].

#### 2.3.1. Electrostatic stabilization

A number of simple wet chemical methods for the preparation of charge-stabilized gold nanoparticles via the reduction of a gold salt with a reducing agent, such as formaldehyde or hydrazine, have been developed [32]. The most widely reported method involves the use of citrate to reduce  $\text{HAuCl}_4$  in water, which was described by Turkevich et al. in 1951 [33]. This method leads to the formation of negatively-charged citrate-stabilized gold nanoparticles ~20 nm in diameter, where the charge-charge repulsion between neighboring nanoparticles inhibits nanoparticle agglomeration. In 1973, Fren described the synthesis of citrate-stabilized gold nanoparticles

with spherical morphologies and with diameters ranging systematically from 16 to 147 nm [34]. Here, stable nanoparticles with selected dimensions can be targeted simply by choosing the appropriate citrate-to-gold ratio. This reaction proceeds via reduction of Au(III) ions by citrate ions to afford atomic gold and then collections of gold atoms leading to nanoparticle growth; importantly, the citrate moieties serve as both reducing agents and stabilizing agents for the consequent nanoparticles [35,36].

#### 2.3.2. Phosphine ligation

In 1981, Schmid et al. reported the synthesis of a monodisperse phosphine-stabilized  $\text{Au}_{55}$  cluster with a core size greater than 1 nm [37]. The reaction involves the reduction of  $\text{AuCl}(\text{PPh}_3)$  with diborane gas in warm benzene. However, these gold nanoparticles decompose readily in solution at room temperature. An additional limitation for this method is the difficulty of large-scale synthesis owing to the use of the diborane gas. In 1993, the synthesis of stable gold clusters having a mean diameter of 1–2 nm was reported by Duff et al. [38,39]. The gold clusters were prepared by aqueous reduction of hydrogen tetrachloride (II) with alkaline tetrakis(hydroxymethyl)phosphonium chloride. This method offers a stable gold cluster without the need of large organic stabilizing molecules. In 2000, Weare et al. discovered an alternative method to synthesize phosphine-stabilized gold nanoparticles that is more easily scalable. This method yields phosphine-stabilized gold nanoparticles with nearly the same small gold core and monodispersity size as the Schmid preparation [40]. The reaction is carried out under phase transfer conditions and uses  $\text{NaBH}_4$  as a reducing agent. However, a key problem with phosphine ligation has been the relative lack of stability of most nanometer-sized particles when compared to alternative stabilization strategies.

#### 2.3.3. Thiol ligation

The production of stable nanometer-sized gold nanoparticles has been accomplished by the development of thiol-stabilization, thus producing MPNs. In 1993, Giersig and Mulvaney were the first to report the stabilization of gold nanoparticles with alkanethiols [41]. One year later, Brust and Schiffrin reported a facile two-phase synthesis of stable, isolable, and organic-soluble gold MPNs with enhanced monodispersity and controlled size [42,43]. The gold nanoparticles were prepared by using borohydride reduction of  $\text{HAuCl}_4$  under phase transfer conditions in the presence of C12SH. These nanoparticles proved to be stable, allowing them to be handled as easily as a normal chemical compound. Due to the relative ease of synthesis and the enhanced stability of these materials, modifications of this method have been applied to the synthesis of gold nanoparticles stabilized by other organosulfur-based ligands such as arenethiols [44], polar aromatic-containing thiols [45], and dialkyl disulfides [46]. The gold MPNs prepared by this method, and/or modifications of this method, typically range in size between 1 and 5 nm. One limitation of a two-phase synthesis method is the need of a phase-transfer catalyst. Shon et al. overcame this problem by using a single-phase synthetic procedure that employs Bunte salts, such as sodium S-dodecylthiosulfate and 2-acrylamido-2-methyl-1-propanesulfonic acid, to generate alkanethiolate protected-gold nanoparticles [47,48].

#### 2.3.4. Ligand-exchange methods

The key advantages of the ligand-exchange method are that it can produce a diverse library of functionalized nanoparticles, and the exchange process preserves the size and optical properties of the gold nanoparticle cores. Several methods have been reported and can be classified based upon the identity of the entering and leaving ligands [31]: thiol-to-thiol [49,50], phosphine-to-phosphine [51,52], phosphine-to-thiol [53,54], phosphine-to-amine [55], citrate-to-thiol [56], and surfactant-to-thiol [57].



The most common type of ligand exchange reaction is the thiol–thiol exchange reaction, which was first reported by Hostetler et al. in 1996 [49]. In this process, as many as one-third of the original *n*-alkanethiolates were replaced by  $\omega$ -functionalized alkanethiols. This type of strategy was employed to synthesize gold nanoparticles with more than two species in the stabilizing ligand shell. The kinetics and a suggested mechanism for the ligand-exchange reaction have been reported [58]; specifically, the exchange reaction was proposed to occur through a predominately associative mechanism in which the ligand is displaced as a thiol. The reactivity of a given thiolate depends upon the type of site to which it is bound. Furthermore, the rate of the exchange reaction depends on the chain length and steric bulk of the initial ligand shell surrounding the gold core.

### 3. Stability of monolayer films on flat gold substrates

Reviewing the fundamental research for SAMs on flat gold can provide valuable insight into the development of stable SAM coatings for two-dimensional (2D) device architectures (e.g., lab-on-a-chip) and for the stabilization of MPNs (i.e., 3D nanomaterials). Early in the pursuit of functional nanoscale films, as knowledge regarding the fundamental structure of alkanethiolate SAMs increased, so did an awareness that these monolayer films were vulnerable to a variety of environmental factors that cause them to degrade. To determine their stability for a variety of proposed applications, a number of research groups turned their attention to both understanding the nature of the causes behind SAM degradation and how these vulnerabilities might be counteracted. The key issues that have received broad attention include: (1) the stability at the surface of the fully formed film when in contact with a liquid drop or other surface mass (influence of the endgroup and methylene spacer on surface stability), (2) the impact of oxidation on the individual adsorbates and the role that ultraviolet (UV) radiation plays in the associated loss of film integrity (influence of the headgroup in conjunction with the methylene spacer on SAM film stability), (3) the influence that variations in temperature and chemical environment have on fully developed films, and (4) the root causes behind the trends in thiol exchange processes and the genesis of the observed displacement of individual adsorbates in chemical displacement studies.

#### 3.1. Factors influencing the stability of monolayer films

Changes in the organization of the endgroups of the adsorbates of a self-assembled monolayer have been observed in several forms. Bain et al. concluded in a 1989 article on reactive spreading that the impact on the contact angle measurements for a pH-buffered aqueous contact liquid, when placed on a series of mixed-thiol SAMs composed of a carboxylic acid-terminated thiol and a normal alkanethiol, provided evidence that the reactivity of the surface-bound acid was reduced when compared to one in solution [59]. This study also revealed how increasing the pH of the drop would lead to a decrease in the contact angle for the contacting liquid. This work was supported by prior acid–base studies involving other forms of monolayer films [60–63]. The authors theorized that the effective acidity of these terminal acid moieties was reduced as compared to that found in bulk solution owing to the restrictive nature of the monolayer interface and as a consequence of the (oriented) polarity of these groups at the chain terminus. But the “restrictive” nature of the terminal moieties of monolayer adsorbates subsequently was determined to be slightly more complex than the simplified depiction of the highly-organized array of perfectly aligned *trans*-extended alkyl chains for a typical well-packed monolayer surface. Lee et al. attributed their observation that such surfaces are less

wettable for a series of contacting liquids with pH values between 3 and 7, as compared to those possessing higher and lower acidity, to conformational changes for the carboxylate termini upon partial ionization [64]. Furthermore, Cooper and Leggett suggested in their studies of exchange reactions on lithographically patterned SAM surfaces that the polar –COOH group provided improved stability to resist displacement [65]. The authors attributed this added resistance to interchain interactions; specifically to H-bonding between the terminal carboxylic acid groups.

In contrast to the stabilizing interchain interactions of terminal carboxylic acid moieties, Evans et al. reported that a series of binary mixed SAMs composed of C12SH (an alkanethiol with a non-polar terminus) and 11-hydroxy-undecane-1-thiol (a polar hydroxy-terminated thiol) exhibited instability for contact angle measurements taken over time [66]. The authors noticed that the extent to which these contact angles varied correlated to the content of the hydroxy-terminated thiol in the monolayer and was influenced by both the temperature and chain length. The authors concluded that surface reorganization was occurring (as supported by XPS studies showing reduced –OH content at the surface), which was driven by the polar moiety at the end of the chain being buried, over time, in the monolayer film. One factor that did not appear to influence the results of the study by Evans et al. was the humidity. But a second study involving Ulman, also utilizing mixed-SAMs of alkanethiols and hydroxy-terminated thiols, revealed that humidity could also alter the results obtained by contact angle measurements when the surface included a terminal hydrophilic species [67]. The variance in measurements occurred with systems exposed to conditions of either 30% or  $\leq 2\%$  relative humidity (the contact angles for hexadecane decreased with increasing relative humidity).

Allara and co-workers used molecular dynamics simulations to support the conclusion that interpenetration of contacting liquids and the resulting interfacial reconstruction could explain sharp transitions in contact angle data with minor variations in the adsorbate chain length of a SAM [68]. Other groups have also noticed a subtle impact on the characteristics of specific SAMs that might be attributable to the influence of contacting liquids intercalating with the array of alkyl chains. Creager and Rowe noted in a 1993 report that a series of aliphatic alcohols influenced the capacitance and redox potential of mixed-SAMs on electrodes where one component of the SAM presented a hydrophobic surface at the monolayer interface [69]. The authors attributed this effect to the alcohols forming “aggregates” at the surface. The authors noted that the effect was maximized when the solution in contact with the surface was saturated with an alcohol and while testing the alcohol with the longest chain length for the series of alcohols. The effect was eliminated when the hydrophobic surface-exposing component was left out of the solution forming the SAM.

Studies that focus on the influence of chain length on monolayer order and surface integrity reveal that SAMs formed from longer chains generate monolayer films with enhanced packing density and conformational order. In an initial study of a series of even-numbered alkanethiol-based SAMs (C2SH–C18SH and C22SH), Porter et al. determined that as the length of the alkyl chain was decreased, the structure of the resulting SAM became more disordered, accompanied by a reduction in packing density, surface coverage, and the capacity to block electron transfer [24]. The authors concluded that the van der Waals forces of the longer alkyl chains appeared to sustain an organizational structure that creates an effective barrier. Poirier et al. showed through a STM study how short alkanethiol-based SAMs (C4SH and C6SH) exhibited 2D liquid-phase properties at room temperature, while longer chains were more crystalline [70]. Another study of monolayer structure, but this time involving alkylsiloxane films on SiO<sub>2</sub> by Allara et al., found that chain length variances impacted contact angle measurements, revealing changes in surface order tied to chain length [71].

### 3.2. Impact of oxidation and UV irradiation

While possessing a basic understanding of the problems that can occur at the air/monolayer interface is useful for the development of practical applications of these systems, the interactions at the monolayer/substrate interface have the most profound implications for alkanethiolate SAM stability. In 1992, Tarlov and Newman, utilizing static secondary ion mass spectroscopy, discovered that SAMs exposed to atmospheric conditions for a prolonged period of time experienced oxidation of the sulfur headgroup, forming sulfonates [72]. Such sulfonate species were not found with SAMs that were examined immediately after forming in the thiol solution. The presence of oxidized sulfur was confirmed with laser desorption ion trap mass spectrometry by Burroughs and Hanley that same year [73], and further validated by the work of Scott et al., who concluded that more than one oxidized species was formed: both alkanesulfonates ( $\text{RSO}_2^-$ ) and alkanesulfonates ( $\text{RSO}_3^-$ ) [74]. Huang and Hemminger utilized a mercury lamp to provide ~25 min of UV radiation to a series of alkanethiolate SAMs and concluded that the oxidation could be related to the exposure to light [75]. In a study by Rieley et al., it was discovered that when SAMs were protected from air and light exposure, no oxidation occurred. In the same report, the authors argued that the photo-oxidation process was possibly mediated by the gold surface [76]. Two studies from 1998 point to ozone as the predominant active agent in these processes [77,78]. Zhang et al. further described how UV radiation can generate ozone from  $\text{O}_2$  *in situ* [77].

Possibly the earliest study that pointed to the oxidation of thiols, by Hemminger and co-workers, utilized laser desorption Fourier-transform mass spectrometry as their tool to uncover the nature of the surface species of SAMs after exposure to air [79]. Their work on a series of alkanethiol-based SAMs, varying from C4SH to C18SH, also revealed that the shorter chains exhibited a greater level of oxidation. Additionally, a collaborative effort involving Whitesides and Nuzzo concluded that long chain alkanethiolate SAMs are more stable to UV degradation than SAMs composed of shorter chains [80]. While the focus of the latter report centered on a structural method of stabilizing SAM films for use in photolithography, the study further concluded that no oxidative damage occurred to SAMs that were stored under nitrogen gas over the course of 2 h and that SAMs formed on other metals helped protect those metal surfaces from oxidation. Whitesides and co-workers had previously reported that Cu could be protected from oxidation by SAMs, and that chain length played a key role in this process [81]. Hutt and Leggett also found that chain length had a strong influence on the level of oxidation, with thiols equal to or smaller than C8SH having significantly more oxidized adsorbates, and those equal to or larger than C12SH having a much slower rate of oxidation [82]. The authors noted that the degree of order of the monolayer film contributes to its resistance to oxidation. In an electrochemical study utilizing C3SH, C12SH, and C18SH, however, Schoenfish and Pemberton determined that the oxidized species formed upon exposure of the SAM to ambient conditions had no effect on the electrochemical blocking characteristics of the films, even after exposing the films to solvent [78].

Cooper and Leggett examined the influence of the nature of the terminal group on oxidative processes [83]. In this investigation, C4SH and C12SH were examined along with their hydroxyl- and carboxyl-terminated analogs. The ratio of the rate constants for the photooxidation was 4:2:1 for  $\text{CH}_3\text{:OH:COOH}$ , respectively, with this ratio applying to both chain lengths. However, these results are at odds with a subsequent study by Brewer et al., where the corresponding carboxyl-terminated SAM was less resistant to oxidation than C12SH [84]. The authors concluded that changes in the reaction conditions (e.g., the light source) might be responsible for the difference. This hypothesis was later confirmed by the same

research group [85]. Additionally, this latter paper argues that the oxidation of SAMs can occur upon exposure to a UV light source even in the absence of ozone. The authors suggested that the type of light source used (e.g., a specific wavelength UV light source vs. a broad-spectrum arc lamp) might dictate the mechanism of the oxidative process.

The idea that the substrate participates in oxidation, as hypothesized above, received support from a study by Lee et al. in 1998 when these researchers concluded that the kinetics of oxidation varied with the morphology of the gold surface (oxidation was observed to increase with a decrease in grain size) [86]. In this report, the authors noted that defect sites are known to enhance reactivity, and that the rate at which a gold film is evaporated can play a role in the nature of the substrate quality: faster evaporation rates led to an increase in the number of defect sites and a corresponding increase in reactivity. The authors also concluded that oxidation of the surface occurs in the dark, provided that the sample is exposed to air. Wang et al. utilized a different method of determining the rate of oxidation as a function of alkyl chain length [87]. These researchers utilized high-resolution photoelectron spectroscopy to observe the impact that a nitrogen-oxygen downstream microwave plasma had on alkanethiol-based SAMs. The authors noted that the oxidation induced by the plasma occurred in a two-step process for the longer chains: (1) penetration of the alkanethiolate array by the reactive oxygen in order to reach the surface-bound sulfur and (2) the oxidation process itself. In contrast, the shorter chains exhibited no film-delaying penetration step.

For all of the preceding studies, the driving force for understanding the influence of oxidation on SAMs was to determine the effect of the oxidized species on the long-term stability of the monolayer film. A 1997 study by Scott et al. [74] demonstrated that a partially oxidized SAM composed of C12SH was displaced by second thiol in a solution of C10SH to the extent of the oxidized species on the surface. Importantly, the displacement of all oxidized moieties occurred within a 30-min timeframe. The utility of selective displacement through targeted oxidation was demonstrated by Leggett and co-workers in several studies where displacement of the oxidized species by a second thiol was used to create patterned monolayers via masking [84], gradients through controlled exposure to light [88], and monolayer lines and grids generated by interference techniques [89].

The vulnerability of thiol-based monolayer systems to oxidation have also led to research specifically addressing their use under biological conditions or as platforms for biological studies [90]. Maciel et al. demonstrated that SAMs formed from alkanethiol adsorbates with terminal hydroxyl groups or terminal ethylene glycol moieties were subject to oxidation at the sulfur headgroup after two weeks of storage in the dark in an oxygen-free atmosphere. However, the  $\text{CH}_3$ -terminated SAMs used in this study proved to be stable for at least nine weeks under the same conditions. This study, along with several others, provides insight into the strong interest in the utilization of SAMs for biological research and the challenges that must be overcome to ensure that these surfaces provide reliable platforms for such applications [91–93].

### 3.3. Impact of exposure to heat and chemical agents

While some issues related to SAM stability are uniquely tied to the nature of the bond between the film and the substrate, many stability problems arise in a number of monolayer formats, providing insight into fundamental concerns that have hampered the development of SAMs in certain industrial applications. The fact that the assembly of well-ordered thin films on a solid substrate relies on interchain attractions that can be easily disrupted by a

relatively small increase in temperature is a concern that has also been noted in the study of LB films [94–96].

In a 1989 article, Bain et al. outlined a thorough investigation of alkanethiol-based SAMs, including a thermal desorption study involving the adsorbates C10SH, C12SH, C16SH, C18SH, and C22SH [20]. The authors found that the alkanethiolates desorbed at about 70 °C with a rate of desorption that was influenced by temperature, environment (air or type of contacting liquid), and chain length. Of the tests conducted, desorption occurred faster in a hydrocarbon solvent, more slowly in ethanol, and even slower in air. Through the use of ellipsometric data, the authors also determined that the longer the chain length, the more thermally stable the SAM. A separate but related IR study in 1990 by Nuzzo et al. of SAMs derived from C22SH found gauche conformations at the end of the chains [97]. Furthermore, the authors reported that fully reversible changes in conformation were observed as the temperature was varied between 300 and 380 K; however, evidence of monolayer degradation was observed above 380 K.

With the development of STM, an alternative approach to analyzing the impact of heat on a SAM surface became available. Delamarche et al. examined SAMs composed of C11SH to evaluate the impact of temperature on scannable surface structures, with an advantage being the elimination of a composite “sampled” value, such as that obtained by infrared spectroscopy or X-ray photoelectron spectroscopy, and its replacement with a visual image that could be dissected and analyzed by its component parts [98]. When using STM in concert with other methods, the authors found that chain-tilt mismatches disappeared at 50 °C, and larger surface domains were formed. At 100 °C, the upper layer of gold atoms became mobile, which in combination with the slow rate of desorption at this temperature led to lateral mobility for the adsorbed species. Above 100 °C, the surface began to decompose, and at 130 °C, thermal desorption of the monolayer was complete.

A subsequent study by Bensebaa et al. utilized reflection-absorption infrared spectroscopy (RAIRS) to analyze the changes occurring in long-chain alkanethiolate SAMs as a function of increasing temperature [99]. Based on the surface selection rules that are associated with surface IR procedures [100] and the relationship between the C–H stretching vibrations and the relative crystallinity of the extended alkyl chains as established in prior studies [24,97,101–104], the authors determined that the chains experience a gradual diminishment in chain tilt from the surface normal, yet remain primarily all *trans*-extended up to about 350 K. Above this temperature, a steady transition to a liquid-like phase occurs that once established in the film is irreversible. The authors also tested SAMs with a variety of terminal groups and determined that the same general trends applied for all SAMs. In a follow-up study, the same research team fine-tuned their analysis of their observations and described the thermal disordering of a SAM as a two stage process: the first stage being a reversible change in the film (a gradual un-tilting with gauche defects developing near the chain termini), and the second being nonreversible (a large number of defects forming below the surface of the film) [27].

With regard to stability upon exposure to harsh chemicals, Bain et al. determined in a study with C18SH SAMs that a well-formed film could be exposed to 1 N HCl or NaOH for one day without detectable deterioration, but after an exposure of one month, both chemicals caused notable damage to the SAM, more so with HCl [20]. Additionally, the authors noted that other chemicals proved to be destructive to the film, including halogens, strong oxidizing agents, and solutions containing either borane or PCl<sub>5</sub>. A 1998 study by Zamborini and Crooks focused on a series of thiol-based SAMs with various chain lengths and terminal groups to determine their chemical resistance to attack by bromide ion [105]. For SAMs with the same tailgroup functionality, the longer the chain, the more resistant the SAM was to corrosion. For SAMs made of

thiols of equivalent length, but possessing different termini, the order of chemical resistance was OH > COOH > CH<sub>3</sub>. Other studies of the chemical stability of SAMs have reviewed the corrosive effects of CN<sup>-</sup> [106], I<sup>-</sup> [107], and a variety of aqueous ions in an electrochemical environment [26].

The resistance of SAMs to chemical etching has been studied extensively by Whitesides and co-workers for use in microcontact printing [108–113]. The process to generate well-defined features involves the patterning of SAMs on a gold substrate using a polymeric stamp followed by etching by reagents such as basic aqueous KCN saturated with O<sub>2</sub> [108,112,113], dilute aqua regia solution [109], or a solution of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, KOH, K<sub>3</sub>Fe(CN)<sub>6</sub> and K<sub>4</sub>Fe(CN)<sub>6</sub> [111]. These studies demonstrated that SAMs can protect gold from a variety of etchants. This research also showed that the length of the alkanethiol chains and the chemical nature of the terminal groups both play important roles in protecting the underlying substrate [112]. Specifically, long chains provide greater protection than short chains, and hydrophobic terminal groups provide greater protection than hydrophilic terminal groups.

### 3.4. Thiol exchange and displacement of thiolate adsorbates

The key role that displacement plays in the formation of a well-ordered SAM can be found in the fact that researchers have concluded that thiols readily displace contaminants from the surface of Au(111) during film formation [3]. This preference for a sulfur–gold bond over other possible bonding combinations has been attributed to “hard” vs. “soft” acid–base chemistry [20]. The fact that most commonly used functional groups fall in the hard category, while gold and sulfur share soft characteristics, has also been credited with the relative ease of incorporation of these terminal functional groups into the structure of well-ordered thiol-based SAMs, even when a competing adsorbate is incorporated into the adsorbate structure at the other end of the methylene spacer. Once such a film is established, the process of displacement of the thiolate-based adsorbates from the SAM formed on a gold surface can occur either as an exchange reaction with another thiol-based adsorbate or as a displacement process by a chemically active species. Simple replacement of one thiolate adsorbate by a thiol of similar architecture has been attributed to either oxidation making a thiolate species susceptible to displacement [74], imperfections in the gold surface creating weaknesses in the SAM film [86], or imperfections in the film coverage providing points of penetration for the attacking species and possible nucleation sites for the new component in the film [114]. With regard to defect-site desorption, Yang et al. concluded in a combined AFM/STM study that the desorption of normal alkanethiols initiates at domain boundaries and vacancy islands, spreading into ordered domains, but also found that such processes could be retarded by the addition of a small amount of one of several specific amphiphilic solvents to the aqueous system [115].

In addition to the typical factors that contribute to the exchange of one thiolate species for another, there appears to be a hierarchy among adsorbates that provides for preferential adsorption of one species over another. Recognition of such preferences can be found in the work of Folkers et al. [116], where the authors concluded that thiol solutions that contain a mixture of adsorbates forming a SAM exhibiting phase separation, would eventually produce a monolayer dominated by one phase, provided adequate exposure time to the development solution. This particular study involved a long chain alkanethiol and a short chain hydroxy-terminated thiol with ethanol as the deposition solvent. The results from a variety of mixed-SAM studies would appear to indicate that an alternative conclusion is also possible [117–119]; namely, that each binary SAM mixture will achieve its own unique surface mixture equilibrium over time depending upon factors such as chain length,

solvent–adsorbate compatibility (solvency), and interchain interactions for the surface bound adsorbates. Articles that address the issue of the hierarchical nature of adsorbates include: (1) the work of Biebuyck and Whitesides, which used a mixed-SAM created by the adsorption of  $\text{HO}(\text{CH}_2)_{16}\text{SS}(\text{CH}_2)_3\text{CF}_3$  to conclude that the  $\text{CF}_3$ -terminated moiety was displaced by  $\text{SH}(\text{CH}_2)_{16}\text{CN}$  in ethanol at a rate  $\sim 10^3$  times faster than the OH-terminated thiolate [120], (2) the work of Baralia et al., which studied SAMs formed from either C12SH or  $\text{OH}(\text{CH}_2)_{11}\text{SH}$  to determine the displacement rates that would occur upon exposure to a solution containing the other thiol, leading to a conclusion that the initial rates of displacement were similar and tied to imperfections in the film [121], and (3) the work of Bain et al., which found from XPS studies involving SAMs formed from solutions containing systematically varying ratios of hydroxy-terminated thiols and normal alkanethiols of the same chain length that the equilibrium surface composition did not necessarily match the solution composition, and that factors such as adsorbate interactions with the solvent and the alkyl chain-dominated surface phase played important roles in the nature of the adsorbate mixture [122].

Biebuyck et al. concluded from a study where a thiol (RS) and a disulfide (RSSR') of similar structure were allowed to form a SAM film within the confines of a competitive adsorption process that the thiol would eventually dominate the surface even though the initial adsorption rates for both adsorbates were similar [29]. From this study, the authors concluded that the processes that form the developing film do not stop with the initial adsorption and formation of a fully-formed film, but continue in a process of adsorbate replacement and ordering that favors the less cumbersome adsorbate. This study followed an earlier one by the same authors that had concluded that thiols ultimately showed a 75:1 advantage over disulfides with regard to competitive adsorption [117].

Schlenoff et al., in a study published in 1995 using alkanethiols bearing radiolabeled  $^{35}\text{S}$  headgroups, determined that while replacement processes are ongoing for a SAM exposed to a thiol-containing solution, there are some thiols on the surface that are not readily displaced [123]. The authors concluded that certain defect sites on the gold surface were resistant to displacement. An electrochemical study by Collard and Fox involving mixed-SAMs of C16SH and 16-(ferrocenylcarbonyloxy)hexadecanethiol provided support for a conclusion that exchange dynamics vary at defect sites by tracking the loss and gain of the electroactive (conducting) species by cyclic voltammetry [114]. The authors noticed that a second electroactive adsorbate could readily displace the first, but when the system was then subsequently exposed to a nonelectroactive adsorbate, the second electroactive species was displaced rather than the first. The authors concluded that the results were consistent with displacement occurring primarily from defect sites, and that these sites remained relatively immobile over time.

#### 4. Strategies for enhancing the stability of monolayer films on gold

Several of the strategies that have been employed to enhance the stability of SAMs have their roots in Langmuir–Blodgett studies decades earlier [124,125]. In many instances, these strategies have been further adopted by the nanoparticle community as described below in Section 5 of this review. The predominant methods used to stabilize monolayer films can be categorized as follows: (1) creating cross-links between adsorbates in the form of physical or chemical bonds, (2) designing multidentate adsorbates that offer multiple surface bonds to reduce or eliminate desorption and exchange processes, and (3) producing adsorbate systems that incorporate aromatic structures that can either enhance surface bonding or create unique rigid film components.

#### 4.1. Inter-chain cross-linking and adsorbate polymerization

An analysis of how the stability of monolayer systems are enhanced by intermolecular attractions or through the initiation of a cross-linking mechanism provides insight into one of the most effective methods of improving the durability of self-assembled monolayer films. However, many common cross-linking procedures have significant drawbacks that must be considered when custom-designing appropriately functional adsorbates. Furthermore, a cross-linking adsorbate that stabilizes a monolayer on flat substrates might fail to produce a stable film on nanoparticles. For the purpose of clarity, we have divided this subsection into three categories: (i) adsorbates where intermolecular bonds form at or near the headgroup, (ii) adsorbates that either hydrogen bond or polymerize based upon functionality built into the methylene spacer, and (iii) adsorbates whose interactions occur at the chain terminus.

##### 4.1.1. Cross-links at the headgroup

Stabilized SAM-on-gold systems in which the stability derives from inter-headgroup bonding or attraction are somewhat rare for at least two reasons. First, due to the defined arrangement of the surface bonding sites on gold, it is often difficult for the adsorbates to adopt low energy conformations within specific bonding networks. Second, similar silane-based systems on oxide substrates are more conducive to forming a successful cross-linked headgroup network with close proximity to the surface [4]. Some of the challenges involved with these silane-based systems can be found in a review by Onclin et al. [17]. Although examples of the development of silane monolayers on gold are rare, they do exist. In a 1994 study by Kurth et al., a trimethoxysilane monolayer was developed on a gold surface, but this monolayer was subsequently modified with poly(ethyl enimine) crosslinked with a diepoxy compound, bisphenol nepichlorohydrin epoxy resin [126]. For this project, the overlying networked system obscured analysis of the effectiveness of the underlying cross-linked surface structure. Similar sulfur-based systems have not been pursued because sulfur is not amenable to developing such a bonding network. There are, however, other thiol-based structures where the adsorbates are designed to possess more than one thiolate bond to the gold substrate, but these systems typically do not create an intermolecular network (see Section 4.2).

##### 4.1.2. Cross-links within the methylene spacer

Insight into the importance of the relative position (in relation to the substrate) of the cross-linking moiety can be found in a study involving diacetylene containing adsorbates, where the alkyne moieties are positioned within the methylene spacer at three different distances from the gold surface in the associated SAMs [127]. The authors, Menzel et al., found that the nature of the photoinitiated bond structures formed between adjacent chains adjusted with the changing position of the cross-linking mechanism such that the bonding structures (conjugated links) that were formed for a system possessing a four-carbon spacer beneath the resulting interconnecting polymer chains exhibited a limited range of bond lengths (shorter in nature) as compared to the SAMs formed from adsorbates with a nine-carbon spacer beneath the cross-linking network. Variances in the nature of the conjugated alkene/alkyne bond lengths were determined by UV–vis spectroscopy, with a typical polydiacetylene SAM possessing bonds adsorbing in the red, violet, and blue regions of the spectrum, and those with reduced bond diversity not adsorbing in the blue. These results appear to be supported by a separate Raman study [128] and further explained by another paper that examined the influence of odd- vs. even-numbered methylene spacers on the resulting conjugated system [129]. One hypothesis is that the variance in bond lengths reflects



a reduction in the number of degrees of freedom for the spacer of a polydiacetylene system possessing a cross-linking network positioned near the metal substrate, limiting the ability for that alkyl chain to adjust to the formation of the conjugated cross-links. These reports are only a few examples of the broad range of research involving polydiacetylene thin-film systems. Because SAMs based upon these networks have been shown to possess a significant increase in overall stability [130], they have been the subject of extensive examination ever since the first report on this type of SAM was published in 1994 [131]. However, prior research on polydiacetylene networks incorporated into Langmuir–Blodgett films laid the groundwork for this research and provided a significant amount of guidance regarding the working parameters for such systems [124,125,132,133].

The improvement in stability afforded by a polydiacetylene cross-linking network includes: (i) barrier properties to electron transfer through the film, where the fully polymerized SAMs show improvement over unpolymerized analogs; (ii) electrochemical stability, where a polydiacetylene film applied to an electrochemical probe withstood more than thirty cycles of cyclic voltammetry scanning in contrast to a normal alkanethiolate SAM that was stripped in two cycles; (iii) thermal stability, where normal alkanethiol SAMs were completely desorbed from a substrate upon application of 200 °C temperature for 5 min, but a polydiacetylene thin film survived the 200 °C heat exposure for an hour; and (iv) chemical stability, where a normal alkanethiol SAM was fully desorbed when exposed for 2 min to a hot basic solution (1:1 mixture of 1.0 M aqueous KOH with EtOH at 100 °C), while the polydiacetylene thin film survived the same test [130,134]. Recognizing the advantages that these polymer networks provide a thin film, researchers have examined a variety of structural changes (and applications) involving these films, including the addition of tailgroups such as –COOH, –OH, and –(CF<sub>2</sub>)<sub>n</sub>CF<sub>3</sub>, and the incorporation of an ester linkage beneath the cross-linking units [135–140]. But there are also disadvantages: diacetylene adsorbates, owing to their propensity to undergo light-initiated polymerization, must be protected from exposure to light before film formation [131], and sterically large surface structures might interfere with efficient film formation [140].

Another route to improving SAM stability by enhancing interchain interactions along the methylene spacer can be found initially in the work of Lenk et al. in 1994, where hydrogen bonds between amide moieties were utilized to improve the stability of an adsorbate with an extended fluorinated segment [141]. Tam-Chang et al. reported in the following year that SAMs possessing an amide moiety β to the thiolate sulfur produced films that were similar in key organizational characteristics to those of comparable normal alkanethiols [80]. The authors also found with their testing an improved stability against desorption and exchange with hexadecanethiol in ethanol. Additional studies involving this architecture include: (i) a review of the barrier properties of an adsorbate in which the amide moiety γ to sulfur has a 15 carbon alkyl alkanethiol tailgroup, but the resulting SAM displayed a reduced ability to block electron transfer when compared to SAMs derived from octadecanethiol [142], (ii) an electrochemical study of amide-containing adsorbates in which the amide moiety enhanced SAM stability in an electrochemical environment [143], (iii) a thermal-stability study in which an adsorbate with three amide groups in the chain induced 2D bonding structures across the film, and the resulting SAM exhibited enhanced resistance to thermal desorption when compared to SAMs derived from an analogous alkanethiol [144], and (iv) several other studies that provide a more complete overall picture of the performance of these adsorbates [145–149]. Among the many studies describing amide linkages incorporated into the alkyl chains of monolayers on flat gold, several have indicated

that the H-bonding sometimes creates films that exhibit reduced conformational order; however, this particular concern might be less significant for monolayers generated on curved surfaces.

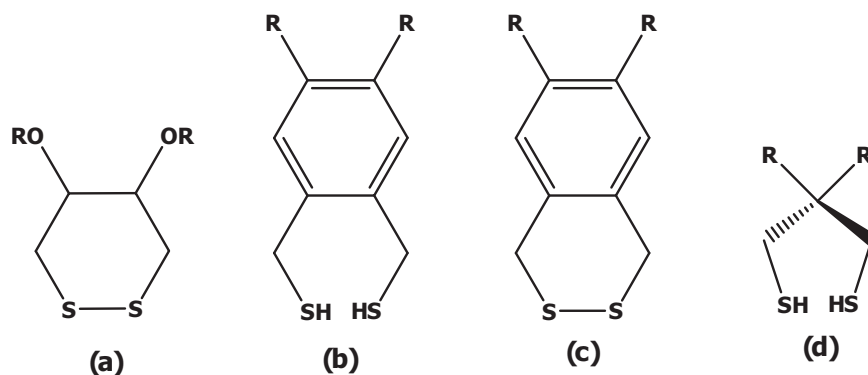
#### 4.1.3. Cross-links at the chain terminus

A description of the impact of the tailgroup on SAM stability can be found in the work of Cooper and Leggett [65], where SAMs derived from alkanethiols possessing a terminal polar group (mercaptopropanoic acid – MPA) were found to be resistant to displacement by C18SH, but SAMs formed from C18SH were readily displaced by MPA. The authors concluded that hydrogen bonding played a key role in this process. But there are limitations to the incorporation of such functional groups at a terminal position, owing to possible interactions with solutions in contact with these surfaces (please see Section 3.1). Because such surface features enjoy the capacity to undergo conformational adjustments, in contrast to functional groups within the methylene spacer, and recognizing that chemical reagents can be readily applied to a SAM surface, it is possible to take advantage of interchain interactions that are not achievable for reactive sites along the methylene spacer. An example can be found in the work of Carey et al., where 11-mercaptopundecanyl-1-boronic acid was found to cross-link upon dehydration to form a surface with structures similar to that found in borate glass [150]. While this structure produces a surface with improved thermal stability, the reversibility of the reaction limits the applications for such thin films. An alternative surface polymerization procedure can be found in a report by Ford et al. involving the cross-linking of a 4-(mercaptomethyl)styrene-based SAM, but analysis of the stability of the resulting film was limited to a laser desorption study [151].

#### 4.2. Chelation: multidentate adsorbates

One of the most versatile and effective strategies for enhancing the stability of SAMs is through the formation of multiple surface bonds for individual adsorbate molecules. Here, the enhancement in stability arises from an entropy-driven process that has been dubbed the “chelate effect” and is generally associated with the tendency of certain ligands to form more than one bond to a metal atom, leading to an improved stability for the ligand–metal complex [152]. In the context of thiol-based SAMs, recognizing that the exchange of thiolate adsorbates at certain points on the surface of gold is a dynamic process during film formation, the presence of a second or third pendant sulfur atom held close to the surface increases the likelihood that the additional sulfur atom(s) will ligate to the surface. Moreover, once bound, the likelihood of two or more headgroups being simultaneously unbound is much lower than that of the potentially successive desorption of two or more individual thiolate chains. A more detailed description of the thermodynamic advantages of multidentate adsorbates can be found in a report by Schlenoff et al. [123]. Furthermore, a recent review outlines the structures of the chelating adsorbates that have been used to generate stable SAMs on flat substrates and on MPNs [153].

Ironically, a bidentate disulfide structure was presented in the pioneering article by Nuzzo and Allara that described the “spontaneous” formation of SAMs on gold [18]. In retrospect, the structure of their disulfides, which were based on alkoxy-functionalized forms of oxidized dithiothreitol (see Fig. 3a), were non-ideal for three reasons: (1) the bond between the two branch points for the resulting dithiolate connects the two alkoxy chains at a dihedral angle that is not conducive to forming tightly packed films, (2) the two oxygen atoms within the adsorbate structure that connects the alkyl chains to the pre-adsorption cyclic disulfide can contribute to disorder in the resulting films, and (3) the relatively unstrained cyclic disulfide structure can provide the adsorbate a possible desorption route, mitigating somewhat the chelate

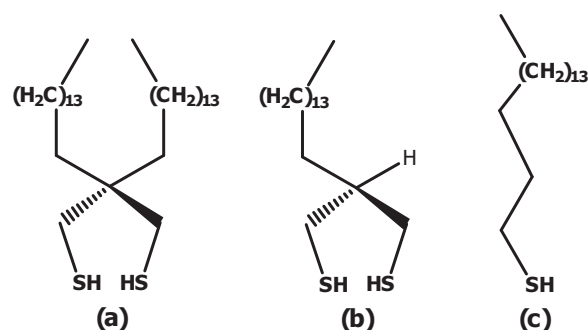


**Fig. 3.** Initial chelating adsorbate structures: (a) the chelating disulfide adsorbate by Allara and Nuzzo [18] (b) the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzene chelating structure by Garg and Lee [154] (c) the disulfide analog for Fig. 6(b), and (d) the branch-point design of the spiroalkanedithiol by Shon and Lee [157].

effect. Consequently, this inception cyclic disulfide adsorbate was abandoned for simpler linear disulfides, which were just as swiftly surpassed by synthetically simpler and more versatile alkanethiol adsorbates. Interestingly, the advantages that surface chelation brings to SAM stability would ultimately lead to the development of thiol structures that resemble the initial dithiothreitol-based chelating structure, albeit with distinct connectivities and efficient surface-binding geometries.

In 1998, Garg and Lee published the results of their initial study on thiol-based chelating adsorbates used to form SAMs on gold [154]. In this paper, which probed the properties of SAMs formed from a bidentate dithiol adsorbate built upon a central aromatic ring (a series of 1,2-bis(mercaptomethyl)-4,5-dialkylbenzene derivatives as shown in Fig. 3b), the authors concluded that the resultant films were densely packed and highly ordered. The authors also determined from preliminary desorption studies that the new chelating SAMs had improved stability characteristics over SAMs formed from normal alkanethiols. A subsequent adsorption study by Garg et al. compared the SAMs formed from the series of aromatic dithiols used in the first study with a disulfide analog, a set of normal alkanethiols of comparable length, and linear disulfides with alkyl chains of similar length [155]. The resulting data indicated that the disulfide analog shown in Fig. 3c formed poorly ordered films – a fact that was attributed to conformational restraints for these adsorbates that make it difficult for a well-ordered final film to form from the initial physisorbed phase during the adsorption process. Additional complexities were also noted and attributed to the rigid, structurally imposed spacing of the two sulfur atoms that contributed to the creation of bonding misalignments with specific sites on the Au(1 1 1) surface. In a third publication involving the 1,2-bis(mercaptomethyl)-4,5-dialkylbenzene derivatives and a series of other aromatic thiols, a desorption study confirmed that the chelating thiol possesses an enhanced stability over the corresponding monothiol adsorbates [156].

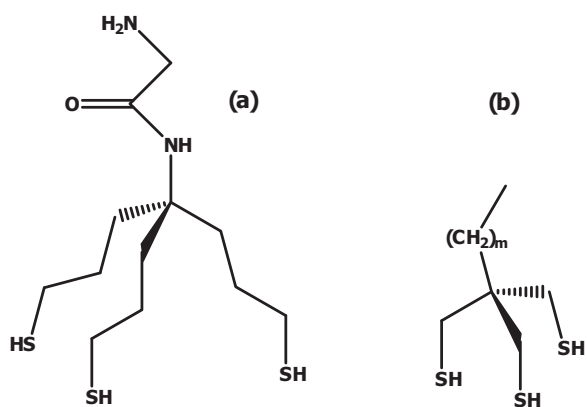
Fig. 3d shows a second-generation class of bidentate adsorbates that contain a single branchpoint for two thiol moieties, and are referred to as “spiroalkanedithiols” [157]. The authors found that the resulting SAMs were highly ordered and well packed, but exhibited a slightly reduced crystallinity when compared to SAMs derived from corresponding normal alkanethiols. The authors also concluded that the branches containing the thiol moieties produced a bonding orientation that was unfavorable to desorption via formation of an intramolecular disulfide ring, creating a structure with improved stability as compared to the SAMs derived from normal alkanethiols. This initial study was followed by a series of reports by Lee and co-workers regarding the systematic analysis of key structural aspects for SAMs formed from a variety of spiroalkanedithiols [158–163]. In particular, a report in 2000 by Shon and Lee described



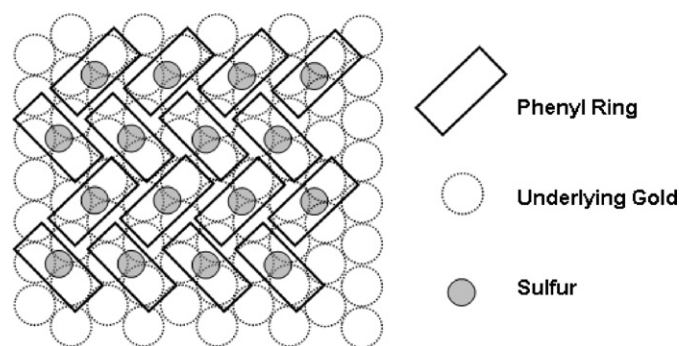
**Fig. 4.** The series of thiol-based adsorbates used by Shon and Lee to examine factors contributing the stability of chelating dithiol adsorbates [164].

the results of a thermal displacement study that included SAMs formed from a symmetrical double-chained spiroalkanedithiol, a single-chained spiroalkanedithiol, and a normal alkanethiol, all of equivalent lengths as shown in Fig. 4. Although both bidentate adsorbates were found to be markedly more resistant to desorption than the normal alkanethiolate, the single-chained dithiolate was surprisingly found to be nearly as resistant to desorption as the double-chained dithiolate [164]. The latter observation was rationalized by the enhanced conformational flexibility of the single-chained adsorbate, which would allow for more efficient binding to the surface. The authors also noted that SAMs developed in solution at 50 °C showed enhanced stability compared to those formed at room temperature.

Trithiol structures are also included in SAM research found in the literature. In 1993, Whitesell and Chang reported on their efforts to form directionally oriented peptide layers on gold and indium-tin-oxide [165]. These layers were attached via aminotrithiol headgroups (see Fig. 5a), which were expected to be more robust than attachment via corresponding monothiol headgroups; moreover, the trithiol headgroups offered the opportunity to increase the spacing between adsorbates due to their sterically larger size. A subsequent electrochemical study in 1998 found that this trithiol headgroup could be modified with terminal ferrocenyl groups to create pinhole-free surfaces [166]. In 2005, a related hydrocarbon-based trithiol adsorbate was reported by Lee and co-workers (see Fig. 5b) [167]. A preliminary ellipsometry-based study compared the solution-phase thermal stability of SAMs on gold derived from analogous monodentate, bidentate, and tridentate adsorbates on gold. The authors found that the tridentate SAMs were more stable than the bidentate SAMs, which were more stable than the monodentate SAMs, but with each increase in the degree of chelation, there was a corresponding decrease in the surface packing density. In 2010, a more thorough study of the thermal stability of these SAMs using X-ray photoelectron spectroscopy (XPS)



**Fig. 5.** Tris-chelating thiol structures studied by (a) Whitesell and Chang [165] and (b) Lee and co-workers [167].



**Fig. 6.** Illustration of the "herringbone" alignment pattern of phenyl bearing adsorbates on the hexagonal lattice of Au(111).

Adapted from Ref. [173].

confirmed the previously reported trend [168]. Separate studies by the Lee group in 2009 examined the electric potential stability and ionic permeability of SAMs derived from hexadecanethiol and several multidentate alkanethiols having analogous chain lengths [169]. These studies found a systematic increase in the potential stability of SAMs as the degree of chelation was increased from monodentate to bidentate to tridentate. The results from the electrochemical impedance spectroscopic measurements were, however, less straightforward, largely due to the loose packing density of some of the multidentate SAMs that were examined.

#### 4.3. Aromatic systems

The incorporation of aromatic moieties into the framework of a typical SAM leads both to unique interchain alignments and to possible deviations in the interaction between the adsorbate and the substrate. The most widely accepted alignment pattern or packing structure of a phenyl-bearing adsorbate assembled on the hexagonal lattice of Au(111) is often referred to as the herringbone structure, which is shown in Fig. 6 [170–173]. Lee et al. determined via atomic force microscopy (AFM) that the periodicity of a series of phenyl-terminated alkanethiol-based adsorbates was  $\sim 4.9 \pm 0.2 \text{ \AA}$  – a number that would indicate the organizational structures adopted by the chains allow the underlying methylene spacers to adopt a densely packed configuration; we note that the periodicity of normal alkanethiol-based SAMs on Au(111) is  $\sim 4.99 \text{ \AA}$  [26,173]. It is further noteworthy that this example is based on terminal aromatic rings attached to extended alkyl chains possessing 12–15 carbons in the methylene spacer. For adsorbates with substantially varying structural segments, issues related to the "commensurability of intraassembly planes" arise, as described

by Ulman and Scaringe in a 1992 article addressing the problems encountered in developing stable two-dimensional molecular assemblies from structurally complex adsorbates [174]. The problems that can occur are best identified by a simple analysis of the component parts of such an adsorbate assembly by comparing the crystal structures adopted by the individual components independently in a pure solid. The key observation derived from the Ulman/Scaringe work is that aromatic structures, if inexpediently inserted into the assembly of a thin film, can destabilize the system. Such an analysis of a SAM is generally based upon a planar assembly; however, structurally complex SAM adsorbates for nanoparticle systems must anticipate the curvature of the surface.

The position of the aromatic ring relative to the sulfur moiety is significant for simple aromatic adsorbates. By studying a series of mono- and biphenyl thiols, Tao et al. concluded that the insertion of a single methylene unit between the sulfur atom and the aromatic ring for thiophenol, forming benzyl mercaptan, improved the resulting monolayer order by providing added flexibility to the adsorbate structure near the metal interface [175]. For films formed from simpler adsorbates without a methylene spacer, there was a reduced surface density. The authors also noted that improvement in the packing density of the adsorbates was obtained by adding a protracted alkyl chain para to the thiol moiety, extending above the ring – a conclusion that has been further supported by the work of Evans et al. [176]. Sabatani et al. concluded in an electrochemical study of a series of simple aromatic thiol-based SAMs in which the number of aromatic rings was systematically increased (i.e., thiophenol, *p*-biphenyl mercaptan, and *p*-terphenyl mercaptan) that the stability of the resulting thin films improved with the increase in the number of rings – an enhancement that might be attributed to greater intermolecular  $\pi$ – $\pi$  interactions [177]. Additional studies involving these structures include mixed, para-functionalized bi-phenyl SAMs [178], absorption kinetics for para-functionalized bi-phenyl SAMs [179], and the utilization of the rigid bi-phenyl thiols to determine their utility in forming ideal surfaces, owing to the absence of the conformational mobility found with normal alkanethiols [180]. In the later article, the authors stressed that the phenyl rings introduced stronger molecule-to-molecule interactions, thereby improving overall SAM stability.

Ulman has been a proponent of the utilization of rigid conjugated systems for the development of stable SAM surfaces. In a short review, a key advantage cited for such systems include the fact that the exposed surface has proven to be stable for months in wetting studies, even when polar functional groups are exposed on the upper phenyl ring, thus allowing for the monolayer interface to be utilized in nucleation and crystal growth studies [181]. There are, however, limitations associated with such surfaces. For example, Ulman and co-workers noted that the intercalation of liquids in the less densely packed surface of the rigid aromatic adsorbates, in combination with the impact of the conjugated dipole arising from the  $\pi$  system of these adsorbates, significantly influenced the contact angles measured for common contacting liquids [182]. This particular characteristic of rigid aromatic adsorbates must be considered when using these types of SAMs in applications where precise control over interfacial wettability is required.

In 1999, Geyer et al. examined the impact of exposure of biphenyl thiol-based SAMs to low energy electrons (50 eV) [183]. The authors concluded that the patterned exposure created increased resistance to etching owing to radiation-induced crosslinking between the phenyl groups. This research was followed by additional studies that have confirmed the crosslinking of neighboring adsorbates upon exposure to low energy electron beams, including an octadecanethiolate SAM, providing a means of producing both positive and negative resists [184–186]. In a recent publication, Turchanin et al. demonstrated that this methodology, when applied to certain aromatic thiol-based SAMs,

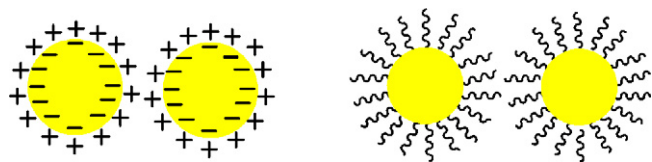


Fig. 7. Illustration of electrostatic (a) and steric (b) stabilization of particles in solution.

Adapted from Ref. [8].

creates surfaces with markedly enhanced thermal stability when compared to normal alkanethiolate SAMs [187]. Specifically, the authors noted that SAMs composed of bi-phenyl thiol desorb from the surface of gold at  $\sim 400$  K. More importantly, the authors also found that bi-phenyl thiolate SAMs that had been cross-linked by exposure to an electron beam desorbed at temperatures as high as  $\sim 1000$  K. The interfacial properties (e.g., wettability and the exact nature of the chemical species at the  $\omega$ -terminus of the films) were, however, not reported.

## 5. Stabilization of monolayer-protected nanoparticles (MPNs)

### 5.1. Dispersion and stability of MPNs

All colloidal systems are fundamentally unstable and suffer from a propensity to undergo aggregation given the natural tendency of such systems to minimize their surface area [188]. Due to Brownian motion in a colloidal system, particles collide with each other, which can lead to the formation of a doublet, which can become a triplet, and with time and an accumulation of mass, precipitation will usually occur. A colloidal system can be stabilized if the repulsive forces between the particles overcome the attractive forces [189], which are predominantly van der Waals in nature. Repulsive forces arise from one or both of the following (Fig. 7): long-range electrostatic repulsion due to the presence of ionic species at the colloidal surface or short-range steric repulsions due to the presence of molecules or polymers on the surface of the colloid [190]. A summary of the various techniques that have been used to stabilize nanoparticles are outlined in the following paragraphs.

With steric stabilization, the contact between the two colloidal particles is physically prevented by the presence of an organic surfactant or polymer on the surface of the particle. For many SAM-functionalized MPNs, the steric repulsion involves a loss of entropy in the surfactant layer due to a loss of chain mobility and an increase in torsional strain. The mechanism of steric stabilization can be illustrated by considering the interaction of two particles that are covered with non-ionic long-chain molecules [191]. As the nanoparticles approach each other, the surfactant layers begin to overlap, and the concentration of the surfactant layer increases in the overlap region, leading to an increase in individual steric interactions and in osmotic pressure. This increase tends to attract solvent from the surrounding medium, creating a consequent force that separates the particles.

Electrostatic stabilization uses charge–charge repulsion to achieve stability [192], where the attractive van der Waals forces are overcome by the repulsive interactions between charged species adsorbed on the surface of the particles. Nanoparticles formed from citrate reduction initially depend upon this form of stabilization to prevent aggregation. A polymer-based electrostatic stabilization strategy can be found in the work of Mayer and Mark, who generated stable gold nanoparticles protected by cationic polyelectrolytes with ammonium side-groups along a hydrophobic polymer backbone [193].

The aggregation or decomposition of unmodified nanoparticles limits their use in technological applications. Without protection, metal nanoparticles degrade quickly and irreversibly into poorly defined aggregated structures. Protection by weakly adsorbed passivating molecules presents a similar problem. As noted above, *n*-alkanethiol monolayers on flat gold exhibit moderate stability at room temperature [81,112], and decompose rapidly at elevated temperatures [20]. Furthermore, such monolayers are generally poor protectants for nanoparticles, not only because they can desorb from the surface and allow the nanoparticle cores to fuse together, but also because of their tendency to pack densely with crystalline order, which leads to a reduction in steric repulsion [123,194].

Although the development of stable alkanethiolate monolayers is clearly one of the key strategies to preventing the aggregation of gold MPNs [195], other classes of molecular adsorbates have shown promising results, such as the dodecylne-coated gold nanoparticles reported in 2007 by Zhang et al., which were stable against aggregation for up to eight weeks [196].

In general, however, the most widely used methods for enhancing the stability of MPNs are based on thiolate headgroups and can be summarized as: (i) the utilization of endgroups to modify the interactions between neighboring MPNs, (ii) the incorporation of ionic functional groups in the adsorbate to provide electrostatic repulsion as described above, (iii) the diversification of the adsorbates (mixed-SAMs) to create chains of varying lengths and thereby enhance steric repulsion, (iv) the development of chelating surfactants that reduce desorption–exchange events, and (v) the addition of cross-links or polymerizable moieties into the adsorbate structure to provide additional stability to the SAM coating.

An example of endgroup modification can be found in a paper from 1998 in which Johnson et al. reported the influence of specific terminal functional groups on the physical properties of thiolate-stabilized gold nanoparticles [197]. The results showed that COOH and NH<sub>2</sub> terminal functionalities were prone to significant aggregation through hydrogen bond formation. In separate studies, Fleming and Walt explored the stability of alkanethiolate monolayers on gold nanoparticle-coated silica microspheres in 2001 [198]. These researchers found that carboxylate-terminated monolayers were more stable than amine-terminated monolayers as monitored by fluorescence microspectroscopy.

The value of electrostatic repulsions can be found in a 2006 article by Zhao et al., which reported an improvement in stability for gold nanoparticles in water by using nucleotides, such as adenosine-5'-triphosphate, as the capping reagents [199]. The nucleotides inhibited the aggregation of gold nanoparticles via the negative charges of their phosphate groups. In 2008, Sistach et al. reported the stabilization of gold nanoparticles in water using bolaamphiphiles having two carboxylate groups separated by a long hydrophobic chain [200]. This study found that the longest hydrophobic chains were the best at stabilizing the nanoparticles against aggregation.

The utilization of mixed adsorbates is another method that has been employed for the stabilization of gold nanoparticles. For example, a 2007 study by Liu et al. described the stability against aggregation of the assembly of poly(ethylene glycol) (PEG) and mixed peptide/polyethylene glycol monolayers on gold nanoparticles in high ionic strength media [201]. The results showed that the stability of the gold nanoparticles increased with increasing PEG length, decreasing nanoparticle diameter, and increasing PEG molar fraction. Moreover, the authors noted that the stability of gold nanoparticles was also affected by the order of assembly: the sequential addition of PEG followed by peptide was more stable than simultaneous co-adsorption.

Using a chelation strategy, Balasubramanian and co-workers explored the use of resorcinarene ligands that had been shown



to inhibit ligand exchange in SAMs on gold [195]. The stability enhancement of this surfactant over short-chain thiols is due to an improved adsorption to the nanoparticle surface by using multidentate interactions, and the greater spacing between their chains provided for higher conformational freedom for the surfactant layer. In related work, Puszta et al. reported the encapsulation of gold nanoparticles within nondesorbing resorcinarene shells crosslinked by olefin metathesis [202]. The results from this study demonstrated that cross-linking of the surfactant layer greatly enhanced the robustness of the encaged nanoparticles against desorption and agglomeration induced degradation. Even though this approach offers enhanced stability for gold nanoparticles, there are several disadvantages, including weak or incomplete adsorbate binding to the gold surfaces, partial desorption and/or displacement by ligand exchange during aging, time-consuming synthesis, and the complexity of the process as a whole.

Other types of multiple gold-sulfur bonds have been employed to stabilize gold nanoparticles. In 2006, Wojczykowski and co-workers reported the stabilization of gold nanoparticles by tridentate alkanethiols and found that the trithiol ligands resisted replacement with normal alkanethiols [203]. A year later, Dougan et al. investigated the enhanced stability of gold nanoparticles coated with thioctic acid-modified oligonucleotides [204]. Also in 2008, Lee and co-workers reported the use of multidentate thiol ligands such as those shown in Figs. 4 and 5 to inhibit the aggregation of large gold nanoparticles (i.e., diameters  $\geq 20$  nm) in organic solution [205]. This study demonstrated that gold nanoparticles stabilized with a tridentate ligand were more stable against aggregation than those stabilized by bidentate and monodentate ligands, while gold nanoparticles coated with the monodentate ligand showed the least stability as determined by UV-vis spectroscopy and dynamic light scattering. Furthermore, two recent studies by Mattoussi's group have shown that the use of PEG-based ligands with multi-thiol anchoring groups enhance the stability of gold nanoparticles in buffered aqueous solution under extreme conditions [206,207].

## 5.2. Thermal stability studies

### 5.2.1. Thermal stability of MPNs in the solid state

There have been several studies describing the thermal stability of ligand-stabilized gold nanoparticles. In 1995, Terrill et al. examined the thermal behavior of alkanethiol-stabilized gold clusters using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) [208]. These studies found that the mass losses by the cluster compounds occurred in a single, well-defined step beginning at 230, 266, and 310 °C for clusters coated with C8SH, C12SH, and C16SH, respectively. The temperature dependence of the mass losses was interpreted to indicate that the thermal stability of alkanethiol-stabilized gold nanoparticles increased with increasing chain length. In 1999, Chen and Murray reported the stabilization of gold nanoparticles by monolayers of arenethiolates [44]. Analysis by TGA showed that gold nanoparticles coated with arenethiolates are less thermally stable than those coated with alkanethiolates.

In 2001 and 2003, Teranishi and co-workers used a heat-treatment method, which was first reported by Maye et al. [209,210], to induce the size evolution of gold nanoparticles in the solid state [211,212]. The initial dodecanethiol-protected Au nanoparticles had a mean diameter of 1.5 nm as measured by transmission electron microscopy (TEM). After removing the solvent, the small nanoparticles were heat-treated at 150–250 °C, and the particle size increased to 3.4–9.7 nm as a function of the temperature. Moreover, when using octadecanol-protected gold nanoparticles,

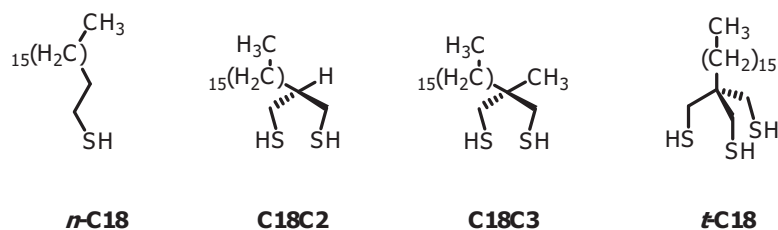
even larger particles could be obtained. The size-evolution process was proposed to include sequential alkanethiol desorption from the particle surface, gold-core coalescence accompanied by a rearrangement of gold atoms, and alkanethiol re-protection of the particle surface [209].

In 2002, Radu et al. reported the thermal decomposition of ligand-stabilized gold clusters on top of graphite and mica substrates by scanning probe microscopy [213]. The ligand-stabilized Au<sub>55</sub> clusters were prepared by using a phosphine-ligation technique [37]. Variable-temperature experiments were performed in ultrahigh vacuum (UHV) at temperatures ranging between 27 and 477 °C. A scanning electron microscope (SEM) was used to investigate gold clusters deposited on graphite before and after annealing for 2 h at several predetermined temperatures. The ligand shells decomposed at about 117 °C on both substrates to form naked gold clusters. Due to differences in cluster mobility at elevated temperatures, large spherical gold aggregates were formed on the graphite substrate, while small uniform islands of gold aggregates were formed on the mica substrate.

In 2004, Luo et al. examined the thermal treatment of alkanethiolate-modified gold nanoparticles assembled as an array on mica and graphite substrates using a variety of analytical techniques [214,215]. The authors found that the capping/linking molecules can be effectively removed to produce gold nanoparticles with controllable surface and optical properties. The authors also found that the particle size and interparticle spacing depended on the chemical and physical nature of the linker molecule and the substrate. One year later, Buettner et al. investigated the thermal stability of normal alkanethiolate-passivated gold colloids [216], where the chain lengths were varied from 3 to 8 to 16 carbon atoms. Temperature-dependent measurements revealed a general tendency for the colloids with longer thiol chains to be more stable in terms of the desorption of the monolayers from the surface.

In 2006, Isaacs et al. explored the thermal stability of thiol-stabilized gold nanoparticles with multilayer assemblies derived from normal and  $\omega$ -functionalized alkanethiols [217]. Analysis by TGA of these MPNs revealed a distinct and well-defined thermal decomposition (mass loss) of the alkanethiolate chains from the 2.2 nm nanoparticle core. The results showed that the MPNs with longer alkyl chains required a higher temperature for complete mass loss. Also, the results indicated that the temperature for the total loss of adsorbate increased linearly with an increase in the alkyl chain length of the protecting organic monolayer. The study further showed that the stability of MPN multilayer films depended on the structure and functionality of the linker molecules (e.g., metal linkers, polymer linkers, and dendrimer linkers) used to build the films.

In 2008, Agasti et al. examined the stability of water-soluble MPNs by varying the substituent along the chain of the adsorbates [218]. The thermal stability of the MPNs was influenced by the packing of ligands, which varied as a function of the position of the substituents. More recently, Srisombat et al. used XPS to study the solid-state thermal stability of gold nanoparticles coated with mono-, bi-, and tri-dentate alkanethiols such as those shown in Fig. 8 [168]. The studies revealed that the MPNs coated with tridentate alkanethiols showed the slowest ligand desorption as the temperature was varied from 35 to 220 °C, while the MPNs coated with *n*-alkanethiols showed the fastest ligand desorption. As a whole, the results from this study demonstrated an enhanced stability for MPNs coated with multidentate adsorbates. Separate studies by Garg et al. have provided support for these conclusions by demonstrating the superior capacity of tridentate alkanethiols to stabilize gold nanoparticles in sensor devices [219].



**Fig. 8.** Structures of *n*-octadecanethiol (**n-C18**), 2-hexadecylpropane-1,3-dithiol (**C18C2**), 2-hexadecyl-2-methylpropane-1,3-dithiol (**C18C3**) and 1,1,1-tris(mercaptomethyl)heptadecane (**t-C18**) [156,168].

### 5.2.2. Thermal stability of MPNs in solution

A 1999 study by Zhong et al. examined the size and shape evolution of alkanethiolate-protected gold nanoparticles in solution [220]. The samples were prepared by a two-phase method [42,43,220] and were then subjected to either solvent evaporation at ~50 °C or heat treatment at ~110 °C under reduced pressure. The results showed that the latter method produced larger particle sizes. A year later, the details of a heating-induced evolution of thiolate-encapsulated gold nanoparticles in solution was reported by Zhong and co-workers [209,210]. Larger core sizes arose from the smaller sized starting particles presumably via sequential ligand desorption, core coalescence, and ligand re-encapsulation. Upon prolonged heating of a solution of alkanethiolate-coated gold nanoparticles (2 nm) at a temperature below 110 °C, the authors observed no significant change in the shape and position of the surface plasmon band. An increase in the intensity of the plasmon band was, however, observed when the temperature reached 138 °C, indicating an increase in core size to 4–6 nm. Prolonged heating of the solution at or above this temperature led to a shift of the surface plasmon band to longer wavelength, which was associated with further growth of the particles.

In a 2004 report, Love et al. described the thermal stability of L-lysine-based dendron-stabilized gold nanoparticles [221], which were dissolved in DMF and then heated in an oil bath. While, no change in the surface plasmon resonance was observed at 100 °C, significant changes were observed at 120 °C. The results showed that the thermal stability of dendron-stabilized gold nanoparticles was influenced by the degree of branching in the protecting dendritic shell and the nature of the dispersion solvent. More recently, the same research group reported gold nanoparticles stabilized by dendritic sulfide ligands with alkene groups at their peripheries [222]. The results showed that intraparticle cross-linking of the ligands enhanced the thermal stability of the gold nanoparticles.

On a different tack, a 2005 study by Isaacs et al. examined the solution-phase thermal stability of tetraoctylammonium-protected gold nanoparticles. The authors found that the stability could be enhanced simply by changing the nature of the counter ions associated with the positively charged ammonium groups. Specifically, the use of thiosulfate anions in place of bromide anions led to an enhancement in stability [223].

Converse to the bulk of the work described in this review, certain studies have found that the adsorption of biomolecules onto the surface of gold nanoparticles leads to an enhancement in the thermal stability of the biomolecules. For example, Jiang et al. reported in 2005 an enhanced thermal stability for cytochrome *c* immobilized on gold nanoparticle surfaces [224]. In separate work, Akamatsu et al. reported in 2006 an enhanced thermal stability for duplex DNA immobilized at modest loadings on gold nanoparticles [225]. Although both of these studies provide evidence that conjugation of the biomolecules to the surface of the nanoparticles increases their thermal stability compared to that of the corresponding non-immobilized biomolecules in solution, the origin of the enhanced thermal stability is specific to the nature of the adsorbed biomolecules.

In 2010, Srisombat et al. investigated the solution-phase thermal stability of gold nanoparticles coated with mono-, bi-, and tri-dentate alkanethiols having similar alkyl chain lengths (see Fig. 8) [168]. In this work, the MPNs were heated in decalin at 120 °C, and the optical properties were monitored as a function of time by UV–vis spectroscopy. The studies found that the evolution of the surface plasmon resonance of the monolayer-protected gold nanoparticles depended on the nature of the monolayer. More specifically, the chelating ligands afforded protection against aggregation according to the following trend: tridentate > bidentate > monodentate. Consequently, these studies demonstrated once again that chelation affords enhanced stability to metal nanoparticles.

### 5.3. Chemical stability studies

Research has shown that cyanide-induced decomposition, where cyanide ions degrade MPCs by reacting with gold clusters to form Au(CN)<sub>2</sub><sup>-</sup> complexes, dialkylsulfides, and dialkyl cyanides [218], can be used to evaluate the degree of protection afforded by alkanethiolate monolayers adsorbed on gold surfaces and colloids [56,109,226]. In the case of most MPNs, the rate of decomposition can be conveniently monitored by UV–vis spectroscopy. Alkanethiolate monolayers protect gold surfaces by providing a barrier against etching by cyanide ion, which, in turn, can be used to probe the corrosion-resisting capacity of the films. The first study of the etching of MPNs by cyanide was reported in 1996 by Weisbecker et al. [56], where the chemical stability of gold colloids coated with HS(CH<sub>2</sub>)<sub>n</sub>OH was examined. The study revealed that the rate of decomposition decreased as the chain length of the adsorbate increased. In 1998, Templeton et al. also showed that the rate of the cyanide-mediated decomposition of MPNs decreased with increasing chain length and steric bulk [227]. A subsequent study from the same group showed that cyanide induced the decomposition of arenethiolate-coated MPNs faster than alkanethiolate-coated MPNs [44]. In 2002, Paulini et al. investigated the impact of branched ligands on the chemical stability of MPNs having amide cross-linking groups within the monolayer chains [228]. This work revealed a correlation between the decomposition rate and the intramonolayer hydrogen bonding and ligand packing density. A year later, Zhu et al. reported the enhanced stability against cyanide etching of 2-mercaptosuccinic acid-coated citrate-reduced gold colloids over unmodified citrate-reduced gold colloids [229]. Furthermore, a 2005 study by Isaacs et al. showed that the chemical stability of tetraoctylammonium thiolate [(Oct)<sub>4</sub>N<sup>+</sup>-O<sub>3</sub>SS]-protected gold nanoparticles was greater than tetraoctylammonium bromide [(Oct)<sub>4</sub>N<sup>+</sup>-Br]-protected gold nanoparticles [223]. A more recent study by Agasti et al. in 2008 demonstrated the steric arrangement of substituents of the ligands correlated to stability against cyanide-induced decomposition [218].

A 2008 report by Srisombat et al. examined the influence of structure on the chemical stability of MPNs by monitoring the cyanide-induced decomposition of small gold nanoparticles

(~2 nm) coated with the mono-, bi-, and tri-dentate ligands shown in Fig. 8 [226]. The differences in chemical stability were attributed to a combination of factors, with the two most important being (1) chelation by the sulfur-containing headgroups and (2) steric bulk of the hydrocarbon tailgroups, where the latter feature impedes the diffusion of cyanide to the underlying gold core. In a related 2009 study, Mei et al. explored the effect of the ligand coordination number and surface curvature on the cyanide-induced decomposition of gold nanoparticles coated with monothiol-terminated PEG–OCH<sub>3</sub> ligands and dithiolane-terminated PEG–OCH<sub>3</sub> ligands [230]. This investigation found that the dithiolane ligands are better at stabilizing small gold nanoparticles (~5 nm), while the monothiol ligands are better at stabilizing larger gold nanoparticles (~15 nm). The authors also concluded that a balance between the level of ligand coordination and packing density of the adsorbates was required to produce stable MPNs. A subsequent study by Browne and Grzybowski suggests that such a situation might be best considered in terms of the surfaces involved [231]. This paper describes how the variance in the density of surface attachment sites as compared to the exposed functional groups at the SAM interface depends on the curvature of the underlying substrate. While the article does not specifically address the issue of MPN stability, it does provide perspective regarding the role of packing density on the properties of MPNs.

## 6. Conclusions

Over the past 25 years, self-assembled monolayers have found widespread use as thin-film coatings in applications ranging from corrosion inhibition to tissue engineering. Similarly, metal nanoparticles have drawn increasing interest due to their potential use in nanoscale optical, electronic, catalytic, and biomedical applications. Many of these applications, however, require exposure to environments that can lead to decomposition of the underlying metal – a concern that has been addressed recently through the development of custom-designed adsorbates that form stable SAM coatings. This review has described the development of such protective SAM films as a method of stabilizing both flat gold substrates and gold nanoparticles. A recurring theme that has emerged from these studies is the critical role played by the headgroup in enhancing the stability of the films. Strong headgroup-substrate binding, including the use of multidentate adsorbates, represents a particularly effective strategy for generating films that offer long-term stability to the underlying metal substrate and/or nanoparticle.

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