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Magnetic and electronic properties of Fe_3O_4 /graphene heterostructures: First principles perspective

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Magnetic and electronic properties of $\text{Fe}_3\text{O}_4(111)$ /graphene heterostructures are investigated by first principles calculations. Different structural models have been considered, which differ in the interface termination of $\text{Fe}_3\text{O}_4(111)$ surface with respect to the same monolayer graphene. In three models, the magnetic moment of Fe(A) has a major change due to less O atoms surrounding Fe(A) atoms than Fe(B). Magnetic moment is enhanced by 8.5%, 18.5%, and 8.7% for models (a), (b), and (c), respectively. Furthermore, the spin polarization of models (a) and (c) is lowered due to the simultaneous occurrence of density of states of spin-up Fe(A) and spin-down Fe(B) at Fermi level. The spin polarization of model (b) remains the same as that of bulk Fe_3O_4 . Our results suggest that different interface terminations and Fe(A) play an important role in determining the magnetism strength and spin polarization. © 2013 American Institute of Physics.

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I. INTRODUCTION

Graphene, a two-dimensional (2D) single atomic layer of graphite, has attracted a great deal of interest due to its novel electronic properties.^{1–6} The band structure of graphene possesses conical electron and hole pockets which meet only at K points of Brillouin zone in momentum space.^{7,8} Due to the linear dependence of energy on momentum, carriers behave as effectively massless and have an effective speed of light of 10^6 m/s, together with a large spin-relaxation length,¹ which makes it a promising candidate for spintronics devices. Recently, many experiments focused on graphene spin-valve devices by utilizing ferromagnetic metal as electrodes.^{9,10} As alternative ferromagnetic materials, ferromagnetic half-metallic oxides are potential to be the spin injection sources because they have high spin polarization, environmental stability, and efficient spin injection.¹¹ Fe_3O_4 was predicted to be half-metallic with a high Curie temperature of 858 K.^{12–15} If Fe_3O_4 was chosen as a spin injector to perform spin injection into graphene, new spintronics devices will be set up. However, the results on Fe_3O_4 /graphene heterostructures have not been widely reported so far. Experimentally, (100), (110), and (111) oriented epitaxial Fe_3O_4 films have been fabricated, in which $\text{Fe}_3\text{O}_4(111)$ plane is composed of atoms with hexagon shape that corresponds to the hexagon of C atoms in graphene. Hence, we choose $\text{Fe}_3\text{O}_4(111)$ /graphene interface to investigate the magnetic and electronic properties of half-metallic oxide/graphene interfaces. In this paper, magnetic and electronic properties of $\text{Fe}_3\text{O}_4(111)$ /graphene heterostructures have been investigated by first principles

calculations. Spin polarization of models (a) and (c) is lowered, but spin polarization of model (b) remains the same as that of bulk Fe_3O_4 . Different interfacial terminations and Fe(A) play an important role in determining the magnetism and spin polarization.

II. CALCULATION DETAILS AND MODEL

All the spin-polarized calculations were performed within projector augmented wave (PAW) method^{16,17} as implemented in the computational code of Vienna *ab initio* simulation package,¹⁸ based on the density-functional theory (DFT). Exchange-correlation potential was treated by generalized gradient approximation, according to Perdew-Burke-Ernzerhof.¹⁹ In order to find the theoretical equilibrium static geometries a standard plane-wave basis set with a kinetic-energy cutoff of 520 eV was used in the geometry optimization process and static calculations. A Γ -centered $5 \times 5 \times 5$ k -point mesh was performed for the bulk calculations of Fe_3O_4 , while we adopted a Γ -centered $5 \times 5 \times 1$ and $10 \times 10 \times 1$ for the static and density of states (DOS) calculations of monolayer graphene, respectively. Calculations were converged to 10^{-5} eV and the structures were relaxed until the largest force became less than 0.03 eV/Å.

Bulk Fe_3O_4 crystallizing in the inverted spinel structure (Space group: $Fd\bar{3}m$) has chemical formula $[\text{Fe}^{2+}]_A[\text{Fe}^{3+}]_B\text{O}_4$ with a experimental lattice constant of 8.39 Å. In inverse spinel structure, the tetrahedron A sites are occupied by Fe^{3+} ions, while the octahedron B sites are occupied by an equal number of randomly distributed Fe^{2+} and Fe^{3+} ions. Magnetic moments of Fe ions in the two sites oppositely oriented, so it can be said that Fe_3O_4 is a ferrimagnet with a

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total magnetic moment of $4 \mu_B/\text{Fe}_3\text{O}_4$, as indicated by the arrows in the chemical formula given above.^{20,21} Graphene is a monolayer of carbon atoms packed into a dense honeycomb crystal structure, which can be obtained by mechanical exfoliation from graphite. Its honeycomb structure contains a bipartite lattice, formed by two interpenetrating triangular sublattices. There are strong covalent bonds between carbon atoms arranged in a honeycomb lattice. The nearest neighbor distance in graphene is $1.42 \text{ \AA}$.²²

$\text{Fe}_3\text{O}_4/\text{graphene}$ interfaces was simulated by building up the bilayers structure consisting of $\text{Fe}_3\text{O}_4(111)$ and monolayer graphene because $\text{Fe}_3\text{O}_4(111)$ plane was composed of atoms with hexagon shape that corresponds to the hexagon of C atoms in grapheme sheet. The supercell was modeled by containing monolayer graphene attached to one unit cell of $\text{Fe}_3\text{O}_4(111)$ with three different terminations plus a vacuum layer of $10 \text{ \AA}$. The supercell contains three models because $\text{Fe}_3\text{O}_4(111)$ surface has three different terminations, as shown in Fig. 1. $\text{Fe}_3\text{O}_4(111)$ is composed of alternate Fe(A), Fe(B), and O layers, while graphene has only one layer. By employing the periodic boundary conditions, each model contains an interface: model (a) contains the O–C interface; model (b) contains the Fe(B)–C interface; model (c) contains the Fe(A)–C interface. In order to make the surface unit cell of $\text{Fe}_3\text{O}_4(111)$ and monolayer graphene lattice matched, the surface unit cell of $\text{Fe}_3\text{O}_4(111)$ has $p(2 \times 2)$ periodicity with a lattice constant of $11.86 \text{ \AA}$, while monolayer graphene has 5×5 periodicity with a lattice constant of $12.3 \text{ \AA}$. There is a minor mismatch in lattice constant between graphene and $\text{Fe}_3\text{O}_4(111)$ surface. Thus, for the present supercells, to compensate lattice mismatch an average lattice constant of $12.08 \text{ \AA}$ is adopted for both the Fe_3O_4 and graphene regions. Density-functional calculations on electronic and atomic structures for $\text{Fe}_3\text{O}_4(111)/\text{graphene}$ heterostructures were performed using $5 \times 5 \times 1$ Monkhorst-Pack mesh of k points in Brillouin zone.

III. RESULTS AND DISCUSSIONS

For monolayer graphene, the calculated band structure shows a zero bandgap semiconductor. The valence band maximum (VBM) and conduction band minimum (CBM) meet at K point called Dirac point, where the effective mass of the hole and electron is nearly zero, leading to the excellent electrical properties. For bulk Fe_3O_4 , the calculated lattice constant is $8.40 \text{ \AA}$, which is consistent with experimental value mentioned above. The calculated magnetic moment for Fe(A), Fe(B), and O ions are approximately

-3.486 , 3.569 , and $0.077 \mu_B/\text{atom}$, as listed in Table I, respectively, leading a net moment of $\sim 4 \mu_B/\text{Fe}_3\text{O}_4$. The results are consistent with the previous theoretical and experimental results.^{23–25} The partial DOS of Fe(A) has a band gap in both the spin-up and spin-down channels, which indicates that Fe(A) ions are insulating. However, DOS of Fe(B) has only finite values at Fermi energy in spin-down channel, and shows a half-metallic feature, as shown in Fig. 2(a). As a result, bulk Fe_3O_4 is half-metallic.^{26,27} In Fig. 2, the symbol “IF-Fe-A-4” is the atomic number, where IF is the “interface”, Fe-A is the Fe ions at A sites, 4 is the atomic number of Fe ions at A sites. The same definition was presented in other figures.

Figure 2 shows the calculated partial DOS of O–C interface contained in model (a), which is obtained by projecting on Fe(A), Fe(B), and O layers from the Fe_3O_4 component in the supercell. When Fe_3O_4 and graphene are contacted to form the interface, the most surprising feature is that the half-metallic behavior of Fe_3O_4 caused by Fe(B) ions on the fifth layer is nearly disappeared, while the partial DOS of Fe(B) ions on the second layer near the interface remains the half-metallic feature, as shown in Fig. 2(a). Meanwhile, it is observed that only the spin-up conduction band (CB) of Fe(A) ions on the forth layer shifts considerably to lower energy and pass through Fermi level, leading to 100% spin polarization, which makes the corresponding magnetic moment of Fe(A) ions decreases as compared to bulk Fe_3O_4 . In addition, the spin-down valence band (VB) of Fe(A) ions on the sixth layer passes through the Fermi level, resulting in 100% spin polarization. Meanwhile, the magnetic moment of Fe(A) ions on the sixth layer decreases as compared to bulk Fe_3O_4 , as shown in Table I. The simultaneous occurrence of pin-up Fe(A) and spin-down Fe(B) leads to low spin polarization as compared to bulk Fe_3O_4 . Figure 2(b) shows the partial DOS of O atoms. The O- $2p$ states on the first layer obviously shift to higher energy by 0.5 eV , and the strong spin splitting DOSs in both the channels indicate that the magnetic moment of O increases as compared to bulk Fe_3O_4 . However, the O- $2p$ states on the seventh layer obviously shift 1.3 eV to higher energy and the VB in spin-down channel comes across Fermi level, and it is relatively symmetrical, which results in the reducing magnetic moment as compared to bulk Fe_3O_4 (seen in Table I). Furthermore, there are two kinds of O atoms on the third layer with different magnetic moment, which is possibly due to the fact that O $2p$ states with large magnetic moment have a stronger hybridization with both Fe(A) and Fe(B) ions $3d$ states than O atoms with small magnetic moment. Figure 2(c) shows the partial DOS of C atoms. It can be clearly seen from the

FIG. 1. The supercell structure of $\text{Fe}_3\text{O}_4/\text{graphene}$: model (a) contains the interface of O–C; model (b) contains the interface of Fe(B)–C; model (c) contains the interface of Fe(A)–C. The left/right side is the $\text{Fe}_3\text{O}_4/\text{graphene}$, respectively. The red spheres stand for oxygen atoms, the blue spheres stand for Fe atoms of Fe_3O_4 , and the dark gray spheres stand for C atoms.

TABLE I. The calculated magnetic moment m (μ_B) of per atom including Fe and O in the supercell $\text{Fe}_3\text{O}_4(111)/\text{graphene}$ model (a), as compared to that of the bulk Fe_3O_4 .

Layer	FO–Fe(A)	FO–Fe(B)	FO–O
1	...	...	0.381
2	...	3.632	...
3	...	...	O(51)0.249 O(63)0.113
4	–3.234	...	...
5	–	3.423	...
6	–3.3285	...	...
7	...	...	–0.0143
Bulk	–3.486	3.569	0.077

figure that the graphene is a zero bandgap semiconductor. Although the C DOS from the interface still remain symmetrical, the VB in both the spin-up and spin-down channels pass through the Fermi level, destroying the particular electronic structure.

Figure 3 shows the calculated partial DOS of the Fe(B)–C interface contained in model (b). The half-metallic

behavior of Fe_3O_4 caused by Fe(B) ions on the first layer is nearly vanished, while the partial DOS of Fe(B) ions on the forth layer far away the interface remains the half-metallic feature, as shown in Fig. 3(a). This is different from the O–C interface. The DOS of Fe(A) ion on the interface has only small change as compared to bulk Fe_3O_4 . All the DOSs of Fe(A) ions remain an insulating behavior. But the magnetic moment of Fe(A) ions on both the second and sixth layer decreases as compared to bulk Fe_3O_4 , as seen in Table II. The above results suggest that the interfacial influence on electronic structure becomes less as the distance between the atoms and interface increases. Figure 3(b) shows the partial DOS of O atoms. All the O–2p states obviously shift to higher energy by 0.5 eV, and DOSs in both the channels remain insulating. The O(65)–2p states on the third layer have a strong spin splitting, resulting in the corresponding magnetic moment increasing as compared to bulk Fe_3O_4 , while O(79)–2p states on the third layer are relatively symmetrical and have the same magnetic moment as compared to bulk Fe_3O_4 . The O atoms on the fifth layer have the similar behavior as that on the third layer. There are two kinds of O atoms with different magnetic moment on both the third layer and fifth layer, which may be due to the fact that O

FIG. 2. (a) The partial DOS obtained for the fully relaxed $\text{Fe}_3\text{O}_4/\text{graphene}$ model (a), as compared to the bulk Fe_3O_4 compounds. The blue/red line stands for Fe(A)/Fe(B) atoms. (b) The contrast between the bulk O atoms and O atoms at the different sites of the interface in the model (a). (c) The contrast between the bulk C atoms and C atoms of the interface in the model (a). The Fermi energy is indicated by the vertical dashed line and the Fermi level is set to 0 eV.

FIG. 3. (a) The partial DOS obtained for the fully relaxed $\text{Fe}_3\text{O}_4/\text{graphene}$ model (b), as compared to the bulk Fe_3O_4 compounds. The blue/red line stands for Fe(A)/Fe(B) atoms. (b) The contrast between the bulk O atoms and O atoms at the different sites of the interface in the model (b). (c) The contrast between the bulk C atoms and C atoms of the interface in the model (b). The Fermi energy is indicated by the vertical dashed line and the Fermi level is set to 0 eV.

atoms with small magnetic moment connect with both Fe(A) and Fe(B) ions, while O atoms with large magnetic moment only connect with Fe(B) ions. The increasing magnetic moment is due to the strong hybridization between O and Fe(B) atoms. Figure 3(c) shows the partial DOS of C atoms. It can be clearly seen that DOS of C at the interface still remains symmetrical, but DOSs in both the spin-up and spin-

down channels have a bandgap of 0.36 eV, destroying the particular electronic structure.

Figure 4 shows the calculated partial DOS of Fe(A)–C interface contained in model (c). We observed the similar behavior as Fe(B)–C interface that the half-metallic behavior caused by Fe(B) ions on the second layer nearly disappears, while the partial DOS of Fe(B) ions on the fifth layer far away the interface remains the half-metallic feature, as shown in Fig. 4. However, the spin-up CB of Fe(A)-83 ions on the first layer shifts considerably to lower energy and pass through the Fermi level, leading to 100% spin polarization, which makes the corresponding magnetic moment of Fe(A)-83 ions decreases as compared to bulk Fe_3O_4 , as shown in Table III. Meanwhile, the spin-down DOS of Fe(A)-84 ion on the first layer pass through the Fermi level, resulting in the 100% spin polarization. The phenomenon is related with the fact that both the edges of monolayer graphene bend toward $\text{Fe}_3\text{O}_4(111)$ surface. The occurrence of spin-up Fe(A) would lower the spin polarization at Fermi level as compared to bulk Fe_3O_4 . DOSs of Fe(A) ions on the third layer display an insulating character, which is consistent with the bulk Fe_3O_4 properties. Figure 5 shows the partial DOS of O atoms. The O-2p states shift to higher energy and the DOSs

TABLE II. The calculated magnetic moment m (μ_B) of per atom including Fe and O in the supercell $\text{Fe}_3\text{O}_4(111)/\text{graphene}$ model (b), as compared to that of the bulk Fe_3O_4 .

	FO–Fe(A)	FO–Fe(B)	FO–O
1	...	3.456	...
2	–3.154	...	...
3	...	...	O(65)0.398 O(79)0.072
4	...	3.688	...
5	...	...	O(51)0.325 O(63)0.091
6	–3.099	...	...
Bulk	–3.486	3.569	0.077

FIG. 4. The partial DOS obtained for the fully relaxed Fe₃O₄/graphene model (c), as compared to the bulk Fe₃O₄ compounds. The blue/red line stands for Fe(A)/Fe(B) atoms. The Fermi energy is indicated by the vertical dashed line and the Fermi level is set to 0 eV.

TABLE III. The calculated magnetic moment m (μ_B) of per atom including Fe and O in the supercell Fe₃O₄(111)/graphene model (c), as compared to that of the bulk Fe₃O₄.

	FO-Fe(A)	FO-Fe(B)	FO-O
1	Fe(83)-2.894 Fe(84)-2.697	...	...
2	...	Fe(91)3.650 Fe(92)3.305	...
3	Fe(87)-3.479 Fe(88)-3.223	...	...
4	...	...	O(55)0.154 O(56)0.392 O(57)-0.06 O(65)0.074 O(67)0.122
5	...	Fe(95)3.519 Fe(96)3.846 Fe(98)2.704	...
6	...	...	O(51)0.488 O(52)0.366 O(63)0.173 O(64)0.060 O(70)-0.015
Bulk	-3.486	3.569	0.077

in both the channel remain insulating. Interestingly, O atoms in the same layer have different magnetic moments, which may be due to the difference of Fe ions surrounding O atoms. Figure 6 shows the partial DOS of C atoms. It can be clearly seen that DOSs of C atoms at the interface changed significantly, and DOSs of C-1 atom have finite DOS and pass through Fermi level only in the spin-up channel. While DOSs of C-4 atom have the similar shape as that of monolayer graphene.

In order to clearly show the magnetic properties, the calculated m for Fe and O ions in the models (a), (b), and (c) are presented in Tables I–III, respectively. The numbers in the parentheses behind the atoms in these tables are presented in Fig. 1. For models (a) and (b), the magnetic moment of the whole supercell is enhanced by 8.5% and 18.5%, respectively, which is attributed to the increased magnetic moment from O and the reduced magnetic moment from Fe(A) atoms in Fe₃O₄. Furthermore, the corresponding magnetic moment of Fe₃O₄ formula unit increases to 4.3413 and 4.7395 μ_B , respectively. Yet, for the model (c), the magnetic moment of the system is also enhanced by 8.7%, which results from the combined action of the increasing magnetic moment of Fe(A) and O atoms as well as the reduced magnetic moment of Fe(B) atoms. Also, we find that the magnetic moment of Fe(A) atoms has a major change in all of the three model because the less O atoms surrounding Fe(A) atoms than Fe(B) atoms.

FIG. 5. The contrast between the bulk O atoms and O atoms at the different sites of the interface in the model (c). The Fermi energy is indicated by the vertical dashed line and the Fermi level is set to 0 eV.

FIG. 6. The contrast between the bulk C atoms and C atoms of the interface in the model (c). The Fermi energy is indicated by the vertical dashed line and the Fermi level is set to 0 eV.

IV. CONCLUSION

We have performed first-principles calculations to investigate the electronic and magnetic properties of $\text{Fe}_3\text{O}_4(111)/$ graphene heterostructure. The magnetic moment enhances

8.5%, 18.5%, and 8.7% for models (a), (b), and (c), respectively. In three models, the magnetic moment of the Fe(A) has a major change, which is caused by the less O atoms surrounding Fe(A) atoms than Fe(B) atoms. Furthermore, spin polarization of models (a) and (c) is lowered due to the simultaneous occurrence of DOS of spin-up Fe(A) and spin-down Fe(B) at Fermi level, while the spin polarization of model (b) remain the same as that of bulk Fe_3O_4 . Therefore, we would possibly tune the interface states by engineering the different interface terminations for optimized performances in spintronics device applications.

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