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Density functional study of the Au-intercalated graphene/Ni(111) surface

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We have studied the effect of Au intercalation on the atomic and electronic structure of the graphene/Ni(111) surface by using density functional theory calculations. Our calculations demonstrate that (1) Au atoms energetically favor interface intercalation over surface adsorption, (2) Au intercalation drastically changes the electronic structure of graphene/Ni(111) so that the graphene π bands almost recover the Dirac cone of ideal free-standing graphene, and (3) the Fermi edge locates closely at the Dirac point, indicating that the underlying Au/Ni(111) substrate is inert. The present theory confirms a recent experimental claim that graphene grown on Ni(111) and intercalated by one monolayer Au can be regarded as quasifree standing.

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I. INTRODUCTION

Since the discovery of its free-standing form in 2004,[1] graphene has been attracting great attention with its peculiar two-dimensional (2D) electronic structure leading to a wealth of exotic physics in electronic transport[2–5] and a variety of potential applications in spintronics and optoelectronics.[6–8] The π states of free-standing graphene feature an interesting band structure called the Dirac cone: the filled-state π and empty-state π^* bands touch at a single point (the Dirac point, E_D) on the Fermi level (E_F) and show linear dispersions near E_F. Underlying this interesting band structure is the unique atomic structure of graphene, a flat 2D honeycomb network of carbon atoms. In real situations, however, the ideal honeycomb network of graphene is susceptible to imperfections such as intrinsic ripples of the graphene plane[9] and charge-donating impurities[10] that would possibly disrupt the subtle Dirac cone band structure. Especially when adsorbed on solid surfaces, the electronic structure of graphene could be affected substantially by the interaction with substrates.[11] Therefore, it has been a fundamental issue to realize a flat graphene layer hardly interacting with surroundings and thus preserving its ideal band structure. Of great interest in this respect is a recent experimental claim for the realization of a metal-supported graphene displaying almost ideal electronic properties of free-standing graphene.[12]

In their angle-resolved photoelectron spectroscopy (ARPES) and scanning tunneling microscopy (STM) study, Varykhalov *et al.*[12] reported that graphene grown on the Ni(111) surface and intercalated by 1 monolayer (ML) Au displays an electronic band structure very close to that of free-standing graphene: the measured π band reproduces well the lower part of the Dirac cone with linear dispersions and the Fermi edge closely at E_D, apart from weak traces of interactions with the substrate appearing in the band dispersion at about 1 eV below E_F and in STM images where the honeycomb shape of ideal graphene was not yet fully recovered. This result is a more elaborated refinement of the findings in an earlier ARPES and electron-energy-loss spectroscopy study of Shikin *et al.*,[13] which was carried out some years before graphene has been spotlighted by the realization of its isolated form: they reported that the strong coupling between a graphene adlayer and the Ni(111) substrate becomes suppressed by intercalation of Au atoms, resulting in a saturation of Ni d bands and a separation of C π and Ni d states. As a matter of fact, the research on metal-supported graphene has a long history tracing back to an early recognition of graphene-layer formation on Pt surfaces via surface segregation of bulk carbon impurities in 1960s.[14] Recent boom of research on free-standing graphene renewed the interest in metal-graphene systems, and, based on extensive studies on a wide variety of metal substrates,[15] we are now at the stage of producing large high-quality graphene films on metal surfaces.[16,17] It is generally known, however, that graphene interacts rather strongly with metal substrates with the strength varying largely depending on the metal serving as support. Thus, in recent researches on metal-supported graphene, the crucial point has been how much the interaction with the substrates modifies the graphene properties, providing a useful database for using graphene as functional materials.[15,18,19] In this sense, the claim for such almost interaction-free graphene by Varykhalov *et al.*[12] is exceptional, indicating that the intercalated Au layer effectively decouples the otherwise strongly interacting graphene and Ni(111). Moreover, the graphene prepared in this way appears to be closer to ideal free-standing graphene than any other preparations on a solid substrate before, such as by mechanical exfoliation from graphite[1–3] or graphitization of SiC by thermal decomposition,[20–22] thus being referred to as quasifree standing.

The ground of the claim for a quasifree-standing graphene by Varykhalov *et al.*[12] is not yet solid because it is based only on the filled-state electronic-structure information. Further studies on the empty-state band structure are required for a complete picture for the Dirac cone, especially for the question for the presence of band gap or not. Moreover, the structural nature including the coverage of the intercalated Au layer is not known, and thus its role in the substrate passivation remains to be verified. First-principles theoretical investigations of both atomic and electronic structure of this graphene/Au/Ni(111) surface would be useful but it is not available yet. There have been density functional theory (DFT) calculations on graphene/Ni(111) (Refs. 18, 19, and 23–25) and graphene/Au(111) (Refs. 18 and 19) but their usefulness in getting insight into graphene/Au/Ni(111) is limited.

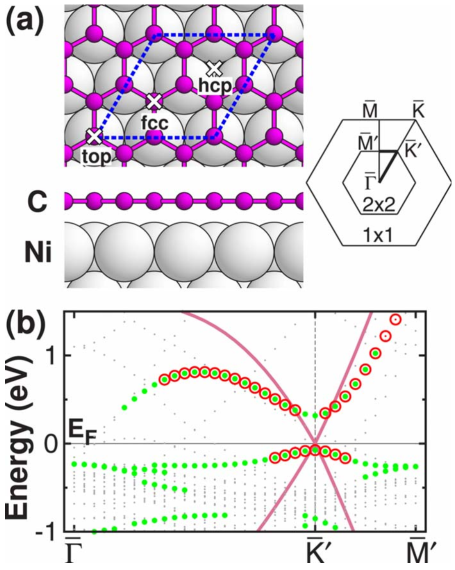

FIG. 1. (Color online) Atomic and electronic structure of the graphene/Ni(111) surface. (a) Equilibrium geometry. Large and small balls represent the Ni and C atoms, respectively. Dashed lines represent a (2×2) unit cell with three high-symmetry surface sites denoted by crosses. C atoms are all above the top and fcc hollow sites. The (2×2) surface Brillouin zone is shown. (b) Band structure of majority-spin states. Open (filled) circles represent the C-derived (Ni-derived) surface states which contain more than 25% (35%) of charge in the graphene (topmost Ni) layer. Solid lines represent the bands of free-standing graphene, given as a reference. The Fermi energy is set to zero.

In this paper, we investigate the atomic and electronic structure of Au-intercalated graphene/Ni(111) surfaces by using DFT calculations. Our DFT study demonstrates that (1) the intercalation of Au atoms is preferred energetically, (2) the Au intercalation makes the graphene layer close to ideal graphene both structurally and electronically, showing π bands with linear dispersions featuring the Dirac cone structure with a negligible band gap and the Fermi edge closely at E_D, and (3) the negligible graphene-substrate interaction is due to the interplay between the Au monolayer and the Ni(111) substrate. These results are in accord with the experimental findings, thus providing a theoretical support for the experimental claim that the graphene on Au/Ni(111) is quasifree standing.

II. METHOD

DFT calculations are performed using the Vienna *ab initio* simulation package.[26] We use the spin-polarized local-density approximation for electron-electron interactions[27] and the projector augmented wave method for electron-ion interactions.[28,29] We expand the electronic wave functions in a plane-wave basis set of 400 eV. The Ni(111) surface is simulated by a periodic slab geometry: each slab consists of five atomic layers and the vacuum spacing is about 16 Å. Graphene and Au-intercalation layers are incorporated on the top of the slab within a Ni(111)-(2×2) supercell, and Brillouin-zone integrations are done with a $4\times4\times1$ k-point mesh. All atoms but the bottom two Ni layers held fixed at bulk positions are relaxed until the residual force components are within 0.03 eV/Å. For bulk Ni, the calculated lattice constant 3.43 Å, bulk modulus 2.51 Mbar, cohesive energy 5.97 eV, and magnetic moment 0.57 μ_B compare well with the experimental values 3.52 Å, 1.86 Mbar, 4.44 eV, and 0.61 μ_B, respectively.[30] For isolated graphene, the calculated hexagonal lattice constant is 2.45 Å, which is close to the lattice constant (2.42 Å) of the Ni(111) surface with a mismatch of 1.2%. In the present supercell calculations, graphene is set to lattice match the Ni(111) surface: the deformation energy of graphene caused by the lattice matching was found to be less than 0.01 eV/C atom. We found that the reverse matching procedure, in which the Ni(111) surface is set to lattice match the graphene, produces no noticeable difference in the calculated graphene π bands of the graphene/Au/Ni(111) surface. Such a negligible effect of the small lattice mismatch on the electronic structure was also reported in a recent calculation for the Ni/graphite/Ni(111) junction system.[31] The used slab thickness, k points, and plane-wave basis were found to produce sufficiently converged interface properties for the graphene/Ni(111) surface: the graphene adsorption energies and the graphene-substrate distances converge well within 0.01 eV and 0.01 Å, respectively.

III. RESULTS

We first discuss the structural and electronic properties of graphene grown on Ni(111) as a reference system. Figure 1(a) shows a structural model for the graphene/Ni(111) system, where the C atoms of graphene are aligned on the top and fcc sites of Ni(111). This model, being referred to as "top-fcc," was proposed in a low-energy electron-diffraction study of Gamo *et al.*[32] and has been supported by several DFT studies as the most stable adsorption configuration.[18,23–25] Our calculations for the top-fcc model are summarized in Table I. The graphene adsorption energy of 0.09 eV/C atom and the separation of 2.08 Å from Ni(111) are in good agreement with 0.1–0.2 eV and 2.0–2.1 Å reported in previous DFT studies.[18,23–25] The Ni(111) substrate does not induce a noticeable breaking of the A-B structural symmetry of graphene with a negligible rumpling of 0.01 Å in the graphene layer. There is, however, a strong electronic coupling between graphene and Ni(111), which is evident from a disruption of the graphene π bands near E_F as seen in the majority-spin band structure shown in Fig. 1(b). The π bands undergo significant changes: the Dirac point disappears with a gap opening of ~0.4 eV at $\bar{K}'$, and the band dispersions are not linear any longer through a strong hybridization with the top-layer Ni d states at about 0.1–0.3 eV below E_F and 0.4–1.0 eV above E_F. The minority-spin band structure (not shown) is similar to that of the majority-spin states except for upward shifts of 0.4–0.6 eV of both graphene π bands and Ni-derived bands. The graphene grown on Ni(111) is thus far from free-standing graphene.

Let us examine the nature and effects of Au intercalation into the graphene/Ni(111) system. Although its effect on the

TABLE I. Energetics and structural details of the graphene/Ni(111) and graphene/Au/Ni(111) surfaces. E (eV) represents the adsorption energy, defined as the energy gain per C (Au) atom relative to free-standing graphene (free Au atom). Δz (Å) represents the rumpling in the given atomic layer (for Ni, the topmost layer), taken as the maximum value of vertical separations among atoms. h (Å) represents their interlayer spacing. Here, the layer height is averaged over all atoms in the layer.

Systems	E_{C}	E_{Au}	Δz_{C}	Δz_{Au}	Δz_{Ni}	$h_{\text{C-Ni}}$	$h_{\text{C-Au}}$	$h_{\text{Au-Ni}}$
Graphene/Ni(111)	0.09		0.01		0	2.08		
Graphene/Au/Ni(111)	0.03	4.45	0.01	0.22	0.05		3.33	2.32

electronic structure of graphene was reported in the previous ARPES study,[12] the coverage and configuration of the intercalated Au atoms are not known but a suggestion that they form a single intercalation layer between the graphene and the Ni(111) substrate. Here, we introduce a simple structural model for the Au-intercalated graphene/Ni(111) surface (see Fig. 2) based on a simplification that Au atoms form a 2D hexagonal layer in commensuration with the Ni(111)-(2 × 2) substrate. In this model, three Au atoms are adsorbed on the Ni top, fcc, and hcp sites in a (2 × 2) unit cell. The coverage of Au corresponds to 0.75 ML (here, 1 ML refers to one Au atom per Ni), and it was found that the intercalation energy per Au atom becomes maximum at this coverage, which is more stable by 0.7–1.4 eV than hexagonal layers with Au coverages of 0.25, 0.33, and 1.0 ML and is also more stable by 0.4–0.9 eV than another possible honeycomb layers with Au coverages of 0.5 and 0.66 ML. In addition, the Au-Au distance of 2.80 Å in our 0.75 ML hexagonal-layer model compares well either with that of the Au(111) surface layers (2.87 Å) or with that of the free-standing 2D hexagonal Au layer (2.63 Å). While there is no structural information about the intercalated Au layer, there was an early STM report that Au atoms adsorbed (*not intercalated*) on Ni(111) form a (9 × 9) moiré overlayer structure.[33] We find that the reported Au-Au distance in the Au/Ni(111)-(9 × 9) structure (2.80 ± 0.10 Å) is in perfect agreement with 2.80 Å in our graphene/Au/Ni(111)-(2 × 2) surface. Thus, the present intercalation model is not only computationally feasible but also physically sound. It was also found in our calculations that the model shown in Fig. 2 is the lowest-energy configuration with respect to relative lateral positions of the graphene, Au, and Ni layers. That is, the configuration is stable with respect to surface-parallel displacements of the Au monolayer relative to the Ni(111) substrate and also with respect to surface-parallel displacements of the graphene layer relative to the Au monolayer.

Table I summarizes the features of the optimized structure for the Au-intercalation model given in Fig. 2. The Au-intercalation energy, defined as the energy gain obtained by intercalation relative to free atom, is 4.45 eV/atom, which is larger than either the adsorption energy on the graphene/Ni(111) surface (3.80 eV) or the bulk cohesive energy of fcc Au (4.28 eV), energetically justifying the preference of the intercalation over the surface overlayer or island formation. The graphene layer is found to interact very weakly with the substrate after the Au intercalation: a negligible adsorption energy of graphene (0.03 eV/C atom), a small rumpling in the graphene layer (0.01 Å), and a large graphene-Au layer distance (3.33 Å), which are all indicative of a substantial weakening of the electronic coupling between graphene and the substrate.

Figure 3(a) shows the majority-spin band structure of the graphene/Au/Ni(111) surface. We find that the graphene π bands are almost the same as those of free-standing graphene. It is clear that the Au intercalation fully saturates the reactive Ni d bands, not allowing C-Ni hybridizations, as was reported in an early Au-intercalation experiment.[13] As a result, unlike the graphene/Ni(111) surface displaying disrupted π bands, the graphene/Au/Ni(111) surface recovers the characteristic Dirac cone with E_{D} closely at the Fermi edge, apart from traces of weak interactions between graphene and the Au/Ni(111) substrate such as a gap opening of 0.02 eV at $\bar{\mathrm{K}}'$, a disparity of 0.07 eV between E_{F} and E_{D}, and partial decreases in carbon character in the π bands. The minority-spin band structure (not shown) also displays a

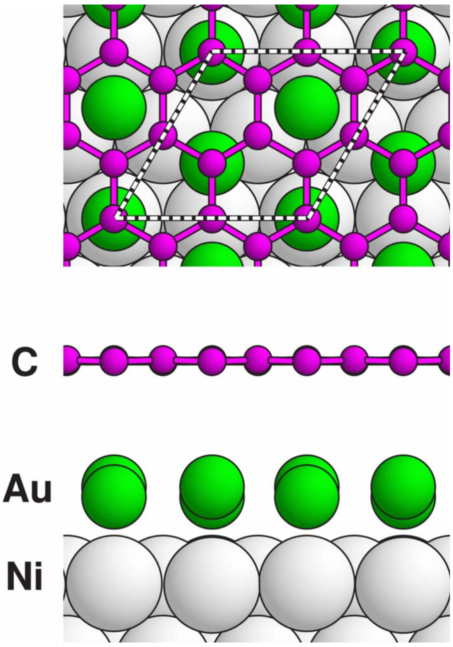

FIG. 2. (Color online) Structural model for the graphene/Au/Ni(111) surface. Large, medium, and small balls represent Ni, Au, and C atoms, respectively. Here, the sizes of atoms are not proportional to their atomic radii but chosen for a better presentation of the geometry. Dashed lines represent a (2 × 2) unit cell. Au atoms occupy the top, fcc, and hcp sites of Ni(111), and the Au coverage corresponds to 0.75 ML. C atoms are above the top and fcc sites of Ni(111).

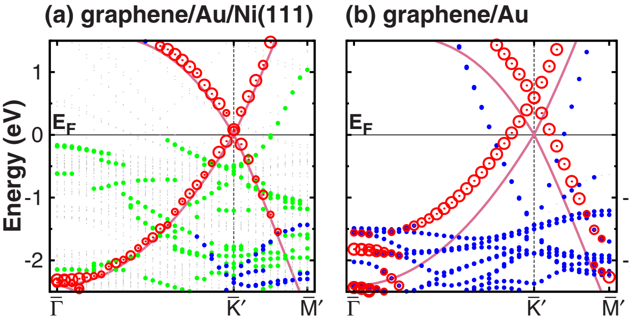

FIG. 3. (Color online) Band structures of (a) graphene/Au/Ni(111) and (b) graphene/Au. In (a), the bands of majority-spin states are shown. In (b), the bands are spin unpolarized and the underlying structure represents the *frozen* graphene/Au/Ni(111) surface with the Ni(111) substrate removed. Large, medium, and small open circles represent C-derived surface states which contain more than 75%, 50%, and 25% of charge in graphene, respectively. Gray (black) filled circles represent Ni-derived (Au-derived) surface states which contain more than 35% of charge in the topmost Ni (Au) layer. Solid lines represent the bands of free-standing graphene.

similar graphene π bands but Ni-derived bands with 0.4–0.6 eV upward shifts from the majority-spin bands. The present calculations are in good agreement with the ARPES study of Varykhalov *et al.*,[12] thus theoretically confirming their claim that the graphene in this system can be regarded as a quasifree-standing graphene.

It is interesting to note that the shape of graphene π bands is sensitive to the amount of intercalated Au atoms. Figure 4 shows the band gap and the relative position of the Dirac point as a function of the Au coverage. At a low coverage of 0.33 ML, the recovery of the Dirac cone shape is still incomplete with a band gap of 0.20 eV and a large shift of the Dirac point by -0.48 eV. As the Au coverage increases, the band gap decreases to zero, indicating a vanishing electronic hybridization between graphene and the Au/Ni(111) substrate, and the Dirac point shifts upward, indicating a more charge transfer from graphene to the substrate for a higher Au coverage. It is thus apparent that the Au-induced recovery of the quasifree-standing graphene π bands requires certain optimal Au coverages. Figure 4 suggests that the quasifree-standing graphene layer is optimally accessible at 0.66–0.75 ML.

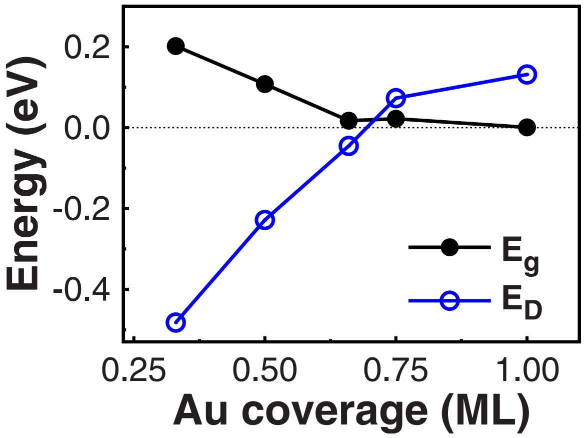

FIG. 4. (Color online) Band gap (E_g) and Dirac point (E_D) relative to E_F in the graphene π bands as a function of the Au coverage. Here, the Dirac point is defined as the midpoint of the band gap. All data were given for the majority-spin band structure.

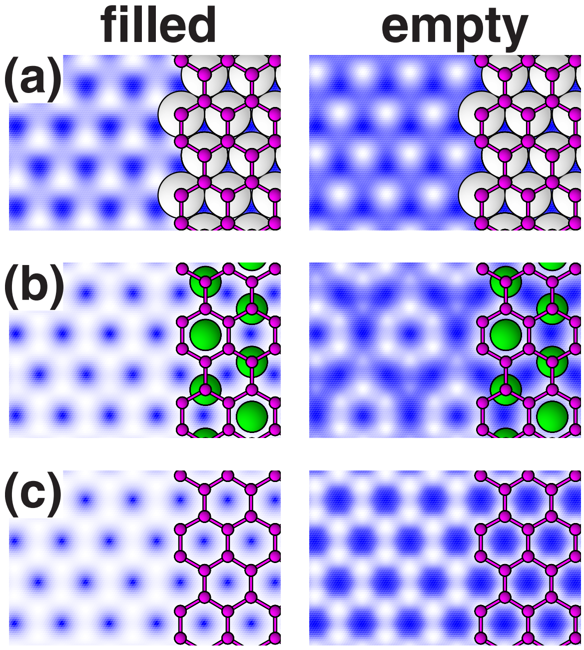

FIG. 5. (Color online) Simulated constant-current STM images: (a) graphene/Ni(111), (b) graphene/Au/Ni(111), and (c) free-standing graphene. The filled-state images were obtained by integrating $\rho(r,E)$ from $E_F-2.0$ eV to E_F, and the empty-state images from E_F to $E_F+2.0$ eV. The images represent the surface of constant density with $\rho=1\times10^{-3}$ $e/\text{Å}^3$.

In order to get an insight into the inertness of the Au/Ni(111) substrate, we examined the band structure of a graphene/Au system [see Fig. 3(b)]. This model system represents the frozen graphene/Au configuration remaining after removing the Ni(111) substrate from the equilibrium graphene/Au/Ni(111) surface. It is shown that the interaction between graphene and the Au monolayer is not strong enough to disrupt the π band structure, but the π bands undergo a uniform upward shift of ~0.5 eV, indicating a charge transfer from graphene to the Au layer. This result is in line with a recent DFT study for graphene on the Au(111) surface: in their six-layer slab representation of the Au(111) surface, Khomyakov *et al.*[19] found that the Dirac cone shifts upward by ~0.2 eV due to a charge transfer from graphene to Au(111). The larger shift in the present study can be attributed to the higher reactiveness of the Au monolayer than the Au(111) surface. Despite a charge transfer from graphene, the Au *d* bands still remain at relatively high energies by about 0.5–1.0 eV with some newly emerging bands that disperse almost linearly over E_F. This rather reactive Au monolayer is passivated by the underlying Ni substrate in the graphene/Au/Ni(111) system. Thus, the inertness of the Au/Ni(111) substrate results not solely from the Au layer but from an interplay between Au monolayer and Ni(111).

Varykhalov *et al.*[12] reported in their ARPES study that the measured π bands deviate a little from those of ideal graphene, resulting in a kink in the linear dispersion at binding energies of ~ 0.95 eV. The origin of the kink was speculated as possibly due to an electron-mass renormalization by graphene-Au interaction. In our band calculations, however, such a change in band dispersion is not evident as seen in Fig. 3(a): the π band just follows the dispersion of ideal graphene down to ~ 1.5 eV below E_F. Nonetheless, it is worth mentioning that, as seen in Fig. 3(a), the filled π bands appear to have noticeably weaker carbon characters compared to the empty π bands, in contrast to the graphene/Au system showing almost the same carbon characters over the whole π bands [see Fig. 3(b)]. In graphene/Au/Ni(111), while Au d states are dispersed at about 1.5 eV below E_F, Ni d states are dispersed at a wide range of energies below E_F in overlap with the π bands. Thus, the graphene π states are likely to resonantly mix with Ni d states, which possibly broadens the spectrum of the π bands in ARPES measurements, being a cause of some inaccuracy in spectral analysis of quasiparticle energies.

Figure 5 shows simulated STM images of graphene in three different configurations. While graphene/Ni(111) shows hexagonal images indicating a break of the A-B symmetry of graphene, graphene/Au/Ni(111) features honeycomb images at both biases, which compare well with the ideal honeycomb images of free-standing graphene. We notice a weak rippling in the empty-state honeycomb image of graphene/Au/Ni(111), which clearly matches the (2×2) periodic arrangement of underlying Au atoms, but it is likely in the image that the A-B symmetry of graphene is preserved on the Au/Ni(111) substrate. In their STM study, Varykhalov *et al.*[12] reported that Au intercalation affects the STM image of graphene/Ni(111), but the images of graphene/Au/Ni(111) still remain predominantly hexagonal. That is, unlike our simulations, this observation implies that the Au-induced recovery of the A-B symmetry of graphene is incomplete. This incomplete recovery of the ideal honeycomb image remains a question because it is not in line with the Au-induced full recovery of the Dirac cone feature in the ARPES measurement.[12] In view of our findings of no strong graphene-substrate interaction and no break of the A-B symmetry, we believe that graphene/Au/Ni(111) has a quasifree-standing nature, but an access to rather ideal honeycomb images may be subject to experimental conditions: it could be readily affected by lattice imperfections such as intrinsic nanoscale ripples of the graphene layer and/or irregular arrangements of the intercalated Au atoms.

IV. SUMMARY

In summary, we have shown by DFT calculations that graphene grown on Ni(111) and intercalated by Au displays electronic features similar to those of free-standing graphene. This study confirms the recent experimental conclusion that the graphene/Au/Ni(111) surface can represent a quasifree-standing graphene layer, and the calculated structural and electronic details give insight into the graphene/Au/Ni(111) system and applications.

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