GOLD ATOM ADSORBED ON GRAPHENE SUPERCELL MODEL

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We performed density functional study for gold adatom on the surface of pristine and graphene supercells with a vacancy. The effect of the adsorption of Au adatom on pristine and defective graphene on the value of the magnetic moment is calculated. The interactions between carbon and gold atom cause a band gap weak opening for the graphene. Using the calculations of the adsorption energy in these structures, its dependence on the deformation of the graphene cell is investigated.

Keywords: graphene supercells, vacancy, Au adsorbed on graphene, local spin density approximation.
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INTRODUCTION

Recently, graphene [1,2] has been extensively investigated by physicists, chemists, and material scientists. According to its large surface area, high electrical conductivity and excellent catalytic activity [3], graphene has been considered as a promising candidate for forming 2D support for loading Pt, Pd, and Au nanoparticles for applications in fuel cells and catalysis [4,5]. Also, graphene offers enormous possibilities for applications in electronics, sensors, biodevices, catalysis, energy storage, etc [6,7] that often involve adsorbed coinage metal clusters. For the utilization of these systems a deeper understanding of their stability and electronic properties is needed. From experiments, it is known that adatoms and small clusters of coinage metals bind weakly to graphite and graphene and are highly mobile [8,9]. In addition, the adsorption of metal atoms has displayed to be an effective way to induce the polarization of charge carriers, an issue of interest in spintronics [10] and to produce local magnetic moments of long-range magnetic coupling [11]. In [12] work devoted to the adsorption of Cu, Ag and Au on a graphene displayed by a slab model and showed that the use of such corrections is essential in certain situations to attain a binding between adsorbate and substrate.

Here, we present a theoretical investigation of Au adsorbed on perfect and graphene supercells with a monovacancy. The results of calculations of the adsorption energy are also displayed. In addition, they are responsible for the semiconductor-metal transitions after the Au atom adsorptions and the creation of energy gaps in this case.

COMPUTATIONAL METHODS

The geometry, electron band structure and magnetic properties of Au adsorbed on pristine and graphene supercells with a vacancy have been studied theoretically. The graphene properties were calculated using the DFT method implemented using the Atomistix ToolKit. In addition, the partial density of states is investigated for the graphene supercell model. The adsorption energies of perfect and graphene supercells containing 50 carbon atoms with a monovacancy have been calculated.

First-principles calculations of graphene properties were carried out on the based on the spin-polarized density functional theory. The local spin density approximation in the Perdew–Zunger (PZ) parameterization was employed for the exchange–correlation functional. The kinetic cut-off energy was 150 Ry. The primitive cell of Graphene was relaxed and optimized with force and stress tolerances of 0.01eV/Å and 0.01eV/Å^3, respectively. A 5x5x5 k point was used for geometry optimization and total energy calculations.

DISCUSSION

In Figure 1 displays schematic of the atomic structure for Au adsorbed on pristine and graphene structure with a single carbon vacancy. Calculations were fulfilled for a variety of initial conditions for Au graphene.

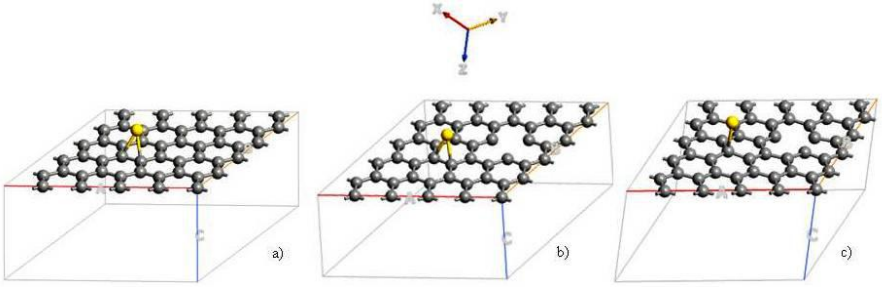

Fig. 1. The positions of Au atoms on a) graphene supercell, b) graphene supercell with carbon vacancy c) graphene supercell with carbon vacancy after relaxed.

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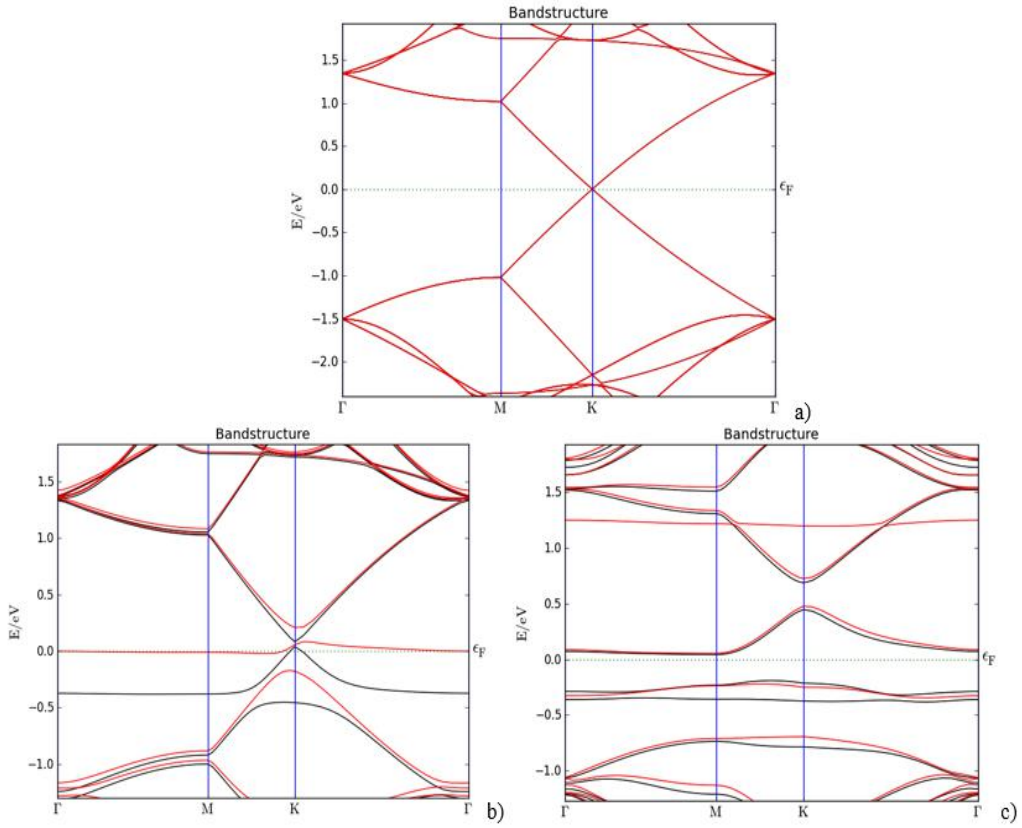


Fig. 2. The electronic band structures of (a) Pristine graphene, gold atom adsorbed (b) graphene supercell (c) graphene supercell with carbon vacancy. The insets present the Dirac Cone of 5×5 supercell.

The electronic band structures of corresponding pristine graphene, gold atom adsorbed graphene supercell and graphene supercell with carbon vacancy were obtained using the DFT as presented in Fig.2. The graphene bands within 1 eV vicinity of the Dirac points can be seen in all of the graphene adsorption orientations considered in this investigation. In addition, graphene-metal interaction cause a band gap weak opening for the graphene. The shift of Fermi energy with respect to the Dirac point corresponds to a p-type doping of graphene.

It was found that Au adsorbed on graphene supercells and 5×5 graphene supercells with vacancy exhibit ferromagnetic spin ordering. In this case the Mulliken population analysis gives the magnetic moments are received different values, as described in Table 1.

Table1.

The value of magnetic moment

Graphene	total magnetic moments	magnetic moments around vacancy
Au adsorbed on 5×5 graphene	$0.8\mu_B$	$0.645\mu_B$ (Au_{50})
Au adsorbed 5×5 graphene with vacancy	$1.005\ \mu_B$	$0.828\ \mu_B$ (C_{25})

The total magnetic moment of the graphene supercell by adsorption Au atom is $0.8\mu_B$. Here the main contribution belongs to Au atom, which the local magnetic moments are acquired $0.645\mu_B$ (Au_{50}). The magnetic moment of Au atom adsorbed on 5×5 graphene supercell with a vacancy is $1.005\mu_B$, and the local magnetic moment around the vacancy is $0.828\mu_B$ (C_{25}).

Furthermore, Figure 3 illustrates the PDOS for spin up and spin down s-,p-,d-electrons of the adsorption states for Au in the 50 atoms supercell with vacancy.

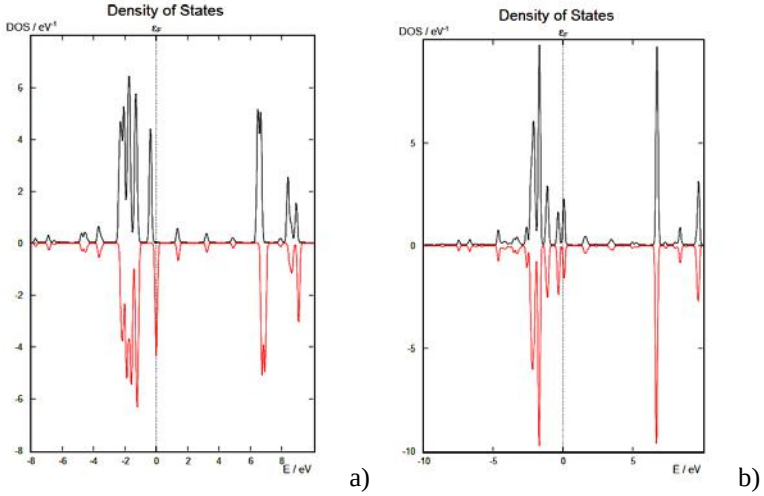
The adsorption energies E_{ads} of Au atom on a graphene are calculated as

$$E_{ads}=E[Au/Gr] - E[Au] - E[Gr]$$

where the E[Au/Gr] are the ground state energies of the adatom on graphene [Au/Gr], graphene [Gr] and gold [Au]. The E_{ads} are negative (positive) when the adsorption is exothermic (endothermic).

Calculated adsorption energies for graphene structures are given in Table 2. We found that the non-local interactions increased the calculated adsorption

energy of Au on graphene by up to 4.1 eV. On the other hand, adsorption energy of Au on 5×5 graphene with vacancy estimation is acquired 3.63eV. The distinctions in the calculated adsorption energies of the graphene/Au system can be related to the use of different graphene supercell models. Another important factor appears to be the different distance between the adsorbed Au atom and C atom in graphene supercell.



a) b)

Fig. 3. PDOS of the Au adsorbed a) 5×5 graphene supercell, b) 5×5 graphene supercell with monovacancy.

Table 2.

Adsorption energy and bond length

Method	E_{ad} (eV)	$d_{Au\text{-}C}$ (Å)	Δh (Å)
Au adsorbed on 5×5 graphene	4.1	2.56 (Au_{50}-C_{23}),	0.54
Au adsorbed on 5×5 graphene with vacancy	3.63	2.21 (Au_4-C_{33}),	0.18

RESULT

We report density functional study for adsorption of gold adatom on pristine and graphene supercells with a monovacancy. These investigations are performed by using local spin density approximation method by employing the ATK program package. In particular, the adsorption energy and magnetic moments for pristine and graphene supercells with a monovacancy adsorbed by Au atom differ from each other. The main contribution of the magnetic moment of the graphene supercell in the adsorption states for Au atom belongs to Au atom. However, the carbon vacancy existence of Au atom adsorbed onto the graphene supercell, the value of the magnetic moment is increased as 1.005 μ_B. The adsorption of a Au atom on graphene supercell the magnetic moment is acquired 0.8μ_B.

Compared to the adsorption energy of gold atom on graphene supercells (E_{ad}=4.1eV) and graphene supercells with a monovacancy (E_{ad}=3.63eV), the adsorption energy of gold on graphene supercells is the largest which corresponds to the most stable configuration.

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АДСОРБИРОВАННЫЙ АТОМ Au НА МОДЕЛИ ГРАФЕНОВОЙ СУПЕРЯЧЕЙКИ

Мы провели исследование функционала плотности адатома золота на поверхности первичных и графеновых суперячеек с вакансией. Рассчитано влияние адсорбции адатома Au на чистом и дефектном графене на величину магнитного момента. Взаимодействия между углеродом и золотом вызывают слабое раскрытие запрещенной зоны для графена. С помощью расчетов энергии адсорбции в этих структурах исследована ее зависимость от деформации графеновой ячейки.

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Au ATOMUNUN QRAFEN SUPERQƏFƏS MODELİNƏ ADSORBSİYASI

Təmiz və vakansiyalı qrafen superqəfəsinin səthində adsorbsiya edilmiş qızıl atom üçün sıxlıq funksional nəzəriyyəsi çərçivəsində tədqiqat həyata keçirilib. Au atomun təmiz və vakansiyalı qrafen səthində adsorbsiyasının maqnit momentinin qiymətinə təsiri hesablanır. Karbon və qızıl atomu arasındakı qarşılıqlı təsir qrafenin enerji zolağının üçün zəif açılmasına səbəb olur. Bu strukturlarda adsorbsiya enerjisinin hesablamalarından istifadə edərək onun qrafen superqəfəsinin deformasiyasından asılılığı araşdırılır.