Density Functional Investigation of the Inclusion of Gold Clusters on a CH3S Self-Assembled Lattice on Au(111)

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We employ first-principles density functional theoretical calculations to address the inclusion of gold (Au) clusters in a well-packed CH 3 S self-assembled lattice. We compute CH 3 S adsorption energies to quantify the energetic stability of the self-assembly and gold adsorption and dissolution energies to characterize the structural stability of a series of Au clusters adsorbed at the SAM-Au interface. Our results indicate that the inclusion of Au clusters with less than four Au atoms in the SAM-Au interface enhances the binding of CH 3 S species. In contrast, larger Au clusters destabilize the self-assembly. We attribute this effect to the low-coordinated gold atoms in the cluster. For small clusters, these low-coordinated sites have significantly different electronic properties compared to larger islands, which makes the binding with the self-assembly energetically more favorable. Our results further indicate that Au clusters in the SAM-Au interface are thermodynamically unstable and they will tend to dissolve, producing Au adatoms incorporated in the self-assembly in the form of CH 3 S-Au-SCH 3 species. This is due to the strong S-Au bond which stabilizes single Au adatoms in the self-assembly. Our results provide solid insight into the impact of adatom islands at the CH 3 S-Au interface.

1. Introduction

Self-assembled monolayers (SAMs) have been examined in a huge variety of applications in the field of materials chemistry or catalysis [1–4]. Methyl thiolate (SCH 3 ) SAMs on gold, and especially on the (111) surface of gold, have been regarded as a model system for the study of these two-dimensional structures [5–7]. SAMs offer the opportunity to tailor surface properties such as adhesion or surface energy, as well as other interfacial characteristics of a metal surface [8–10]. Despite the remarkable interest in the properties of SAMs, one of the topics widely overseen in the field is the presence of defects and imperfections in the self-assembly, especially when the control of the SAM quality is crucial for many SAM technological applications [11].

Self-assembly is often accompanied by the formation of surface defects such as disordered boundaries between crystalline regions within the SAM and vacancy pits or islands [12]. Such variances in surface structure can influence self-assembly stability, and this is indeed one of the most serious constraints of SAM. On one hand, atomic steps in the gold substrate play an active role during the self-assembly process, and in one of our recent studies we demonstrated that step edges are feasible sources of defects during self-assembly [13]. The presence of both monatomic high gold islands and vacancy pits has been extensively observed during the self-assembly of a large number of molecules on Au(111) [14–17]. We recently suggested that one of the roles of vacancy pits is to stabilize the self-assembly, reducing the number of free surface vacancies [13]. The properties of gold islands, on the other hand, have been less studied, and there is little information on the role of those features produced during self-assembly. The self-assembly process on Au(111) produces single gold adatoms [18–20]. These gold atoms can incorporate into alkanethiol monolayers forming gold-thiolate species with reduced mobility. Gold adatoms can also be deposited onto a self-assembled monolayer by means of physical vapor deposition. STM experiments have
demonstrated that deposited Au atoms penetrate through the self-assembly and preferentially nucleate either at the intersection of different domains or inside domains of less dense striped phase [15, 16].

In this contribution, we present a first-principles, plane wave density functional theory (DFT) study of the inclusion of small gold clusters in the well-packed (\(\sqrt{3} \times \sqrt{3}\))-R30\(^\circ\)-CH\(_3\)S self-assembled lattice. We characterize the self-assembled lattice in the presence of gold clusters of increasing size at the Au-CH\(_3\)S interface. We use SAM adsorption energies to characterize monolayer stability and gold adsorption and dissolution energies to quantify the structural stability of the gold clusters at the interface. Our results show that the inclusion of small gold clusters, with less than four Au atoms, enhances the binding of CH\(_3\)S species, hence making the SAM energetically more stable. Larger clusters tend to destabilize the self-assembly, diminishing the CH\(_3\)S binding. A density of states analysis indicates that the presence of low-coordinated gold atoms is responsible for the stabilizing effect of small clusters. Our results further reveal that clusters located in the SAM-Au interface are thermodynamically unstable towards dissolution, and they will tend to dissolve producing Au adatoms incorporated in the self-assembly. Our results provide solid insight into the impact of adatom islands at the CH\(_3\)S-Au interface.

2. Theoretical Approach

The metal substrate is modeled by means of periodic slabs separated by a vacuum space of ~1.0 nm containing four (111) atomic planes. The vacuum space was found enough to converge the binding energies within 0.01 eV. The lattice parameter of 4.177 Å has been optimized for bulk Au and has been kept fixed in the slab calculations. The two outermost atomic layers of the substrate were allowed to relax.

We employed a 3(\(\sqrt{3} \times \sqrt{3}\))-R30\(^\circ\)-9CH\(_3\)S unit cell to model the CH\(_3\)S adsorption onto the Au(111) surface. This is the original adsorption model discovered by means of He diffraction and atomic force microscopy studies [21, 22]. Even when further studies discovered the existence of more complex superlattices [23, 24], for example, c(4 × 2), the original model is still observed in different metals and for different adsorbates and constitutes a convenient model system to systematically characterize the impact of Au clusters on SAM stability, which supports our choice [25–27]. It contains nine SCH\(_3\) species adsorbed via the sulfur (S) head group on the bridge position, with a slight shift towards the face-centered-cubic (fcc) hollow site of the Au(111) surface. The atomic coordinates of SCH\(_3\) (MT) moieties were allowed to relax without further constraints.

The DFT calculations are carried out using the Vienna Ab initio Simulation Package (VASP) [28–31]. The exchange-correlation energy and potential are described using the generalized gradient approach for exchange-correlation functional within the Perdew-Wang (PW91) implementation [32, 33]. The one-electron wave functions have been expanded on a plane wave basis with a cut-off of 400 eV for the kinetic energy. The Brillouin zone sampling is carried out at \(\Gamma\) point, which is a reasonable approach for large enough supercells. The projected augmented wave (PAW) method [34, 35] has been employed to describe the effect of the inner cores of the atoms on the valence electrons. The tolerance used to define self-consistency is 10\(^{-4}\) eV for the single-point total energy and 10\(^{-5}\) eV for the geometry optimization. The energy minimization for a given atomic configuration is carried out using a Davidson-Bloch iteration scheme.

We calculated average SAM adsorption energies (\(\Delta E_{\text{SAM}}\)) with respect to the SCH\(_3\) radical, according to the following equation:

\[
\Delta E_{\text{SAM}} = \frac{(\Delta E_{\text{SAM}} - \Delta E_{\text{Au}})}{N_{\text{Au}}},
\]

where \(\Delta E_{\text{SAM}}\) is the total energy of the SAM containing a gold cluster, \(E_{\text{SAM}}\), \(N_{\text{Au}}\), and \(E_{\text{Au}}\) are the total energy of the Au slab, the number of SCH\(_3\) species in the unit cell, and the total energy of the SCH\(_3\) radical, respectively.

The calculated average binding energy of the self-assembly in the absence of Au clusters (\(\Delta E_{\text{SAM}}^0\)) defined as the energy needed to adsorb the monolayer per adsorbed SCH\(_3\) species as compared to gas-phase SCH\(_3\) and the gold substrate was found to be ~1.96 eV. This value is close to those previously found in the literature [36]. The adsorption energy of gold clusters is defined as in the following equation:

\[
\Delta E_{\text{Au}} = \frac{(E_{\text{cell}} - E_{\text{cell}} - N_{\text{Au}} E_{\text{Au}})}{N_{\text{Au}}},
\]

where \(E_{\text{cell}}\) is the total energy of the Au slab containing the gold cluster and \(E_{\text{cell}}\) and \(E_{\text{Au}}\) are the total energy of the Au slab, the number of Au atoms in the cluster, and the total energy of bulk Au, respectively. Finally, the absorption energy of the gold clusters to the self-assembled phase is defined as

\[
\Delta E_{\text{Au}} = \frac{(E_{\text{SCH3}} - E_{\text{SCH3}} - N_{\text{Au}} E_{\text{Au}})}{N_{\text{Au}}},
\]

and the SCH\(_3\) vacancy energy is defined as

\[
\Delta E_{\text{SCH3}} = - \frac{(E_{\text{SCH3}} - E_{\text{SCH3}} - E_{\text{SCH3}})}{N_{\text{Au}}},
\]

where \(E_{\text{SCH3}}\) is the total energy of the SAM containing a gold cluster with SCH\(_3\) vacancy.

3. Results and Discussion

We study the incorporation of clusters of increasing size in the well-packed (\(\sqrt{3} \times \sqrt{3}\))-R30\(^\circ\)-CH\(_3\)S self-assembled lattice and address (i) the impact of those clusters on the molecular network properties and (ii) the impact of the self-assembly on the properties of the Au clusters. We report geometrical parameters characterizing both the molecular network and the clusters in Table 1 and average SCH\(_3\) binding energies in Table 2. The geometries of the Au clusters at the SAM interface are depicted schematically in Figure 2.

To begin with, we address the impact of small gold clusters with sizes ranging from Au\(_1\) to Au\(_3\) on SAM stability,
corresponding to Au coverage of 0.11 and 0.33 monolayers (ML), respectively. Gold adatoms (labeled Au$_{ad}$) incorporate into the SCH$_3$-gold interface at the most stable fcc adsorption sites, in which the Au adatom is bonded to two different SCH$_3$ species on top-fcc sites. The average binding energy of the SAM containing a single Au adatom is $-1.99$ eV. This value is slightly more exothermic than $\Delta E_{SAM}^{Au}$ for the Au-free SAM ($\Delta E_{SAM}^{Au} = -1.96$ V). This indicates that Au adatoms stabilize the self-assembly. The inclusion of gold dimers and trimers (labeled Au$_2$ and Au$_3$) also stabilizes the SAM, and $\Delta E_{SAM}$ is $-1.99$ and $-1.98$ eV, respectively. These values are more exothermic than those for the Au-free SAM. $\Delta E_{SAM}$ is an average binding energy which includes the binding contribution of all CH$_3$S species in the unit cell and hence the energy changes due to clusters are small. In order to gain a deeper insight into the stabilizing effect of small gold clusters on the SAM, we use the gold substrate containing Au$_4$ cluster and compute SCH$_3$ vacancy energies $\Delta E_{V}^{SAM}$, defined as the energy needed to generate a vacancy in the molecular assembly. The lower this energy is, the stronger the Au-SCH$_3$ bond will be. We compute $\Delta E_{V}^{SAM}$ for two different SCH$_3$ sites on the substrate: a site on the Au(III) terrace with $\Delta E_{V}^{SAM}$ of $-1.96$ eV and a site directly on the Au$_3$ gold cluster with $\Delta E_{V}^{SAM}$ of $-2.48$ eV. SCH$_3$ species directly attached to the Au$_3$ gold clusters are strongly bonded to the Au substrate. Differently, Au$_4$ cluster has a small impact on the bonding of SCH$_3$ species on the Au(III) terrace, and SCH$_3$ vacancy energy is very similar to the average binding energy for the atom-free SAM ($\Delta E_{SAM}^{Au} = -1.96$ V). These results are consistent with a decrease in the lateral coordination of the Au atoms in the Au$_4$ cluster with respect to the Au(III) surface (3 versus 6).

The presence of larger gold clusters with sizes ranging from Au$_4$ to Au$_{12}$ (0.44 and 0.77 ML, resp.) destabilizes CH$_3$S bond and $\Delta E_{SAM}$ is more endothermic than that for the Au-free SAM. This energy change is in contrast to smaller clusters, which tend to stabilize the SAM. In order to gain more insight into the destabilizing effect of larger Au cluster, we use the substrate with the Au$_3$ cluster as an example and carefully analyze the binding properties of the CH$_3$S species on the structure by means of CH$_3$S vacancy energies. This substrate contains three distinct adsorption sites: a top site on the island (labeled island-top site), an edge site of the island (labeled island-edge site), and the sites on the Au(III)
Figure 2: Plain view of the self-assembled structures containing Au clusters of increasing size. Au atoms in each cluster are colored white, SCH$_3$ atoms are colored in light grey, and bottom metal layers are colored black with transparent planes representing the surface. On some of the structures (Au$_3$ and Au$_7$), we label different SCH$_3$ adsorption sites on top of the cluster or on the Au(111) terrace.

We now turn to analyze geometric and electronic properties of the Au clusters in the self-assembly. In order to do this, we compute binding energies for the adsorption of the Au clusters on the SAM-free Au(111) substrate, $\Delta E_{\text{Au}}$, which quantify the stabilizing impact of the Au substrate on the cluster. We also compute binding energies for the adsorption of the Au clusters on the SAM-covered Au(111) substrate, $\Delta E_{\text{Au-SAM}}$, which quantify the stabilizing contribution of the SAM on the gold cluster. Both $\Delta E_{\text{Au}}$ and $\Delta E_{\text{Au-SAM}}$ values are displayed in Figure 3(b). Our results indicate that the...
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Figure 3: (a) Binding energy values, $\Delta E_{\text{SAM}}$ in eV, for the adsorption of SCH$_3$ SAM to Au(111) substrate containing gold clusters of increasing size. The horizontal line represents the adsorption energy value of the self-assembly to the cluster-free Au(111) surface ($\Delta E_0^{\text{SAM}} = -1.96$ V), whereas the shaded region below the line indicates the energy values lower than $\Delta E_0^{\text{SAM}}$. (b) Calculated values for the adsorption energy of gold clusters to the clean Au(111) surface $\Delta E_{\text{Au}}$ (solid line, squares) and to the SAM-covered substrate $\Delta E_{\text{Au}}^{\text{SAM}}$ (dashed line, diamonds) in eV. The shaded region indicates the lowest energy values for each cluster size.

![Figure 3](image_url)

The energy needed to include a single adatom in the self-assembly ($\Delta E_{\text{SAM}} = 0.13$ eV) is more exothermic than the energy needed to adsorb the adatom on the bare Au(111) surface ($\Delta E_{\text{Au}} = 0.43$ eV). We found similar results for Au$_2$ and Au$_3$ clusters, indicating that the SAM also stabilizes these clusters. Differently, we found an opposite trend for clusters larger than Au$_3$. For these clusters, $\Delta E_{\text{SAM}}$ becomes more exothermic than $\Delta E_{\text{Au}}$. As an example, for Au$_7$ (i.e., the largest gold cluster we considered), $\Delta E_{\text{Au}}^{\text{SAM}}$ is 0.43 eV, with this value being larger than $\Delta E_{\text{Au}} = 0.25$ eV. This indicates that an Au$_7$ cluster is more stable on the bare Au(111) surface than on the SAM interface. The gold clusters suffer in general minor geometrical changes in the interface and the average height of Au $z$(Au) is unaffected by the presence of any SAM (see results from Table 1).

We further carried out a density of states (DOS) analysis in order to gain insight into the electronic structure differences for gold clusters of increasing size included in the self-assembly. We display the DOS plots projected on the CH$_3$S species in Figure 4 (top inset) and on the Au(111) surface in Figure 4 (bottom inset). We also display a DOS plot projected on the Au clusters for the SAM structures containing Au$_4$, Au$_5$, and Au$_7$ clusters in the central panel. The results indicate that the states of the Au clusters progressively shift towards positive energies for increasing cluster sizes. This shift correlates with a decrease in the hybridization energy between the Au clusters and the CH$_3$S species and an increase in hybridization energy between the Au clusters and the Au(111) surface and indicates that the Au-CH$_3$S bonds weaken, while the Au-Au(111) bonds strengthen. These observations explain the different trends found between $\Delta E_{\text{SAM}}^{\text{Au}}$ and $\Delta E_{\text{Au}}^{\text{Au}}$ with increasing cluster size: $\Delta E_{\text{SAM}}^{\text{Au}}$ increases and $\Delta E_{\text{Au}}^{\text{Au}}$ decreases when the Au cluster size increases (Figure 3(b)). A similar effect has been found for Pd nanoparticles with increasing particle size [37].

![Figure 4](image_url)
Finally, we evaluate the stability of Au clusters 1–7 towards dissolution and compute each dissolution energy $\Delta E^{\text{Disl}}$, which is defined as the energy needed to dissolve SAM-covered Au cluster and produce SAM-covered gold adatoms (see Figure 5(a), bottom panel). We display $\Delta E^{\text{Disl}}$ values for different cluster sizes in Figure 5(a) (top panel) and the numerical values in Table 3. The computed $\Delta E^{\text{Disl}}$ values are exothermic, which indicates that aggregated Au islands are in general energetically less favored than structures containing separate Au adatoms in the self-assembly. This suggests that Au clusters will tend to dissolve in the self-assembled phase, forming Au adatoms that will integrate in the SAM. These results are consistent with previous experimental observations finding that Au adatoms deposited on a packed SAM dissolve and nucleate preferentially only at the intersections of different self-assembled domains. In order to provide further information of the energy contributions involved in the cluster dissolution process, we break down $\Delta E^{\text{Disl}}$ for some selected cluster sizes in two different terms, $\Delta E^{\text{Diss}} + \Delta E^{\text{Dil}}$. The first represents the energy needed to dissociate an Au cluster, producing Au adatoms homogeneously distributed in the SAM, and the second, $\Delta E^{\text{Dil}}$, represents the energy needed to dilute the adatoms in the SAM (see Figure 5(b)). We schematically represent the two contributions to $\Delta E^{\text{Dil}}$ in Figure 5(a) (bottom panel), whereas in Table 3 we report the numerical values. The results displayed in Figure 5(a) (bottom panel) indicate that $\Delta E^{\text{Diss}}$, the dissociative contribution to $\Delta E^{\text{Disl}}$, is exothermic and larger than the dilution energy $\Delta E^{\text{Dil}}$, making $\Delta E^{\text{Dil}}$ exothermic for all cluster sizes considered here. Our results are consistent with the experimental observations finding island nucleation rarely within densely packed SAM [15].

4. Conclusion

Periodic density functional calculations have been carried out to gain insight into the inclusion of gold clusters on the ($\sqrt{3} \times \sqrt{3}$)-R30°-CH$_3$S self-assembled lattice on Au(111). Our results have demonstrated that the inclusion of gold clusters with less than four Au atoms enhances the binding of
Table 3: Calculated dissolution energies of the Au clusters adsorbed in the Au-SAM interface to produce gold adatoms. For some selected clusters, we break down the dissolution energies in two different energy contributions needed to dissociate the cluster and dilute the gold adatoms. Figure 5(b) provides a graphical representation of the dissolution, dissociation, and dilution processes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Au-free</th>
<th>Au$_3$</th>
<th>Au$_4$</th>
<th>Au$_5$</th>
<th>Au$_6$</th>
<th>Au$_7$</th>
<th>Au$_8$</th>
<th>Au$_9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E^\text{Diss}$, meV</td>
<td>$-$18</td>
<td>$-$13</td>
<td>$-$22</td>
<td>$-$24</td>
<td>$-$33</td>
<td>$-$30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Delta E^\text{Dis}$, meV</td>
<td>$-$53</td>
<td>$-$46</td>
<td>$-$44</td>
<td>$-$37</td>
<td>$-$36</td>
<td>$-$33</td>
<td>$-$30</td>
<td>$-$27</td>
</tr>
</tbody>
</table>

$\Delta E^\text{Dis}$, dissolution energy, in meV, to form Au adatoms diluted in the SAM; $\Delta E^\text{Diss}$, dissociation energy, in meV, to form Au adatoms homogeneously distributed in the SAM; $\Delta E^\text{Dis}$, dilution energy, in meV.

CH$_3$S species in the self-assembled lattice. In contrast, larger gold clusters destabilize the self-assembly. We attributed this effect to the presence of low-coordinated gold atoms with significantly different electronic properties compared with larger clusters, which makes the binding energetically more favored. Our results further indicate that all gold clusters are thermodynamically unstable at the SAM-Au interface and that they will tend to dissolve, producing Au adatoms. This was consistent with experimental evidence from the literature. Our results provide solid insight into the impact of adatom islands at the CH$_3$S-Au interface.

Competing Interests
The authors declare that there are no competing interests regarding the publication of this paper.

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