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Au_nPt_n clusters adsorbed on graphene studied by first-principles calculations

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In this work, we present the adsorption of Au_nPt_n clusters on graphene surface by using the density-functional theory within localized density approximation (LDA), and generalized gradient approximation (GGA). We calculate the adsorption energy, geometries, band structure, charge differences, and magnetization up to $n=3$. We observe that graphene can be metallic or semiconducting depending on number of Au and Pt atoms in the cluster and the charge transfer between cluster and the graphene. LDA and GGA results are given and compared for all cases. We find that Au_3Pt_3 and AuPt graphene can have half metallic properties within GGA.

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I. INTRODUCTION

Graphene is becoming the center of increasing attention because of its unusual transport and electronic properties.[1] It is the two-dimensional (2D) form of carbon densely packed in a honeycomb crystal lattice. Graphene is produced and isolated, at room temperature rather easily.[2–4] It is found that it has high structural quality[2,5–9] and electrons can travel in it thousands of interatomic distances without any scattering.[2,5,9] Graphene is a conductor with remarkable electronic properties.[6,7,10–12] It is found that epitaxial graphene has good properties for coherent nanoscale electronics applications.[13] Graphene is therefore finding application in areas, such as hydrogen storage,[5,14–20] gas sensors,[21–23] and spin-valve devices.[21,24,25]

There are several investigations on metal atom adsorption and impurities on graphene.[26–32] Metal-graphene interface is important in understanding the electronic transport through a graphene sheet.[26,33–35]

The research on interaction between adatoms, molecules, and graphene are developing rapidly.[36–45] This is important in controlling the modification of graphene.[36]

H. Sevincli *et al.*,[42] investigated electronic and magnetic properties of graphene and graphene nanoribbons functionalized by three-dimensional (3D) transition-metal (TM) atoms. They found that binding energies of adsorbed TM atom depends on their species and coverage density. Graphene is found to become a magnetic metal after the adsorption of TM atoms.

K. T. Chan *et al.*,[36] investigated the adsorption of 12 different metal adatoms on graphene by using density-functional theory (DFT) with the generalized gradient approximation (GGA). They investigated transition, noble, and group IV metals and found that the calculations are in agreement with covalent bonding, and strong hybridization between adatom and graphene.

The problem of gold atoms and dimers on the surface of graphene is investigated by R. Varns and P. Strange[37] using DFT. They found that the gold-gold interaction is stronger than the gold-graphene interaction and the stable configuration of single gold atom is when Au is directly above a carbon atom. The dimer, on the other hand, is directly above a carbon-carbon bond.

G. M. Wang *et al.*,[46] have investigated the interaction of deposited gold adatoms and dimers with multilayer relaxed graphite surfaces by using DFT with numerical orbitals and a relativistic core pseudopotential.

The adsorption of single Pt atom and Pt clusters on graphene and carbon nanotube is investigated by D. H. Chi *et al.*,[47] by using DFT within GGA. They found that the Pt-Pt bond length and the charge transfer from Pt clusters to the nanotube change as a function of cluster size. The catalytic activities of Pt cluster adsorbed on the nanotube are found to be better than that of the free cluster.

Y. Okamoto[48] investigated Pt_{13} or Au_{13} cluster on graphene sheets and flakes by using DFT. It is found that the stability of the interface increases by introducing five or seven member rings into the graphene.

The cluster-graphene interface can be used to test our understanding of the fabrication of electronic devices.[36,37,49]

We are especially interested in Au and Pt. Au has poorer catalytic properties than Pt. Au-Pt clusters show different catalytic and magnetic properties.[50,51] To the best of our knowledge, there is no work on interaction between Au_nPt_n clusters and graphene surface up to $n=3$. Catalytic activity increases as the cluster size is getting smaller. This is why we calculate the adsorption of Au_nPt_n on graphene. In this work, adsorption energy, band structure, charge transfers, are investigated by using DFT within LDA and GGA. We have also included spin polarization in our calculation. We observe that Au_nPt_n adsorption on graphene influences the electronic structure drastically.

This paper is organized as follows. In Sec. II, the computational method is described briefly. In Sec. III, our results are given. Finally, the conclusion is given in Sec. IV.

II. COMPUTATIONAL DETAILS

The total energy and electronic structure calculations are performed within DFT pseudo potential approach using the plane-wave-self-consistent field package (PWSCF).[52] The kinetic energy cutoff of plane waves is taken as 612 eV. We have used the ultrasoft pseudopotentials within GGA [Perdew-Burke-Ernzerhof exchange-correlation (xc)] and LDA.[53–56] The Brillouin-zone (BZ) sampling is done by using $9\times9\times1$ grid of Monkhorst-Pack[57] special k points and using a Methfessel and Paxton method.[58]

The structures investigated include a single graphene layer with (4×4) unit cell to minimize the interaction between clusters on repeating slabs and a Au_nPt_n cluster adsorbed at different sites on the surface. First, we obtain the stable configurations of Au_nPt_n clusters in vacuum. We find similar structures for Au_nPt_n within GGA and LDA. Then, the adsorbate+graphene system is relaxed to equilibrium. The Hellmann-Feynman forces and conventional minimization techniques are used to determine the equilibrium structures. Hellmann-Feynman forces after the ionic relaxation, are smaller than 0.001 eV/Å.

The adsorption energy is calculated as

$$E_a = -(E_{gc} - E_g - E_c) \quad (1)$$

where, E_{gc}, E_g, and E_c are energies of graphene cluster, the free-standing graphene and the cluster, respectively. Convergence criteria of total energy between two self-consistent field steps is taken to be 10^{-6} eV.

The charge difference is defined as:

$$\Delta\rho = \rho_{\text{total}} - \rho_{\text{graphene}} - \rho_{\text{cluster}} \quad (2)$$

where ρ_{total}, ρ_{graphene}, and ρ_{cluster} are the total charge on Au_nPt_n graphene, graphene and the cluster or atom, respectively. We have also included the spin polarization into our calculations.

We have investigated the charge transfer by using the Löwdin analysis. It is claimed that there are two charge-transfer mechanisms. First, it is the relative position of the HOMO and LUMO of the adsorbate with respect to Dirac point in pure graphene that determines the direction of charge transfer for paramagnetic adsorbates.[22,44,59] O. Leenaerts *et al.*,[22] have shown that if the highest occupied molecular orbital (HOMO) is above the Dirac point, there will be charge transfer to graphene. If the lowest unoccupied molecular orbital (LUMO) is bellow the Dirac point, there will be charge transfer to substrate. Second, the charge transfer could also be determined by using hybridization of the HOMO and LUMO with graphene orbitals. This orbital mixing with graphene orbitals results in effective charge transfer and it occurs for all adsorbates.[22,44,59]

There are some computational problems in the calculation of charge transfer by DFT.[44,59] O. Leenarts *et al.*,[44,59] has shown that the charge transfer between paramagnetic molecules and graphene layer may crucially depend on the size of the supercell used in the calculation.

III. RESULTS

We consider three possible sites for each adsorbate, namely, the top site (T) which is directly above a C atom, the bridge site (B) at the midpoint of a C-C bond and hollow site (H) on the center of the hexagon.

A. Au and Pt on graphene

We have done a DFT study of Au and Pt adsorption on graphene, as test cases. We find that wherever we start, Au atom always end up at the T site on graphene within LDA as seen in Fig. 1(a). Pt atom, on the other hand, prefers to stay on the B site as seen in Figs. 1(b) and 2(b) within LDA and GGA. These results are in agreement with available literature.[36,37,47]

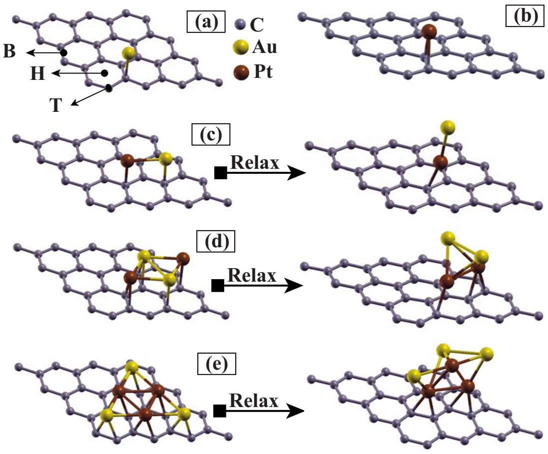


FIG. 1. (Color online) The Au_nPt_n-graphene structures within LDA. B: bridge site, H: hollow site, and T: top site (a) the stable configuration of Au graphene. (b) The stable configuration of Pt graphene. (c) Initial (left) and final (right) configurations of AuPt graphene. (d) Initial (left) and final (right) configurations of Au_2Pt_2 graphene. (e) Initial (left) and final (right) configurations of Au_3Pt_3 graphene.

The calculated binding energies, bond lengths, and the charge transfer from the adsorbate to graphene are given in Table. I

As can be seen in Table I. LDA binding energies are consistently larger than GGA ones. The corresponding bond lengths are therefore shorter for LDA. These results are in

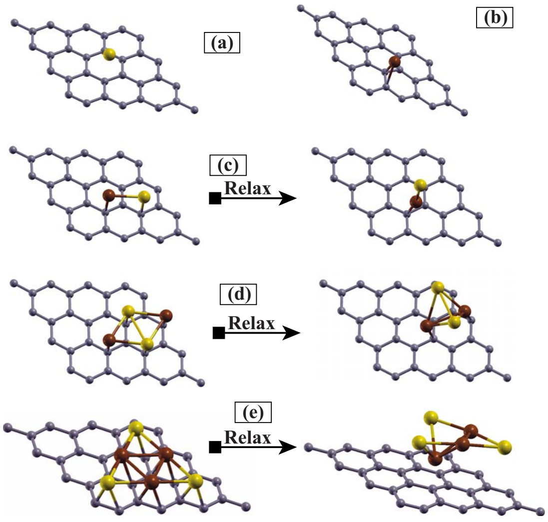


FIG. 2. (Color online) The Au_nPt_n-graphene structures within GGA. (a) The stable configuration of Au graphene.(b) The stable configuration of Pt graphene. (c) Initial (left) and final (right) configurations of AuPt graphene. (d) Initial (left) and final (right) configurations of Au_2Pt_2 graphene. (e) Initial (left) and final (right) configurations of Au_3Pt_3 graphene. (f) Initial (left) and final (right) configurations of Au_3Pt_3 graphene.

TABLE I. Au and Pt on graphene: the bond length (d) the adsorption energy (E_a) and the total charge transfer from the graphene to Au and from Pt to graphene for the most stable relaxed position calculated by using LDA and GGA.

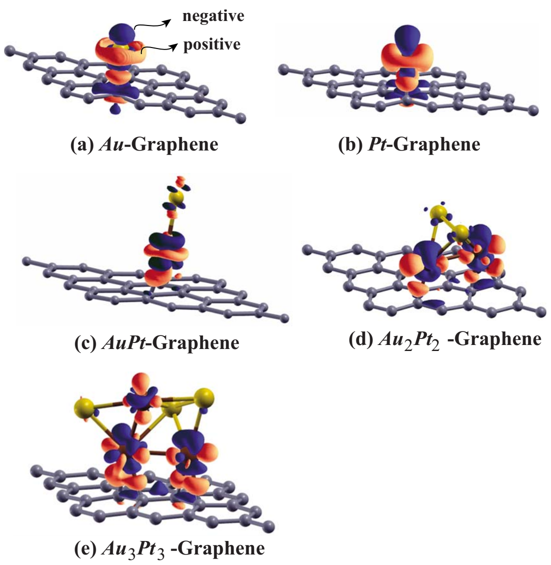
Adsorbate/xc	Position	d (Å)	E_a (eV)	Total charge transfer (e)
Au/LDA	T	2.20	0.98	−0.19
Au/GGA	B	3.64	0.14	−0.20
Pt/LDA	B	2.06	2.74	0.14
Pt/GGA	B	2.10	2.17	0.08

agreement with the available literature.[37,46] Pt atom has higher adsorption energy than Au. The reason that Pt atom has large adsorption energy may be due the strong hybridization between Pt and adjacent C atoms.[47] As seen in Fig. 2(a) there is no chemisorption between Au and C atoms for Au graphene within GGA. The initial configuration is given as B site but after the interaction we observe that Au atom is moving up to a higher position as seen in Fig. 2(a).

The charge differences are also as expected. There is a charge transfer from graphene to gold, whereas Pt is found to be a donor, transferring charge to the graphene in agreement with available literature.[37,46,47] The charge transfer is shown in Figs. 3 and 4 in more detail. The negative regions in this figure correspond to decrease of charge from the vicinity. The spin-polarized calculations yield lower binding energy for Au in LDA (0.50 eV). Total magnetization of the Pt graphene (Au graphene) the system is found as zero μ_B/cell ($0.82\mu_B$/cell) for GGA.

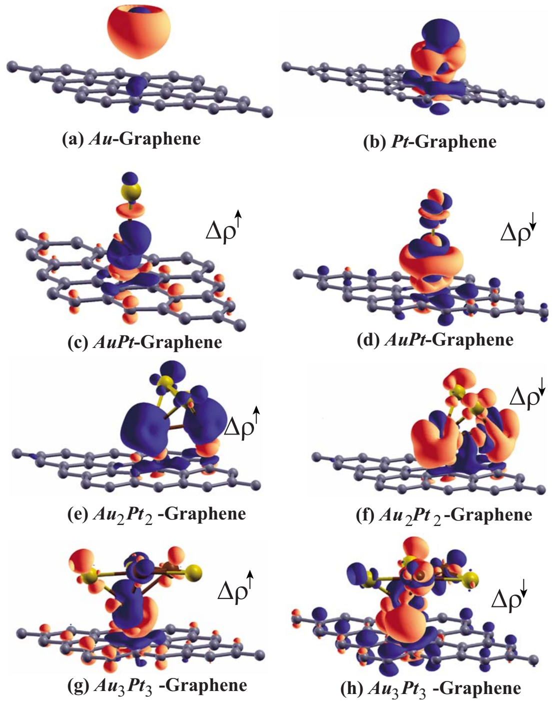
B. AuPt on graphene

The calculated binding energies, bond lengths, charge transfers, and the magnetization of the adsorbed AuPt are given in Table II. There is a charge transfer from graphene to AuPt. Excess charge is more localized around the Au atom (−0.26e). The accompanying magnetization to the charge transfer is calculated as $0.95\mu_B$/cell.



(a) ***Au*-Graphene** (b) ***Pt*-Graphene** (c) ***AuPt*-Graphene** (d) ***Au_2Pt_2* -Graphene** (e) ***Au_3Pt_3* -Graphene**

FIG. 3. (Color online) The charge differences between adsorbates and the graphene within LDA. The negative (positive) regions correspond to decrease (increase) in charge.



(a) ***Au*-Graphene** (b) ***Pt*-Graphene** (c) ***AuPt*-Graphene** (d) ***AuPt*-Graphene** (e) ***Au_2Pt_2* -Graphene** (f) ***Au_2Pt_2* -Graphene** (g) ***Au_3Pt_3* -Graphene** (h) ***Au_3Pt_3* -Graphene**

FIG. 4. (Color online) The charge differences between adsorbates and the graphene within GGA. The negative (positive) regions correspond to decrease (increase) in charge. The charge differences are decomposed into their spin components.

The adsorption energy (bond length) is 1.96 eV, (2.12 Å) in LDA, 1.14 eV, (2.17 Å) in GGA.

The starting position of AuPt cluster on graphene surface is taken as the T site. The relaxed position in LDA (GGA) is shown in Fig. 1(c) [Fig. 2(c)]. As can be seen from these figures, AuPt cluster is shifted to a position in between T and B sites.

The charge differences for AuPt graphene calculated within LDA is shown in Fig. 3(c). It is clearly seen that AuPt receives some charge from graphene which is in line with our total charge-transfer results.

The spin-polarized GGA results are shown in Figs. 4(c) and 4(d) for spin-up and spin-down states, respectively. These are similar to our LDA charge difference results.

There is also a charge transfer from Pt to Au, as can easily be seen in Figs. 4(c) and 4(d).

TABLE II. AuPt on graphene: the bond length (d) the adsorption energy (E_a) and the total charge transfer from the graphene to AuPt for the most stable relaxed position calculated by using LDA and GGA.

Adsorbate/xc	Position	d (Å)	E_a (eV)	Total charge transfer (e)
AuPt/LDA	T/B	2.12	1.96	−0.08
AuPt/GGA	T/B	2.17	1.14	−0.003

TABLE III. Au_2Pt_2 on graphene: the bond length (d) the adsorption energy (E_a) and the total charge transfer from the Au_2Pt_2 to graphene for the most stable relaxed position calculated by using LDA and GGA.

Adsorbate/xc	Position	d (Å)	E_a (eV)	Total charge transfer (e)
Au_2Pt_2/LDA	T/B	2.15	3.20	0.31
Au_2Pt_2/GGA	T/B	2.17	1.81	0.08

C. Au_2Pt_2 on graphene

Our results for Au_2Pt_2 adsorbed on graphene are given in Table III. For this case, charge is transferred from Au_2Pt_2 to the graphene. Au atom receive less charge [−0.18(e)] than given by the Pt atoms (+0.49e).

The relaxed position of Au_2Pt_2 within LDA (GGA) is given in Fig. 1(d) [Fig. 2(d)]. The structure of cluster is modified from planar to 3D and shifted from T site (GGA) [B site (LDA)] to somewhere in between T and B sites.

The charge differences for Au_2Pt_2 graphene calculated within LDA is shown in Fig. 3(d). There is a charge transfer from Pt to graphene and also between interacting orbitals of Au and Pt. The spin-polarized GGA results are shown in Figs. 4(e) and 4(f) for spin-up and spin-down states, respectively. These are similar to our LDA charge difference results.

Total magnetization of the system is found as $0.01\mu_B$/cell.

D. Au_3Pt_3 on graphene

The calculated quantities for Au_3Pt_3 are given in Table IV. The charge is transferred form graphene to Au_3Pt_3. Total magnetization of the system is found as $2.95\mu_B$/cell.

The relaxed position of Au_3Pt_3 within LDA (GGA) is given in Fig. 1(e) [Fig. 2(e)]. After the relaxation, the structure of cluster is modified from planar to 3D as seen in Figs. 1(e) and 2(e). GGA adsorption energy is much smaller than that in LDA and there is no chemical binding to the surface within GGA.

The charge transfer is similar to the case of AuPt as can be seen in Fig. 3(e) and Figs. 4(g) and 4(h).

The interaction properties of the graphene and adsorbate that is summarized up to now may also be seen in the calculated band structures. LDA and GGA results are given in Figs. 5 and 6, respectively. We observe that the band structure of bare graphene[5,14,42] and the charge-transfer results for all the cases studied are in agreement with the available literature.[37,46,47] Charge transfer from graphene to cluster or atoms may make graphene metallic. We observe that there is

TABLE IV. Au_3Pt_3 on graphene: the bond length (d) the adsorption energy (E_a) the total charge transfer from the graphene to Au_3Pt_3 for the most stable relaxed position calculated by using LDA and GGA.

Adsorbate/xc	Position	d (Å)	E_a (eV)	Total charge transfer (e)
Au_3Pt_3/LDA	T/B	2.15(av.)	3.61	−0.25
Au_3Pt_3/GGA	T/B	3.89(av.)	0.54	−0.05

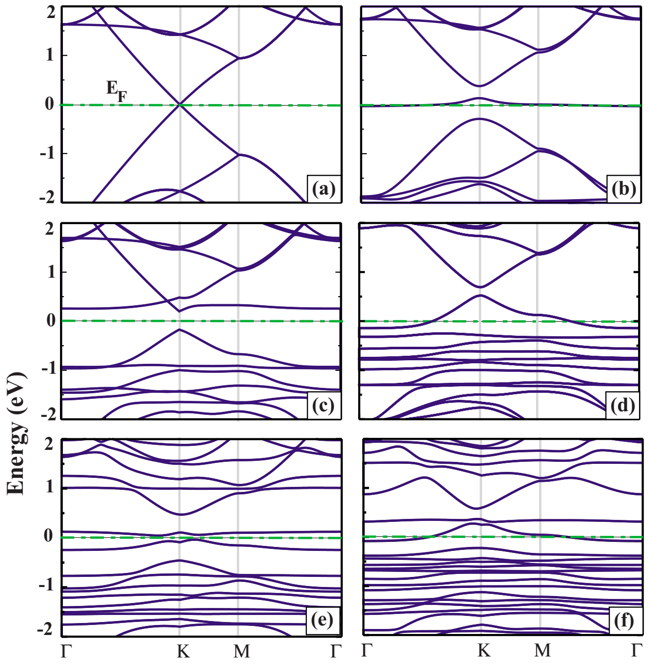


FIG. 5. (Color online) The energy band structures within LDA. (Note that spin-up and spin-down bands overlap exactly in LDA). (a) Graphene. (b) Au graphene. (c) Pt graphene. (d) AuPt graphene. (e) Au_2Pt_2 graphene. (f) Au_3Pt_3 graphene.

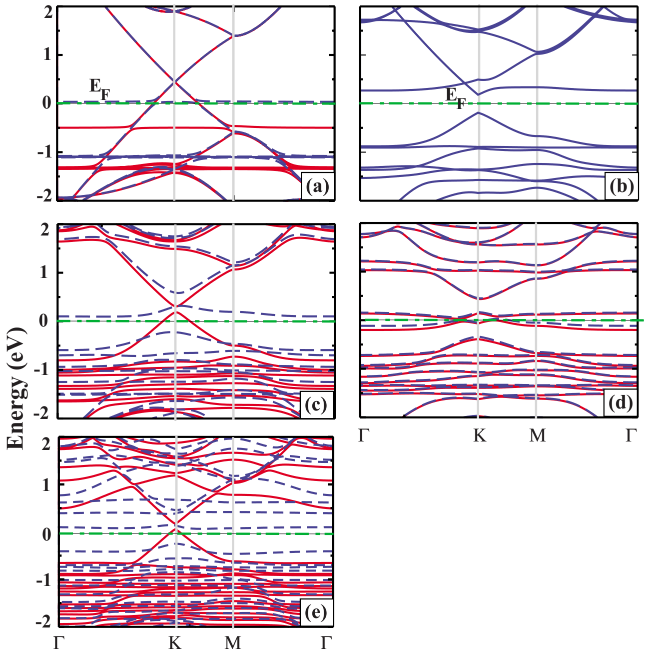


FIG. 6. (Color online) The energy band structures within GGA (a) Au graphene. (b) Pt graphene (Note that spin-up and spin-down bands overlap exactly). (c) AuPt graphene. (d) Au_2Pt_2 graphene. (e) Au_3Pt_3 graphene (red line; spin-up bands. Blue-dashed line; spin-down bands).

a charge transfer from graphene to the adsorbed entity for Au, AuPt, and Au_3Pt_3. These results are in agreement with the available literature.[37,46] We observe that GGA and LDA correctly predicts the direction of charge transfer between adsorbate and the graphene.

The bands are also decomposed into contributions by different spins. We find, for AuPt and Au_3Pt_3 graphene within GGA, that while spin-up bands show metallic properties and spin-down bands show semiconducting properties. Thus, the corresponding systems show half metallic properties.

We note that the band structures around the Dirac point are affected by cluster adsorption on graphene. The presence of adsorbates results in flat, molecularlike levels around the Fermi energy. Usually, a small band gap opens. For Au, AuPt, and Au_3Pt_3, electrons are transferred from the upper valance band of the graphene to the adsorbate so that the Fermi energy intersects the valence band. For Pt and Au_2Pt_2, electrons are given to the graphene which shifts the Fermi energy into the conduction band. The linear dispersion around the Fermi level seems to survive in cases Au, AuPt, and Au_2Pt_2 on graphene. This is equivalent to doping the graphene with donors and acceptors.

IV. CONCLUSION

We have shown that the presence of Au_nPt_n clusters on graphene changes the electronic properties in an important way by using the first-principles DFT-LDA/GGA method. In almost all cases we find moderate adsorption energies corresponding to physisorption.

We find a downward shift of the Fermi level relative the Dirac point for Au, AuPt, and Au_3Pt_3 on graphene and upward shift for Au_2Pt_2 graphene and Pt graphene on graphene.

We find, for AuPt and Au_3Pt_3 graphene within GGA, that they show half metallic properties.

Although the band gaps are problematic in DFT, the trends may come out to be correct. The band gap turns out to be tunable by the adsorption of Au_nPt_n clusters. This changes the electronic properties of graphene which is important in applications such as gas sensors and electronic devices.

DFT is rather efficient in finding different geometries. But finding different energies and bond lengths in LDA and GGA signals that energy results are questionable. The real values may be somewhere between the LDA and GGA results. LDA and GGA are also known to be problematic for charge-transfer studies.[60–62] This problem can only be handled if one goes beyond the simple first-order approach.[63]

Molecular dynamics and Monte Carlo simulation approaches are also used to study the cluster-substrate interaction.[64–66] There are successful interatomic potentials, such as the quantum Sutton-Chen potentials[64] that enable researchers to investigate dynamic processes at the surface. The work of D. H. Seo *et al.*,[64] on the relative strength of interatomic bonding of Au and Pt on carbon nanotubes is in agreement with our work.

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