Small gold clusters on graphene, their mobility and clustering: a DFT study

Martin Amft, Biplab Sanyal, Olle Eriksson and Natalia V Skorodumova

Department of Physics and Astronomy, Uppsala University, Box 516, S-751 20 Uppsala, Sweden

E-mail: martin.amft@fysik.uu.se

Received 18 November 2010, in final form 5 March 2011
Published 4 May 2011
Online at stacks.iop.org/JPhysCM/23/205301

Abstract
Motivated by the experimentally observed high mobility of gold atoms on graphene and their tendency to form nanometer-sized clusters, we present a density functional theory study of the ground state structures of small gold clusters on graphene, their mobility and clustering. Our detailed analysis of the electronic structures identifies the opportunity to form strong gold–gold bonds and the graphene-mediated interaction of the pre-adsorbed fragments as the driving forces behind gold’s tendency to aggregate on graphene. While clusters containing up to three gold atoms have one unambiguous ground state structure, both gas phase isomers of a cluster with four gold atoms can be found on graphene. In the gas phase the diamond-shaped $\text{Au}_4^D$ cluster is the ground state structure, whereas the Y-shaped $\text{Au}_4^Y$ becomes the actual ground state when adsorbed on graphene. As we show, both clusters can be produced on graphene by two distinct clustering processes. We also studied in detail the stepwise formation of a gold dimer out of two pre-adsorbed adatoms, as well as the formation of $\text{Au}_3$. All reactions are exothermic and no further activation barriers, apart from the diffusion barriers, were found. The diffusion barriers of all studied clusters range from 4 to 36 meV only, and are substantially exceeded by the adsorption energies of $-0.1$ to $-0.59$ eV. This explains the high mobility of $\text{Au}_1$–$\text{Au}_4$ on graphene along the C–C bonds.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Historically, carbon allotropes, e.g. graphite, carbon nanotubes and fullerene, have been extensively used for studying the absorption processes of finite-sized particles on them. Small coinage metal clusters on single layers of carbon, i.e. graphene, were first used to model the adsorption on graphite surfaces or single-walled carbon nanotubes [1–3]. After the experimental evidence for the existence of graphene was found by Novoselov et al [4, 5], now even awarded with the Nobel Prize in Physics, the study of cluster adsorption on graphene became important in its own right.

Graphene stands as an extraordinary material that offers enormous possibilities for applications in electronics, sensors, biodevices, catalysis and energy storage [6–9]. The unique electronic structure of graphene with a linear dispersion of the electronic structure at Dirac points not only plays an important role in charge transport but in verifying theoretical predictions in quantum electrodynamics by table-top experiments too. As graphene is a zero-bandgap material, one of the routes to make use of graphene in the electronics industry is to create a small bandgap by means of functionalization with external chemical agents [10–12].

By means of density functional theory (DFT), the effect of Au nanoparticles on the electronic structure of graphene has been studied [13]. The authors showed that $\text{Au}_{38}$ nanoparticles covered with methylthiolate molecules introduce new Dirac-type points due to charge transfer but keeping the graphene layer metallic whereas the bare nanoparticle opens up a small bandgap at the Dirac point of graphene. A recent work [14] has emphasized the effects of the distribution of Au atoms on the charge carrier mobility of graphene. They have concluded that the formation of Au clusters increases the mobility whereas a homogeneous distribution reduces the mobility.
The adsorption and diffusion of gold adatoms on highly oriented pyrolytic graphite (HOPG) have been studied for decades, first by means of the desorption flux from the surface [15], and later on directly with scanning tunneling microscopy [16] and transmission electron microscopy [17]. Also ab initio calculations on the adsorption of small gold clusters and the diffusion of adatoms and dimers on HOPG have been reported [18–20].

Very recently the growth of gold nanoparticles on few layers of graphene by physical vapor deposition has been monitored [21]. The growth process stopped at an average particle size of 6.46 ± 0.68 nm on a single graphene sheet. As atomic-scale manipulation is nowadays possible in experiments, the study of small clusters and their effects on the electronic properties is highly relevant for the future realizations of nanoscale devices.

A systematic theoretical study of the size variation of small Au clusters adsorbed on graphene is missing. Here we address this issue by means of DFT. We study the adsorption of Au1−4 on graphene, focusing on an analysis of the electronic structures. Diffusion barriers are calculated from the total energies and confirm the high mobility of Au1−4. We study in detail the stepwise formation of a gold dimer out of two pre-adsorbed adatoms, as well as the formation of Au3,4. We show how both Au4 isomers from the gas phase can be produced on graphene by two distinct clustering processes.

This paper is organized as follows. In section 2 we summarize the computational details of this work. In section 3 the ground state structures of Au1−4/graphene, their adsorption energies, charge transfers and electronic structures are discussed. Starting from these structures the mobility, i.e. diffusion barriers, and clustering processes have been studied and are presented in section 4. Finally, section 5 summarizes and concludes the paper.

2. Computational details

The scalar-relativistic ab initio DFT calculations were performed using the projector augmented wave (PAW) [22, 23] method as implemented in VASP [24, 25]. The exchange–correlation interaction was treated in the generalized gradient approximation (GGA) in the parameterization of Perdew, Burke and Ernzerhof (PBE) [26]. Recently, it has been shown that this level of accuracy is sufficient for the systems at hand [27]. A cutoff energy of 600 eV was used and a Gaussian smearing with a width of σ = 0.05 eV for the occupation of the electronic levels.

The graphene sheet was modeled by a 5 × 5 supercell, i.e. 50 carbon atoms, using the calculated C–C bond length of 1.42 Å. The repeated sheets were separated from each other by 20 Å of vacuum. A Monkhorst-Pack Γ-centered 5 × 5 × 1 k-point mesh (13 k-points in the irreducible wedge of the Brillouin zone) was used for the structural relaxations. Spin polarization was taken into account for all calculations and the relaxation cycle was stopped when the Hellmann–Feynman forces had become smaller than 5 × 10−3 eV Å−1. Spin–orbit coupling was not taken into account, since calculating the electronic structures of the previously relaxed Au1/graphene with spin–orbit coupling increased the adsorption energies by 30 meV only. Furthermore, structural relaxations are expected to be negligible, since the Hellmann–Feynman forces were already well converged.

We also used a finer k-point mesh, i.e. 16 × 16 × 1 k-point mesh (130 k-points), and found the changes in the geometry of the systems to be negligible. Therefore we decided to use the relaxed structures obtained with the 5 × 5 × 1 k-point mesh for total energy (E0) and density of states (DOS) calculations. However we used a finer k-point mesh, i.e. 20 × 20 × 1 with 202 k-points, to accurately calculate E0 and the DOS of these structures. Note that cluster adsorption energies, \( E_{\text{ads}} = E_0(\text{Au}_{1−4}/\text{graphene}) - E_0(\text{Au}_{1−4}) - E_0(\text{graphene}) \), are negative when the adsorption is exothermic. The projected DOS were calculated within Wigner–Seitz spheres of radii 0.863 Å (carbon) and 1.503 Å (gold), using for illustrative purposes a higher Gaussian smearing of 0.1 eV.

In order to obtain the diffusion barriers the total energies of the gold clusters on different binding sites were calculated. In the calculations the x–y coordinates of the gold atom binding to carbon, as well as the carbon atoms in the rim, were fixed, while the rest of the structure could fully relax. Since the calculated diffusion barriers are less than 36 meV, we checked their dependence on the GGA exchange–correlation functional used. Compared to PW91 [28] and RPBE [29], we found only negligible differences.

The change distributions and transfers were analyzed by means of the Bader analysis [30].

3. Ground state properties of Au1−4/graphene

There are different ways to obtain clusters of a certain size on a substrate. Here we consider two possibilities: first, mass-selected clusters soft-landed onto graphene and, second, the clustering of smaller fragments, already pre-adsorbed on the graphene sheet.

When exploring the first scenario, we obtain the ground state structures of Au1−4/graphene, see figures 1(a)–(d), by fully relaxing the gas phase cluster ground state structures [31–33] in various ways on graphene. As will be shown in section 4, the same structures for Au2−4 are formed when starting from smaller pre-adsorbed fragments, i.e. by the second scenario.

The tetramer shows an interesting peculiarity. In the gas phase the diamond-shaped isomer, \( \text{Au}_{4}^{D} \), is the ground state [31–33]. According to our calculations, it is 43 meV lower in energy than the Y-shaped isomer, \( \text{Au}_{4}^{Y} \), cf [31, 33]. On graphene the situation is reversed: \( \text{Au}_{4}^{Y} \) is 137 meV lower in energy than \( \text{Au}_{4}^{D} \) on graphene. The overall geometry of both isomers is conserved on graphene, cf figures 1(d) and (e). In addition to soft-landing, both isomers can be formed on graphene by clustering of smaller pre-adsorbed fragments, i.e. \( \text{Au}_{4}^{D} \rightarrow \text{Au}_{4}^{D} \) and \( 2\text{Au}_{2} \rightarrow \text{Au}_{3}^{D} \), see section 4 for more details. Note that two of the bonds in \( \text{Au}_{3}^{D} \) are comparable to the inter-dimer bond, i.e. 2.55 and 2.6 Å compared to 2.67 and 2.72 Å, cf figures 1(b) and (e).
terraces. On MgO the gold trimer and tetramer form two
in contrast to the adsorption of small gold clusters on MgO
of the trimer and tetramers on graphene, figures 1(c)–(e), is
from the gas phase. The isomer AuY
3.1. Binding sites and energies, charge redistribution
The adatom, dimer and Y-shaped tetramer prefer the binding
site on top of a carbon atom, whereas the trimer and diamond-
shaped tetramer bind right above a carbon–carbon bond, see
figure 1 for an illustration. It is interesting to observe a trend to
minimize the number of gold atoms binding to graphene for all
five clusters, i.e. only one Au atom is close to the graphene
layer. This already indicates that the Au–Au interaction is
stronger than the Au–C interaction, which will be discussed
in greater detail below.

The ground state structures of Au1.2/graphene, see
figures 1(a) and (b), resemble the adsorption behavior of Au1,2
on MgO and graphite [34, 18, 35]. The adsorption behavior
of the trimer and tetramers on graphene, figures 1(c)–(e), is
in contrast to the adsorption of small gold clusters on MgO
terraces. On MgO the gold trimer and tetramer form two
bonds between gold and surface oxygen. Furthermore only the
diamond-shaped Au4 isomer is stable on that substrate [34].

Care must be taken when comparing our results with
earlier studies of Au1–4 on HOPG [18–20]. First of all, the
authors relied on the use of the local density approximation
(LDA), which only coincidently describes the bulk properties
of graphite better than GGA. Second, the number of k-
points was eight at best, making a meaningful calculation
of, for instance, the DOS impossible. Last, but not least,
spin polarization was neglected in [18, 20]. We find spin
polarization especially important for open shell systems like
Au1,4/graphene. They have two distinct peaks, for spin up
and down states, respectively, close to the Fermi level, cf figures 4
and 5. Despite all these methodological differences one can
conclude that the ground state structures of Au1–3 adsorbed on
HOPG and graphene seem to be very similar. Note that Au3,4
have not been studied on graphene before. The second isomer,
AuY, figure 1(e), has not even been considered on graphite
before. Note that the tetrahedral structure of Au4 is known
to be unstable in the gas phase [33, 36] and neither did we find
this structure on graphene.

Figure 2(a) shows the cluster adsorption energies Eads
of the Au1–3 ground state structures, as well as of both Au4
isomers. AuY 4 has the highest Eads of −0.59 eV and the adatom
having with −0.1 eV the lowest. As mentioned above, AuY
is not only the ground state structure on graphene, but also
adsorbs stronger on it than AuD, i.e. Eads = −0.59 versus
−0.41 eV, respectively.

In all five cases the whole gold cluster receives, according
to our Bader analysis, a small charge of up to −0.12 e− from
graphene, see figure 2(b). Hence adsorbing Au1–4 on graphene
corresponds to a p-doping of the material. A clear odd–even
oscillation, depending on the number of gold atoms in the
cluster, can be seen in the charge transfer. It is generally
known that the electronic characteristics of low-dimensional
gold structures can exhibit odd/even oscillations depending on
the parity of the number of Au atoms, which are determined by
the opening/closing of the s shell [37, 38, 34].
Figure 3. Buckling, i.e. vertical distortion, of the first three coordination shells around the adsorption sites of Au$_1$−4. Full symbols: gas phase structures adsorbed on graphene, cf figures 1(a)–(d). Open symbols: Au$_Y$/graphene, cf figure 1(e).

In addition to the charge transfer into the clusters, there also occurs a significant charge redistribution within the clusters themselves, see Bader charges of the individual atoms in figure 1. The insets in figures 4–8 also illustrate it by showing isosurfaces of the charge density redistribution, i.e. \( \Delta \rho = \rho(\text{Au}_n/\text{graphene}) - \rho(\text{Au}_n) - \rho(\text{graphene}) \), upon the cluster adsorption on graphene. The actual tetramer ground state geometry Au$_Y$/graphene breaks these trends, showing a significantly smaller distortion of the C atom positions than Au$_D$/graphene, see figure 3 (open symbols).

Along with the buckling comes a polarization of the graphene sheet, i.e. charge deviations from an otherwise neutral charge state of the carbon atoms, of up to \( \pm 0.18 \) e−. For the systems under consideration the polarization does not show such a clear pattern as observed on HOPG [18, 20]. For coordination shell around the adsorbate, cf figure 3. Let us consider for the moment only the gas phase structures adsorbed on graphene. The full symbols in figure 3 show that the vertical distortion of the carbon atoms binding to the Au atom scales approximately linearly with the size of the gold cluster. On the other hand, the buckling in the second and third coordination shell does show a clear odd–even oscillation, depending on the number of Au atoms, figure 3 (full symbols). But the actual tetramer ground state geometry Au$_Y$/graphene breaks these trends, showing a significantly smaller distortion of the C atom positions than Au$_D$/graphene, see figure 3 (open symbols).

Concerning the adsorption strength of these small gold clusters on graphene we can summarize that two effects exist, which can compete with each other. First, the attraction due to the formation of chemical bonds between gold and carbon. Second, there also exists a Coulomb interaction between the charged gold atoms in the cluster and the carbon atoms in the proximity of the adsorption site. Mostly this Coulomb interaction is repulsive in nature, as can be seen from the extra charge in the clusters that tends to be concentrated as far away from the graphene sheet as possible, see figures 1(a)–(c).

Although the extra charge density concentrates on the two outer atoms in Au$_D$/graphene, those two atoms are repelled away from the graphene sheet, recognizable from the 5% stretched bonds with the bottom gold atom, see figure 1(d). In contrast to these four systems, the Coulomb interaction between the adsorbed Au$_Y$ and the underlying graphene sheet is predominately attractive, i.e. between the leftmost gold atom, cf figure 1(e), carrying most of the additional charge, and the positively charged carbon atoms under it, cf the inset in figure 7.

The comparatively small adsorption energy of the single gold atom is also explained by these competing effects, see figure 1(a), which is manifested in the 5–9% longer Au–C distance of Au$_1$/graphene compared to the other clusters.

It has, predominantly qualitatively, been reported in the literature that the adsorption of Au$_1$−4 on HOPG [18–20, 39] and of Au$_{1,2}$ on graphene [40, 41] leads to a shift of the carbon atoms in the vicinity of the adsorption site towards the gold. Due to the strong sp$^2$ interatomic C–C bonds the vertical distortion is not solely restricted to the carbon atoms underneath gold. Instead it spreads at least to the third coordination shell around the adsorbate, cf figure 3. Let us consider for the moment only the gas phase structures adsorbed on graphene. The full symbols in figure 3 show that the vertical distortion of the carbon atoms binding to the Au atom scales approximately linearly with the size of the gold cluster. On the other hand, the buckling in the second and third coordination shell does show a clear odd–even oscillation, depending on the number of Au atoms, figure 3 (full symbols). But the actual tetramer ground state geometry Au$_Y$/graphene breaks these trends, showing a significantly smaller distortion of the C atom positions than Au$_D$/graphene, see figure 3 (open symbols).

Along with the buckling comes a polarization of the graphene sheet, i.e. charge deviations from an otherwise neutral charge state of the carbon atoms, of up to \( \pm 0.18 \) e−. For the systems under consideration the polarization does not show such a clear pattern as observed on HOPG [18, 20].
instance, the carbon atom binding to Au$_{1,3}$ and Au$_{4}^{D}$ gains additional electrons, whereas it stays neutral when binding to Au$_{1}^{B}$ or even loses some charge if under Au$_{2}$. Also in the second and third coordination shells around the binding sites a general pattern could not be observed, i.e. charge losses and gains could be observed within the same coordination shell. In the case of Au$_{1}$ the charge redistribution leads to a loss of charge in the second coordination shell and a charge donation into the gold adatom and partially into the carbon atom of the first coordination shell as well.

3.2. Electronic structure of Au$_{1,3}$/graphene

Both the gold adatom and trimer possess an unpaired 6s electron that gives rise to a total spin moment of 1 $\mu_B$ in the system.

Figures 4 and 5 show the total spin-polarized DOS of Au$_{1,3}$/graphene and, for comparison, also the total DOS of pure graphene. For illustration the atomic energy levels of an isolated gold atom are shown as arrows in figure 4. Only in this simple case can the origin of the electronic states of the adsorbed adatom be easily identified from the gas phase species.

From the lm and site-decomposed DOS (not shown) we identified the character of the labeled structures 1–4 in the DOS of Au$_{1}$/graphene and accordingly for the bigger clusters as well.

In figure 4 structures 1 (2) are gold 5d states with spin polarization up (down). The higher peaks in 1 and 2 consist partially of d$_{z^2}$ states that overlap with p$_z$ states of the underlying carbon atom. Also the gold 6s state near the Fermi level, i.e. peak 3, hybridizes with the p$_z$ state to form a $\sigma$ bond. The unoccupied states in peak 4 are of similar character as those in 3. Compared to the atomic states, i.e. arrows 1’ and 2’ in figure 4, the d states are split upon adsorption of the gold atom on graphene. Furthermore they are shifted approximately 0.7 eV downwards in energy. The gap between the highest occupied states and the lowest unoccupied states $\Delta E_G$, i.e. between peaks 3 and 4, is 0.15 eV narrower than in the gas phase, i.e. 3’ and 4’.

For the bigger clusters, we concentrate our efforts on the identification of the most important features of the densities of states, i.e. figures 5–8, and their contribution to the formation of the clusters and their bonding to graphene.

Already at a first glance at the DOS of Au$_{3}$/graphene, figure 5, one can recognize the higher complexity of the structure. The two peaks are labeled with one comprised predominantly of d$_{z^2}$ and d$_{x^2−y^2}$ states of the gold atom closest to carbon, hybridizing with its p states. Peaks 2 are predominantly d$_{x^2−y^2}$ states located at the two gold atoms at the top. The main features, 3, mostly contain d states of all characters from the top gold atoms. Most of the d$_{z^2}$ states of all three gold atoms are concentrated in this peak, forming the chemical bond to carbon by hybridizing with its p$_z$ states. Peak 4 consists of intracluster d$_{z^2}$–d$_{z^2}$ states. Peak 5 directly below the Fermi energy contains the 6s states of the top gold atoms that interact only indirectly, via d$_{z^2}$ states of the gold atom closest to graphene, with the carbon p$_z$ states. Clearly, most of the spin moment of the whole system is concentrated in these states. Finally, peaks 6 and 7 in the unoccupied DOS are overlaps of empty 6s states and carbon p$_z$ states from the top gold atoms and the bottom one, respectively.

From the shown DOS, especially the peaks near the Fermi energy, one can conclude that even a small external bias of less than ±0.5 V will significantly increase the electrical conductivity of these systems.

The charge density redistributions upon adsorption $\Delta \rho$ are shown as insets in figures 4 and 5. The earlier mentioned polarization of the carbon atoms in the first three coordination shells around the adsorption sites can be seen. The extra charge in Au$_{1}$ also leads to a charge density redistribution within the gold atom, whereas the gold atoms in the trimer seem to equally share the additional charge from the substrate. Therefore it is important to take the Bader analysis, figure 1, into consideration as well that shows a charge depletion of the bottom gold atom.

3.3. Electronic structure of Au$_{2,4}$/graphene

Obviously, the total magnetic moment of the closed-shell structures Au$_{2,4}$ must be zero in the gas phase. This is unchanged by adsorbing them on graphene.

Upon adsorption the symmetry of the electronic structure of the dimer is broken, see figure 6. From the lm and site-decomposed DOS (not shown), we see that peak 1 consists of d$_{z^2}$ states. The broader feature 2 and peak 3 are d$_{xy}$, d$_{yz}$ and d$_{x^2−y^2}$ states, predominantly from the gold atom closest to carbon, hybridizing with carbon p$_{xy}$ states. Peaks 4 and 5 do not contribute to the chemical bonding to graphene, as they are s–d states localized at the cluster, whereas 6, mostly s–d$_{z^2}$ states at the top gold atom, indirectly interacts with carbon p$_z$ via d$_{z^2}$ at the bottom gold atom. Finally, the two peaks at 7 are predominantly unoccupied 6s states of the gold atom close to carbon, overlapping empty p$_z$ states of carbon. Note also that the states in peaks 4–7 substantially narrow the cone in graphene’s DOS around the Fermi energy, leaving it only undisturbed in the interval $E_F$ ± 0.5 eV, figure 6.  

Figure 6. Projected total DOS of Au$_{1}$/graphene (black line) and for comparison pure graphene (red line). Note: the Fermi energies of both systems were shifted to 0 eV. Inset: charge density redistribution due to adsorption of Au$_{2}$ on graphene; increase (decrease) of the charge density in red (blue). The shown isosurfaces correspond to $\pm 7 \times 10^{-4}$ e$^−$ Å$^{-3}$.
To summarize the predominant nature of the labeled peaks in the DOS of Au4/graphene, figure 7, we label the gold atoms in the following way, see figure 1(e): Au4 (left), Au4m (middle), Au4 (top) and Au4b (bottom). The carbon atom under Au4b, forming the chemical bond with the cluster, is named Cb.

Peaks 1 and 2 consist of s–d states and dxy states, respectively, localized on the cluster only. Peak 3 consists of d states that contribute to the chemical bond by overlapping with px states of Cb, i.e. d3z states on Au4m and d3z states on Au4b. Peak 4 and its shoulder consist mainly of dxy and d2−2z on Au4, overlapping with carbon p states as well. Peak 5 are d2−2z states solely localized within the cluster, while 6 are s−d2 states of Au4b hybridizing strongly with px of Cb. The highest peak 7 consists of dxy and d2−2z states of Au4, Au4m and Au4, i.e. a major part of the strong gold–gold bonds that hold the cluster together. Peaks 8 and 9 are d states almost exclusively localized on Au4m and Au4, respectively, as well as peaks 10 (d2−2z states) and 11 (s−dy states) which are localized on Au4. As we saw for the other clusters the unoccupied states at peak 12 are s states, in the present case of Au4 and Au4b, overlapping with unoccupied px states of Cb.

Despite its more symmetric geometry the DOS of Au4/graphene, figure 8, has many features which can be recognized from the other isomer, cf figure 7. For convenience we label the gold atoms in Au4/graphene again: Au4 (bottom), Au4m (middle) and Au4 (top), see figure 1(d). The two carbon atoms, forming bonds with the cluster, have a very similar electronic structure and we therefore simply name them both Cb.

The relatively broad peak 1 consists mainly of dxy states of Au4 and Au4b. The shoulder below peak 2 is d2−dy cluster states of Au4b and Au4, with a smaller amount of intermixed s states that hybridize with the p states of Cb. The actual shoulder and the double peak 3 are predominantly dxy and d2−2z states of Au4 and Au4, respectively. The lower peak 4 contains s−dy states of Au4 that also overlap with Cbpx states. The high peaks 5–7 are the strong intracluster bonds, formed out of d states. Peak 8, on the other hand, consists mainly of d2z states of Au4m, as well as dxy states of Au4 and Au4b, contributing to the chemical bond to carbon by hybridizing with px states of Cb. The highest occupied states, peak 9, are again intracluster bonds, formed out of s states of the Au4m and d2z states of Au4 and Au4b. As for the other clusters the lowest unoccupied states, peaks 10, are unoccupied s states on all the four gold atoms, that overlap with unoccupied Cbpx states.

The gap between the highest occupied states and the lowest unoccupied cluster states ΔE in figures 7 and 8 is very similar, but smaller than that in the dimer case, figure 6. Hence, in contrast to Au1/graphene, an external bias of more than ±0.5 V is needed to see a significant increase in the electrical conductivity.

4. Mobility and clustering

In this section we discuss the mobility and initial clustering processes of gold on graphene. First experiments on the diffusion and desorption of gold atoms on graphite date back almost three decades [15]. With the rise of scanning tunneling microscopes, quantitative estimates of the diffusion and desorption barriers became feasible. These experiments revealed that the binding energies of Au1/graphene exceed their diffusion barriers [16]. Computations of gold adatoms and dimers on HOPG supported these experiments [19].

4.1. Diffusion along the C–C bonds

We determined the diffusion barriers for Au1–4 on graphene from the total energies on the top (t) and bridge (b) positions, as well as from one position in between those two (tb). These energies are sufficient, since none of the five clusters was found to bind to graphene at the hollow sites, i.e. in the center of a carbon hexagon.

Figure 9 shows the differences in the total energies, ΔE0i, of the five clusters with respect to the total energy at their
Figure 9. Difference in the total energies $\Delta E_0$ at the top (t), bridge (b) and a position in between (tb) of Au$_1$ and Au$_Y$, $D_4$ on graphene. $E_0$ of the respective cluster ground state was subtracted to show the diffusion barriers along the C–C bonds (also given in parentheses). Note the smaller scales for Au$_3$, 4.

Figure 10. Changes in the total energy $\Delta E_0$ when forming Au/graphene from two pre-adsorbed adatoms (solid symbols) and for the dimer formation in the gas phase (open symbols). The $x$–$y$ coordinates of the Au adatoms were kept fixed for positions 1–6. The system relaxes without an additional activation barrier from position 6 to 7, the dimer ground state structure (figure 2(b)). The Au–Au distances for the different positions are given on the top axis.

binding site, i.e. top (Au$_{1,2}$ and Au$_Y$) and bridge for the remaining two.

Note that only Au$_2$ binds on both the top and bridge position, while the other four clusters have a saddle point at the bridge (Au$_1$ and Au$_Y$) or top (Au$_3$ and Au$_D$) position, respectively, i.e. if allowed, they relax to their stable binding site. These transition states define the diffusion barriers of the gold clusters along the C–C bonds. For convenience the diffusion barriers are also explicitly given in figure 9. They range from only 4 meV for Au$_2$ and Au$_D$, making them highly mobile, to 36 meV for the least mobile trimer.

The adsorption energies of all five gold clusters on graphene, cf figure 2(a), exceed their diffusion barriers by at least one order of magnitude. Hence, while these small gold clusters will rather strongly adsorb onto the graphene sheet, they will easily diffuse even at very low temperatures.

Figure 11. Changes in total spin-polarized DOS (solid lines, spin up; dashed lines, spin down) when two pre-adsorbed adatoms come stepwise closer to each other to form Au/graphene, cf figure 10. The diagonal line marks the Fermi energies at the different positions.

Figure 12. Changes in the total energy $\Delta E_0$ during the formation of AuY/graphene out of (a) two pre-adsorbed dimers and (b) Au$_D$ out of four adatoms (solid squares). For comparison $\Delta E_0$ for the formation of Au$_2$ in the gas phase is shown as well (open circles). The dotted horizontal line marks the highest gain in energy.

4.2. Clustering of pre-adsorbed fragments

We modeled the initial clustering processes of gold on graphene in two steps. First, we simulated the formation of a dimer out of two pre-adsorbed gold atoms, cf figures 10 and 11. Second, two possible pathways for forming a tetramer, cf figure 12, were explored. At the same time, the formation of a trimer out of a dimer and adatom was studied, too.

In order to simulate the clustering of two pre-adsorbed gold atoms, they were initially placed as far away from each other as possible on a 5 × 5 graphene sheet, i.e. 7.1 Å. This configuration is named position 1 in figures 10 and 11. Since the total energy of the system decreases only marginally between positions 1 and 2, we omitted intermediate steps, cf figure 10.

In the subsequent steps, i.e. positions 2–6, the second gold atom was brought closer to the fixed one along two C–C bonds, see the inset in figure 10. For each of the positions 1–6 only the $x$–$y$ coordinates of the adatoms and one carbon atom at the rim were kept fixed, while $z$ coordinates of the adatoms and the rest of the graphene sheet could fully relax. In a final
step we allowed the system to freely relax from position 6 and without an additional activation barrier it converged to the dimer ground state (position 7). This final structure is identical to the one we found in section 3 by soft-landing the dimer on graphene, see figure 1(b).

Both in the gas phase and on graphene, the formation of a gold dimer is exothermic with a gain in total energy per gold atom of $\Delta E_0 = -1.14$ and $-1.29$ eV, respectively, see figure 10. The higher energy gain on graphene is a result of the higher adsorption energy of Au$_2$ compared to two adatoms, see $E_{ads}$ in figure 2(a). $\Delta E_0$ largely exceeds both the adsorption energy as well as the diffusion barriers of Au$_1$/graphene. Thus the driving forces behind the clustering of two pre-adsorbed gold adatoms is the opportunity to lower the total energy of the system by forming strong gold–gold bonds, i.e. the strongly hybridized d states in figure 6. At positions 3–6 forces act on the two adatoms that try to pull them towards each other. This attractive, graphene-mediated interaction has a maximal range of approximately 4.3 Å, i.e. the Au–Au distance in position 3. At this distance the two gold atoms are still well separated in the gas phase.

Note that the last two positions represent a dimer that is parallel (position 6) and perpendicular (position 7) to the graphene sheet. Obviously, in the gas phase the total energies have to be identical for positions 6 and 7.

Figure 11 shows the changes in the spin-projected total DOS during the intermediate steps of forming a gold dimer on graphene, cf positions 1–7 in figure 10. Note that, even for the largest possible separation of the two adatoms in the 5 × 5 supercell, i.e. 7.1 Å (position 1), there is still an electrostatic interaction between the charged gold atoms, cf figure 1(a). This can be seen from their 6s states near the Fermi level that should exactly coincide without any mutual interaction. At an Au–Au distance of 4.9 Å (position 2) the 6s peak splitting becomes more visible. But still the 6s states below the Fermi level belong solely to the spin-up channel. When the graphene-mediated attraction between the adatoms becomes obvious at a distance of 4.3 Å, see $\Delta E_0$ at position 3 in figure 10, one of the 6s spins flips, leaving the total system with no total magnetic moments, as we saw above for the closed-shell system Au$_5$/graphene. Upon further approach of the two gold atoms the two atomic 6s states form a molecular orbital that moves to lower energies. Finally, it hybridizes with the d$_z^2$ states, cf peaks 4 and 6 in figure 6, in the dimer ground state structure (position 7). Meanwhile the unoccupied 6s states directly above the Fermi level in positions 3–6 move up in energy to finally form peak 7 in figure 6.

Our next aim was to study the formation of Au$_{1,4,4}$ on graphene. We accomplished this by allowing two pre-adsorbed fragments to fully relax from an initial state corresponding to position 6 in figure 10. There are two different reaction pathways for forming a tetramer, resulting in the two isomers Au$_4^0$ and Au$_4^3$, see figures 1(d) and (e). In the first reaction pathway two dimers cluster from their perpendicular ground state into the Y-shaped tetramer, 2Au$_2$ → Au$_4^3$. The energy gain per gold atom during this step is $\Delta E_0 = -0.27$ eV, see figure 12(a). Nonetheless, per dimer this energy gain is still bigger than the dimer adsorption energy of $-0.47$ eV, see figure 2(a), overcompensating the breaking of one Au–C bond to form Au$_4^3$/graphene.

The second pathway includes two intermediate steps to form Au$_4^0$ out of four single gold atoms. To begin with, a trimer is formed, Au$_1$ + Au$_2$ → Au$_4$. Then, by adding yet another adatom, one forms the tetramer: Au$_1$ + Au$_3$ → Au$_4^0$. The energy gain $\Delta E_0$ during the whole reaction is shown in figure 12(b). This process is exothermic and the fragments only have to overcome their diffusion barriers, see figure 9. As for the dimer formation, the energy released by forming the strong Au–Au bonds is the driving force behind the clustering, which is for all steps bigger than the cost of breaking an Au–C bond or overcoming diffusion barriers.

Although we did not explicitly calculate the stepwise movement of the different fragments, as we did in the case of the two adatoms, see figure 10, we expect a similar behavior due to the high mobility of the pre-adsorbed clusters, see section 4.

A comparison of $\Delta E_0$ in figures 12(a) and (b) shows, as mentioned in section 3, that Au$_4^3$/graphene is 137 meV lower in energy than Au$_4^0$/graphene. The open symbols in figure 12 show the energies of the reaction steps in the gas phase. Since Au$_4^0$ is the gas phase ground state structure, we assumed that both reaction pathways give this structure. The end points in figure 12(b) seem to coincide, i.e. the energy gain by clustering in the gas phase and on graphene appears to be the same. That is actually the case since the adsorption energy of four Au$_1$ on graphene is $-0.4$ eV, which is almost identical to $E_{ads}$ of Au$_4^3$ with $-0.41$ eV.

5. Summary and conclusions

By means of density functional theory, the adsorption of Au$_{1,3,4}$ clusters on graphene, their mobility and clustering from pre-adsorbed fragments have been studied. This allowed us to explain the initial steps in the experimentally observed formation of bigger gold aggregates on graphene. While Au$_{1,3,4}$ adsorb similarly on graphene as on graphite, the tetramer turns out to be more peculiar. In the gas phase it has two isomers, the diamond-shaped Au$_4^0$ being the ground state and the Y-shaped Au$_4^3$. On graphene Au$_4^3$ becomes the ground state instead. Although Au$_4^3$ binds stronger to the substrate and also receives more charge from it than Au$_4^0$ does, it disturbs the graphene sheet substantially less.

The cluster adsorption energies on graphene of all studied clusters range from $-0.1$ to $-0.59$ eV and substantially exceed their diffusion barriers, which are 4–36 meV, only. All clusters diffuse along the C–C bonds, since none of them binds to the hollow sites in the centers of the carbon hexagons.

Our detailed analysis of the densities of states shows which states contribute to the strong intracluster bonds, predominantly the 5d states, and which to the chemical bond between gold and carbon, i.e. mostly s–d$_z^2$ cluster states hybridizing with p$_z$ states of carbon.

The formation of the strong Au–Au bonds is the driving force behind the tendency to form bigger clusters from smaller pre-adsorbed fragments. We studied these processes in
detail for the stepwise formation of a dimer out of two pre-adsorbed adatoms, including the evolution of the electronic structure during the clustering. The exothermic reaction has no additional activation barriers apart from the small diffusion barriers of the fragments moving along the C–C bonds. We find the graphene-mediated, attractive interaction of two gold adatoms to have a range of approximately 4.3 Å, which is clearly longer than in the gas phase.

Finally, we have also studied the formation of the trimer and tetramers by the reactions \( \text{Au}_4 \rightarrow \text{Au}_3 \rightarrow \text{Au}_2 \rightarrow \text{Au}_1 \). Both reactions are also activation-barrier-free. As for the dimer, the energy gained clearly longer than in the gas phase.

Note that both tetramer isomers, i.e. \( \text{Au}_4 \) and \( \text{Au}_4 \), are formed on graphene, depending on the actual reaction pathway.

Acknowledgments

This research was supported by the Swedish Energy Agency (Energimyndigheten) and the Swedish Research Council (Vetenskapsrådet). Computation time on the Neolith Cluster (Energimyndigheten) and the Swedish Research Council (SNIC). OE is grateful to the European Research Council (ERC) for support.

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