

Adsorption of molecular oxygen on doped graphene: Atomic, electronic, and magnetic properties

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Adsorption of molecular oxygen on B-, N-, Al-, Si-, P-, Cr- and Mn-doped graphene is theoretically studied using density-functional theory in order to clarify if O₂ can change the possibility of using doped graphene for gas sensors, electronic, and spintronic devices. O₂ is physisorbed on B-, and N-doped graphene with small adsorption energy and long distance from the graphene plane, indicating the oxidation will not happen; chemisorption is observed on Al-, Si-, P-, Cr- and Mn-doped graphene. The local curvature caused by the large bond length of X-C (X represents the dopants) relative to C-C bond plays a very important role in this chemisorption. The chemisorption of O₂ induces dramatic changes of electronic structures and localized spin polarization of doped graphene, and in particular, chemisorption of O₂ on Cr-doped graphene is antiferromagnetic. The analysis of electronic density of states shows the contribution of the hybridization between O and dopants is mainly from the *p* or *d* orbitals. Furthermore, spin density shows that the magnetization locates mainly around the doped atoms, which may be responsible for the Kondo effect. These special properties supply a good choice to control the electronic properties and spin polarization in the field of graphene engineering.

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I. INTRODUCTION

Graphene has been becoming a new star in a lot of fields after its successful fabrication,¹⁻³ especially for the application of two aspects below because of the many reasons for the renewed interest: first, it is very potential to apply graphene as gas sensors with high sensitivity because the transport properties exhibit large changes upon exposure to several gases such as NO₂.⁴ Graphene can be used as an excellent sensor material because of its special properties such as two-dimensional property maximizing the interaction of adsorbates on the layer, low Johnson noise,^{2,5-7} and few crystal defects.^{2,5,6} This tells us the electronic properties of graphene system can be sensitive to the adsorption of gases. Second, there is an extraordinary interest in the electronic band properties and magnetic order in graphene-related materials that can be put into use as the next-generation electronic devices and recording media, magnetic inks, spin qubits, and spintronic devices,^{3,8,9} which can use the advantages of high mobility of electrons in graphene and long coherence times in carbon-based materials. A few investigations have been performed until now to search for the potential application of graphene or graphene nanoribbons as gas sensors.^{10,11} However, it has been shown that intrinsic graphene can only physisorb most of gas molecules¹¹⁻¹³ and has no band gap and spin polarization. This, for example, prevents the use of graphene in making gas sensors, transistors and spintronic devices.

In order to improve the sensitivity for gases and the electronic structures in graphene and carbon nanotubes (CNTs), the method of doping is usually used. B- and N-doped graphene can also improve gas sensing of CO, NO, NO₂, and NH₃ (Ref. 14); Al-doped graphene can be sensitive to most of common gases in air;¹⁵ H₂O on Ti-doped graphene,¹⁶ chlorophenols on Si-doped CNTs (Ref. 17) are also reported. Meanwhile, the electronic structures and magnetic properties in graphene and graphene nanoribbons can be changed by doping different atoms such as boron,¹⁸ sulfur, and phosphorus,¹⁹ transition metal atoms,²⁰⁻²² or by defect engineering,²³ functionalized with different atoms, mol-

ecules, and clusters²⁴ and so on. Experimentally, several CNTs and graphene-based materials with different dopants such as nitrogen,²⁵ boron,²⁶ phosphorus²⁷ were also synthesized. It has been shown by these studies that the doped graphene or CNTs materials are very potential for gas sensors, electronics and spintronics.

However, in order to use these materials in reality, the effect of O₂ should be considered, since O₂ is one of the most important gases taking up more than 20% in air. Meanwhile, it has been shown that O₂ can hole-dope semiconductors.²⁸ Also, gas molecules can change the electronic and magnetic properties of graphene and graphene nanoribbons.²⁹ Previous calculations¹² and experiments³⁰ have shown that O₂ in the triplet state is physisorbed on the surface of single-walled carbon nanotubes (SWCNTs) and graphene, and the transport properties could not be significantly affected. On the other hand, the electronic properties of carbon-doped boron nitride nanotubes can be changed dramatically by the chemisorption of O₂ molecule.³¹ This indicates that the dopants can improve the reactivity of materials, and the O₂ molecules can give rise to very different properties. Therefore, how O₂ molecule can affect the properties of doped graphene is necessary to be understood in the fields of both gas sensing and electronics.

In this paper we study from first principles the adsorption of molecular oxygen on B-, N-, Al-, Si-, P-, Cr-, and Mn-doped graphene. In order to illuminate easily, these materials are abbreviated to be BG, NG, AG, SG, PG, CG, and MG. BG and NG retain a planar form, while other atoms protrude out of the graphene layer and induce a local curvature in graphene. Furthermore, O₂ molecule is physisorbed on BG and NG with relatively small adsorption energy and large distance of X-O (X represents the doping atom), comparing with chemisorption on the doped graphene with other dopants. In the end, the chemisorption induces dramatic change for the electronic structures of doped graphene, and injects magnetic moments into the system except O₂ on PG. Especially, the system of O₂ on CG is antiferromagnetic (AFM).

II. COMPUTATIONAL METHODS

Spin-polarized density-functional theory (DFT) calculations are performed using the Perdew-Burke-Ernzerhof (PBE) (Ref. 32) generalized gradient approximation (GGA) for the exchange-correlation potential. A supercell of 6×6 graphene including 72 C atoms with a doped atom substituting a C atom and a single O_2 molecule adsorbed onto it is constructed. With this model, the dopant concentration in our calculations is $\sim 1.4\%$. Experiments have shown the existence of these types of single-atom doped materials.³³ Besides, a method to synthesize the transition metals doped graphene has been proposed.²¹ In the direction normal to the surface, 29.5 Å length in the supercell is sufficient to minimize the interaction between graphene layers. Ultrasoft pseudopotentials³⁴ and a plane-wave basis setup to a kinetic energy cutoff of 25 Ry for the wave function and of 200 Ry for the charge density are chosen in all simulations (for transition metals Cr and Mn, a cutoff of 35 Ry for the wave function and 300 Ry for the charge density). The Brillouin zone is sampled using a $3 \times 3 \times 1$ Monkhorst-Pack³⁵ grid and Methfessel-Paxton³⁶ smearing of 0.01 Ry. A denser $11 \times 11 \times 1$ Monkhorst-Pack grid and the tetrahedron method³⁷ are used for the calculation of density of states (DOS) and partial DOS (PDOS). Atomic positions are optimized until the maximum force on any atom is less than 0.001 a.u. All calculations are performed using the QUANTUM-ESPRESSO package.³⁸ We carefully test this supercell for the convergence of energy, magnetic properties, comparing a larger supercell as in Ref. 21, and there is few difference found.

Here, we would like to point out that the usage of GGA, the consequent neglect of van der Waals interactions, leads to an incorrect description of physisorption, but this is of little concern for us since we are interested in chemically bound molecules. In fact, in physisorbed systems, LDA results look “better” than GGA, but they are just “wrong in a different way.” For chemically bound systems, GGA is usually a better choice.

In this calculation, only the triplet O_2 molecule is considered, which is the ground state of O_2 . The adsorption energy is defined by $E_a = E_{tot} - E_{dg} - E_o$, where E_{tot} is the total energy of the doped graphene with a bound O_2 molecule, E_{dg} is the energy of doped graphene, and E_o is the energy of isolated O_2 molecule. In order to minimize systematic errors, the same supercells and k -point grids are used for all calculations.

III. RESULTS AND DISCUSSION

The bond length of O_2 molecule in ground state is 1.2350 Å (experimental value is 1.207 Å) and the magnetic moment is $2 \mu_B$ in our calculations. O_2 molecule is placed at the top of the doping atoms, and slightly inclined to the graphene plane at the beginning. After relaxation, O_2 molecule is found to be physisorbed on the top of B and N atoms, while chemisorbed on the top of Al, Si, P, Cr, and Mn atoms. After relaxation, O_2 is parallel to graphene plane, which is the most stable configuration according to the test of our calculations. The configurations of MG and O_2 adsorption on MG are shown in Fig. 1, where the Mn atom

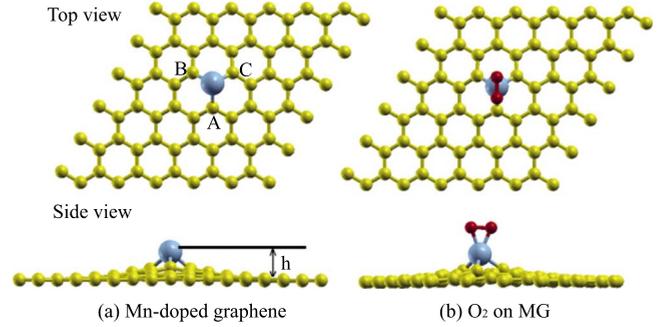


FIG. 1. (Color online) The most stable configurations of MG with an elevation h of 1.555 Å (a); and of O_2 on MG with h of 1.652 Å (b).

protrudes out of the graphene plane. All configurations here are very similar to Fig. 1, except for BG and NG with all atoms in the same plane and physisorbed O_2 . In fact, a meta-stable configuration with all atoms in one plane can be obtained if the dopant is set to be in the same plane of graphene, but it is very easy to transform to the stable one. Meanwhile, the results of O_2 adsorption on all doped graphene are shown in Table I, which will be discussed detailedly below.

A. Adsorption of oxygen on CG and MG

We first discuss the adsorption of O_2 on CG and MG. The atomic and magnetic structures of CG and MG have been discussed in Ref. 21. As shown in Fig. 1 and Table I, the elevation of Cr and Mn atoms is 1.6487 and 1.5555 Å; the Cr-C and Mn-C bond lengths are 1.8559 and 1.8317 Å; the magnetic moments are $2.00\mu_B$ and $3.00\mu_B$, respectively. These are in good agreement with the results using a larger supercell in Ref. 21. The unpaired electrons in transition metals (Cr and Mn) induce magnetic moments, and the direction of spin polarization of Cr or Mn is opposite to that of the nearest carbon atoms, that is, C_A , C_B , and C_C in Fig. 1(a).

From Table I, we can learn the configurations are changed dramatically after O_2 adsorption. The molecular oxygen is chemisorbed on CG and MG with large adsorption energies of -2.6098 and -2.0918 eV, respectively, indicating very stable adsorption of O_2 . The bonds of Cr-O and Mn-O are formed with short lengths of 1.7935 and 1.8641 Å; The elevation of Cr above graphene plane is shortened to 1.6188 Å, while the elevation of Mn is extended to 1.6520 Å. The O-O bond extends to 1.4088 and 1.3993 Å for CG and MG. Interestingly, CG become AFM by the adsorption of O_2 , i.e., with zero total magnetic moment but $0.34\mu_B$ absolute magnetic moment. We calculate the magnetic moment of every atom in the system, and find the magnetic moment of Cr atom (-0.1435) is opposite to other atoms such as O ($0.0411\mu_B$, $0.0421 \mu_B$), the three nearest C atoms C_A ($0.0133 \mu_B$), C_B ($0.0169 \mu_B$) and C_C ($0.0169 \mu_B$). At the same time, the absolute magnetic moment of Cr and the sum of magnetic moment of O, C_A , C_B , and C_C is very close. These two properties make the system AFM, and the magnetization very localized, as shown in Fig. 2(a). For MG, O_2 adsorption reduces the magnetic moment

TABLE I. Summary of atomic structures of the compounds, including adsorption energy E_a (eV), the shortest bond length of X-C d_{X-C} (Å), shorter bond length of X-O d_{X-O} (Å), bond length of O-O d_{O-O} (Å), the elevation of the dopant atoms above the graphene plane h (Å) (negative value means the dopants protrude out of the plane in opposite direction to O_2 molecule), magnetic moments of the system M_B (μ_B), and Löwdin charge (Ref. 39) transfers from doped graphene to O_2 molecule c (e^-).

		Cr	Mn	Al	Si	P	B	N
Doped	h	1.6487	1.5555	1.7584	1.4579	1.4591	0.0000	0.0000
Graphene	d_{X-C}	1.8559	1.8317	1.8528	1.7611	1.7689	1.4794	1.4079
	M_B	2.0000	3.0000	0.0000	0.0000	1.0500	0.0000	0.0000
O_2	E_a	-2.6098	-2.0918	-1.5589	-1.3132	-1.0359	-0.0232	-0.1228
Adsorption	h	1.6188	1.6520	1.9026	1.6607	1.4840	-0.2457	-0.0541
	d_{X-C}	1.8159	1.8464	1.9284	1.8284	1.7501	1.4810	1.4066
	d_{X-O}	1.7935	1.8641	1.8770	1.7109	1.6275	3.5099	3.3196
	d_{O-O}	1.4088	1.3993	1.4000	1.5103	1.5584	1.2354	1.2577
	M_B	AFM	1.4500	1.0000	0.3300	0.0000	1.9900	1.8000
	c	0.2166	0.1865	0.4367	0.9184	0.8181	-0.0863	0.0235

of the system to $1.45 \mu_B$, which is caused by the decrease of unpaired electrons due to the hybridization between Mn and O atoms. Similar to O_2 on CG, the magnetic moment is located around the Mn atom, as shown in Fig. 2(b), which may be a Kondo system.

In order to understand the electronic properties of the system, DOS and PDOS of O_2 -CG and O_2 -MG are calculated, as shown in Figs. 3 and 4, respectively. It is well known that intrinsic graphene is semimetal. In Fig. 3, it is obvious that CG is a metal. After adsorption of O_2 , the O, C, and Cr hybridize strongly. There is one DOS peak for spin-down electrons appearing at the Fermi level, which comes from the hybridization of Cr atom and O_2 molecule. One peak disappears below the position of -1.5 eV, which mainly belongs to the contribution of $3d$ electrons in Cr atom. Löwdin charge analysis shows there is $0.2166e^-$ transfer from CG to O_2 molecule, that is to say, O_2 is an acceptor here. Therefore, O_2 can actually p -dope the host CG, which is consistent with the effect of O_2 on organic semiconductors.²⁸ Similarly, O_2 can p -dope MG through accepting $0.1865e^-$. From Fig. 4, we can learn that the change of electronic properties of MG induced by O_2 adsorption is mainly around the Fermi level,

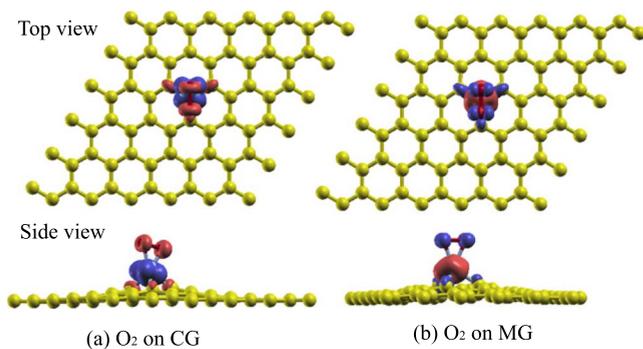


FIG. 2. (Color online) Spin density in O_2 adsorption on doped graphene. (a) In O_2 -CG chemisorption system with isovalues of ± 0.01 a.u.; (b) O_2 -MG chemisorption system with isovalues of ± 0.001 a.u.

where the DOS peak of spin-down electrons of MG before adsorption above the Fermi level disappears, which is contributed by the $3d$ electrons in Mn atom hybridizing with $2p$ electrons in O atom. Meantime, one peak for spin-up electrons appears at the Fermi level, which is made up of hybridized Mn d and O p orbitals according to the PDOS analysis in Fig. 4. Similar to the analysis of spin density (Fig. 2), the magnetization is also localized and then O_2 adsorbed on Cr or Mn may exhibit as Kondo impurities as well as Cr or Mn doped into graphene²¹ and Ni impurity in a Au nanowire.⁴⁰

B. Adsorption of oxygen on AG, SG, and PG

Al, Si, and P elements contain $3p$ orbital, and they have 3, 4, and 5 valence electrons, respectively. Discussion about

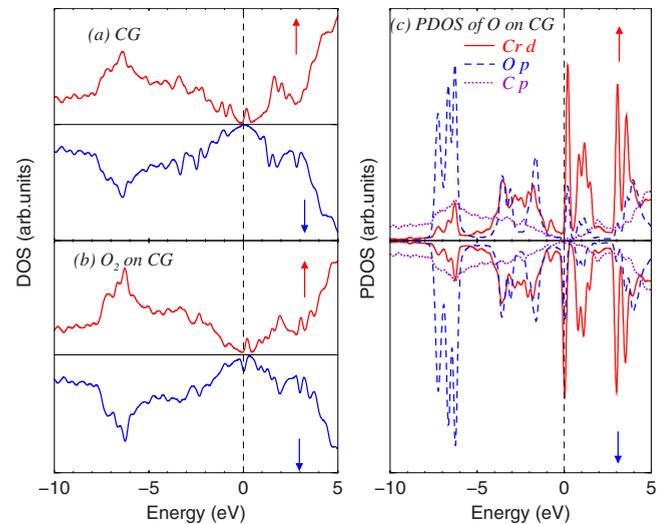


FIG. 3. (Color online) Total and partial DOS for CG and O_2 -CG chemisorption system. (a) Total DOS of CG before adsorption of O_2 ; (b) Total DOS of CG after adsorption of O_2 ; (c) PDOS of atoms in O_2 -CG chemisorbed system. PDOS of O_p is the average of two O atoms, and C_p is the average of all C atoms in the system. The arrows denote the spin-down (\downarrow) states and spin-up (\uparrow) states. The zero energy is the Fermi level.

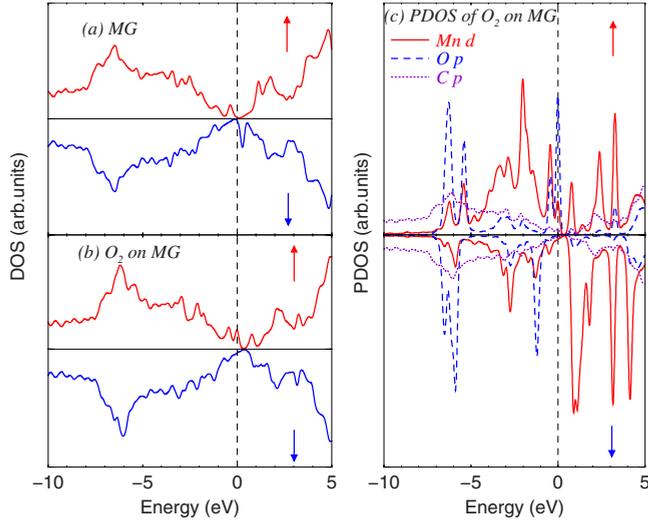


FIG. 4. (Color online) Total and partial DOS for MG and O_2 -MG chemisorption system. (a) Total DOS of MG before adsorption of O_2 ; (b) total DOS of MG after adsorption of O_2 ; (c) PDOS of atoms in O_2 -MG chemisorbed system. The arrows denote the spin-down (\downarrow) states and spin-up (\uparrow) states. The zero energy is the Fermi level.

their doping into graphene and nanotubes has been reported recently, which show that they are potential resources for detecting toxic molecules and modulating the electronic structures of graphene.

From Table I, we can learn that Al, Si, and P atoms introduce a local curvature of graphene, with elevation of 1.7584, 1.4579, and 1.4591 Å, respectively. Meanwhile, the bond lengths of Al-C, Si-C, and P-C is 1.8528, 1.7611, and 1.7689 Å, respectively, which basically decrease with the increase of electrons of the elements. In fact, for atoms which have the same configurations of orbitals, the covalent bond length decreases with the increase of group number. This indicates that the extension of electron states plays a very important role in the structures of doped graphene. Specially, P dopant introduces spin polarization into the PG with magnetic moment of $1.05 \mu_B$, while no magnetization exists for AG and SG. It is noticed that a metastable configuration of PG with all atoms retaining in one plane can be observed, in which there is no spin polarization induced. It seems that the local curvature has a very important effect for the magnetic property. O_2 molecule can be chemisorbed on the atoms of Al, Si, and P in graphene, with large adsorption energies of -1.5589 , -1.3132 , and -1.0359 eV, respectively. Meantime, the atomic structures change much. For AG, Al atom has an elevation of 1.9026 Å, and C-Al bond extends to 1.9284 Å, Al-O to 1.8770 Å, and O-O to 1.40 Å. For SG, Si atom protrudes out of graphene plane with elevation of 1.6607 Å. C-Si, Si-O, and O-O bonds also elongate, which are 1.8284, 1.7109, and 1.5103 Å, respectively. On the contrary, chemisorption of O_2 on PG shorten the P-C bond to 1.6286 Å from 1.7691 Å before adsorption, and the bond O-O is broken completely with the long distance of 1.5598 Å. The P atom almost retains the place above graphene with 1.4796 Å and does not protrude outward more. It is interesting that chemisorption of O_2 introduces

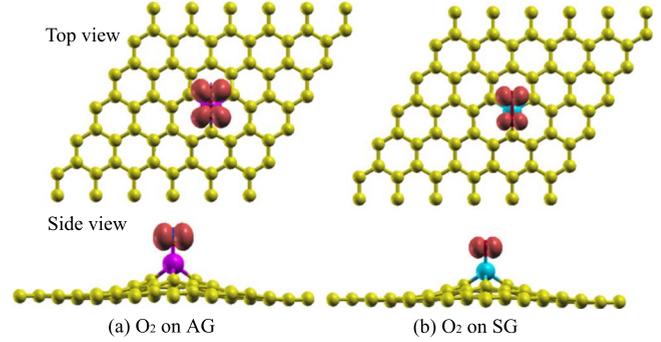


FIG. 5. (Color online) Spin density in O_2 adsorption on doped graphene. (a) In O_2 -AG chemisorption system; (b) O_2 -SG chemisorption system. The isovalues are ± 0.002 a.u.

spin polarization for AG and SG with magnetic moments of $1.00 \mu_B$ and $0.33 \mu_B$, but the magnetization in PG vanishes after O_2 adsorption. For AG and SG, the spin polarization is mainly located in the O atoms, which is also very localized as shown in Fig. 5. Therefore, O_2 adsorption may introduce Kondo effect into AG and SG systems.

The electronic properties are also investigated by the analysis of DOS (PDOS) and Löwdin charges. For AG after adsorption, the analysis of Löwdin charges shows that O_2 molecule accepts $0.44e^-$ from Al atom, and $0.72e^-$ transfers from Al to the three nearest C atoms (0.24 per atom). The DOS of AG before and after adsorption of O_2 is shown in Fig. 6. Al has three valence electrons, and therefore can be hole doping for graphene, as shown in Fig. 6(a), where the minimum of DOS shifts above the Fermi level. Chemisorption of O_2 introduces spin polarization, which creates the difference of the DOS mainly around the Fermi level, as shown in Fig. 6(b). The peak at Fermi level for spin-down electrons is contributed by the O_p orbital according to the PDOS analysis, shown in Fig. 6(c).

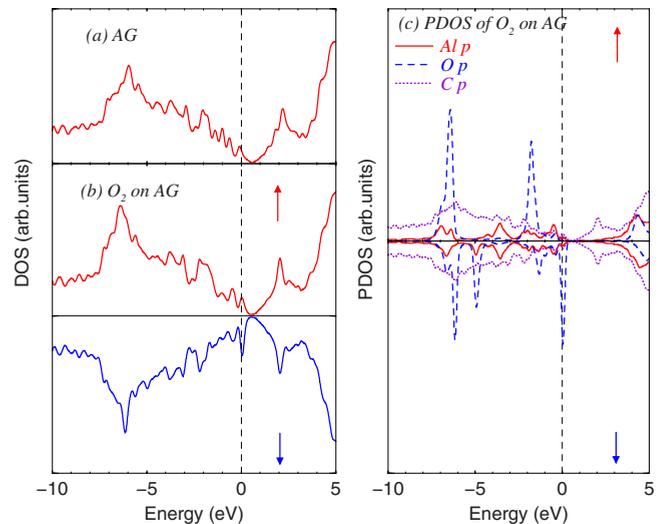


FIG. 6. (Color online) Total and partial DOS for AG and O_2 -AG chemisorption system. (a) Total DOS of AG before adsorption of O_2 ; (b) total DOS of AG after adsorption of O_2 ; (c) PDOS of atoms in chemisorbed system. The arrows denote the spin-down (\downarrow) states and spin-up (\uparrow) states. The zero energy is the Fermi level.

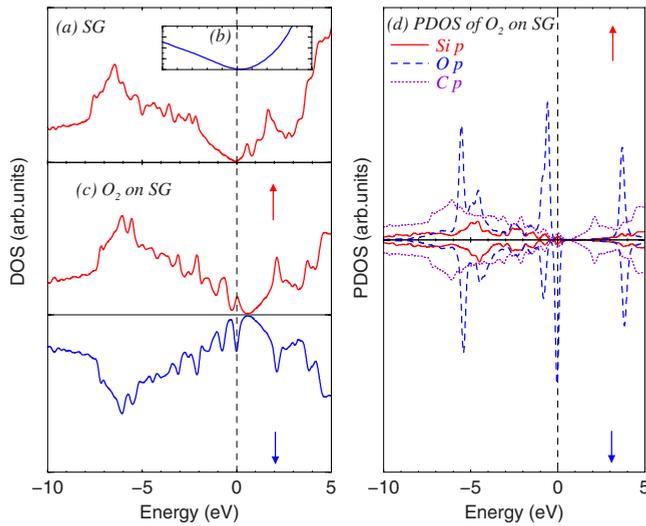


FIG. 7. (Color online) Total and partial DOS for SG and O₂-SG chemisorption system. (a) Total DOS of SG before adsorption of O₂; (b) DOS of SG with 3% concentration; (c) total DOS of SG after adsorption of O₂; (d) PDOS of atoms in chemisorbed system. The arrows denote the spin-down (↓) states and spin-up (↑) states. The zero energy is the Fermi level.

For chemisorption of O₂ on SG, O₂ molecule accepts about 0.92e⁻ from Si atom, and about 0.23e⁻ transfers from Si atom to every nearest C atom. Si has four electrons, the same as C atom. Therefore, the doping of Si should not shift the Fermi level of graphene, as shown in Fig. 7(a). It is worth pointing out that the electronic structures are dependent on the dopant concentration, as shown in Fig. 7(b), and the electronic band of SG system is open with a gap of 0.1 eV. Nevertheless, it does not affect the configuration of chemisorption of O₂ on SG. O₂ adsorption introduces magnetization with 0.33 μ_B. As shown in Fig. 7(c) and 7(d), the difference of the DOS between spin-up and spin-down electrons is mainly caused by O*p* orbital. The DOS peak of spin-up electrons at the Fermi level is caused by the p_z orbital in C atom, while the peak of spin down by O*p*. Moreover, the hybridization of Si*p*, O*p*, and C*p* orbitals also happens here.

For O₂ on PG, about 0.82e⁻ transfers from P atom to two O atoms, and about 0.24e⁻ from P atom to every nearest C atom. Before O₂ binding, PG is magnetic with 1.05μ_B. Here, charge analysis shows us that every nearest C atom accepts about 0.18 e⁻ from P atoms, and about 4.3 e⁻ remains in P atoms. That is to say, there is about one electron unpaired, inducing about 1μ_B magnetic moment. After adsorption of O₂, the hybridization between P and O, even including C, employs the unpaired electron, and then the spin polarization vanishes. According to the DOS of PG before adsorption of O₂, as shown in Fig. 8(a), the difference of DOS between spin-up and spin-down electrons mainly locates around the Fermi level. The binding of O₂ evaporates the magnetization and creates a peak at the position of -0.75 eV, as shown in Fig. 8(b), which is caused by the hybridization of P*p*, O*p*, and C*p* orbitals, as shown in Fig. 8(c).

C. Adsorption of oxygen on BG and NG

B and N belong to the second group elements in the periodic table, which have 2*s*2*p* configurations for electrons

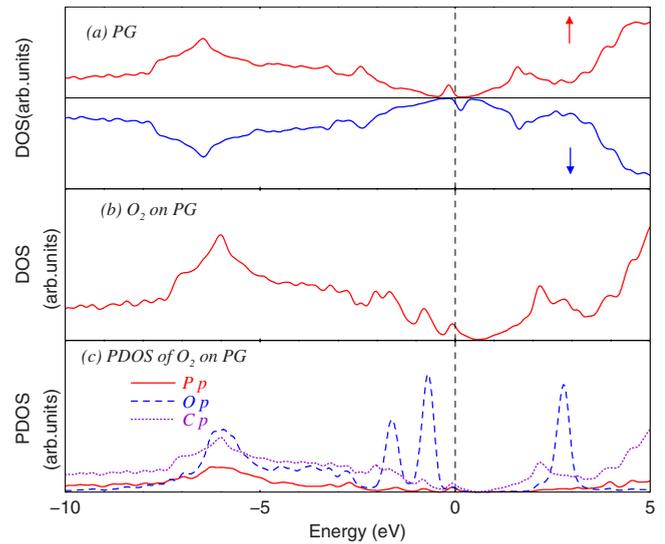


FIG. 8. (Color online) Total and partial DOS for PG and O₂-PG chemisorption system. (a) Total DOS of PG before adsorption of O₂; (b) total DOS of PG after adsorption of O₂; (c) PDOS of atoms in chemisorbed system. The arrows denote the spin-down (↓) states and spin-up (↑) states. The zero energy is the Fermi level.

and are the nearest elements for C. The extension of electrons of B, C, and N is similar. Therefore, there is no local distortion when B and N are doped in graphene. The length of B-C is 1.4794 Å, larger than that of N-C with 1.4079 Å. B and N atoms do not have elevation above graphene, and there is also no spin polarization. O₂ is physisorbed on BG and NG, which is the same as O₂ on B-doped graphite.⁴¹ The physisorption does not change the structures of BG and NG significantly, and the magnetic moments of O₂ is also almost retained, as shown in Fig. 9(a). The spin density of O₂-NG is very similar. The spin density of O₂-BG system concentrates in the O₂ molecule, which is almost the same as the spin density of isolated O₂ molecule, shown in Fig. 9(b). The O₂ molecule is far away from graphene with a distance larger than 3.5 Å and a relatively small adsorption energy. Furthermore, B and Al, N and P belong to the same group elements and have very similar valence electron configurations, and

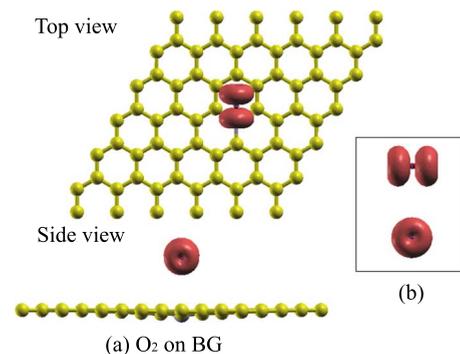


FIG. 9. (Color online) Spin density in O₂ adsorption in (a) O₂-BG physisorption system, and (b) isolated O₂. The isovalues are ±0.005 a.u.

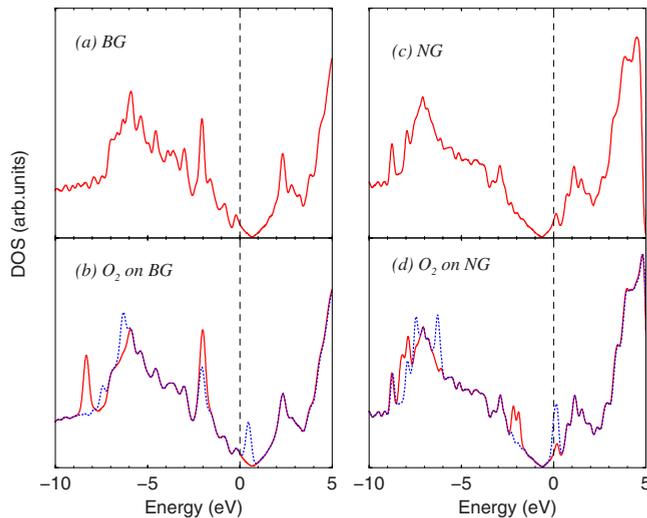


FIG. 10. (Color online) (a) Total DOS of BG before adsorption of O_2 ; (b) total DOS of BG after adsorption of O_2 ; (c) total DOS of NG before adsorption of O_2 ; (d) Total DOS of NG after adsorption of O_2 ; red solid line represents spin-up states and blue dashed line spin-down states in (b) and (d). The zero energy is the Fermi level.

their behaviors caused by O_2 molecule are so different, it can be induced that one important reason for this phenomenon is the local curvature in AG and PG. This is also in agreement with the conclusion of local curvature enhancing chemical reactivity of doped graphene.¹⁹ About this local curvature, as in Table I, only the B and N dopants are not elevated, and the B-C and N-C bond lengths are close to C-C bond in graphene. By contrary, other dopants are elevated, and the X-C bonds are much longer than C-C bonds. Therefore, it can be concluded that dopant X is elevated only when the length of X-C is appreciably larger than that of C-C.

Although O_2 cannot bind stably on BG and NG, it can still affect the electronic properties at low temperature at least. The dopant of Boron can hole-dope graphene and Nitrogen electron-dope graphene, as shown in Figs. 10(a) and 10(c), where the Dirac point shifts above (BG) or below (NG) the Fermi level. After adsorption of O_2 , the spin polarization is introduced and the DOS is changed. One DOS peak around Fermi level appears for spin-down electrons of BG and NG physisorbed O_2 molecule, caused by O_p orbital; but the DOS of spin-up electrons is very similar to that of

BG before adsorption. This means that the change in DOS is concentrated on the O_2 molecule. However, this effect should not exist at room temperature because of the very weak adsorption and the long distance between O_2 and graphene. Furthermore, the charge transfer between O_2 and BG or NG is very small compared with the chemisorption, indicating the small change for the conductance of the system. It should be noticed that O_2 acts as a donor for BG through donating $\sim 0.08 e^-$ to BG system. Although the charge transfer of the physisorbed system using the figure of the single electron Kohn-Sham equation is under debate, the trend of this small charge transfer is reliable.

IV. CONCLUSION

In conclusion, our simulation studies reveal that most of doped graphene are sensitive to O_2 molecule. The local curvature caused by doped atoms is very important to the reactivity for gas molecules. BG and NG are inert to molecular oxygen, while graphene with Al, Si, P, Cr, and Mn doping allows O_2 to form stable chemisorption states, which affects the magnetic, electronic, and atomic properties of graphene. O_2 acts as an acceptor in all chemisorbed configurations, and introduces localized spin polarization except on PG. In particular, O_2 on CG is AFM, and O_2 can retain its magnetic moments on B- and N-doped graphene. Significantly, O_2 adsorption may introduce Kondo effect into CG, MG, AG, and SG systems. Most of systems with O_2 on doped graphene behave as metallic materials. Therefore, a combination of foreign atom doping followed by exposure to air may be an effective way to tune the electronic and magnetic properties of semimetal and unpolarized graphene. However, the potential usage of doped graphene as gas sensors should be dependent on the sensitivity to O_2 molecule in air. When chemisorption of O_2 on doped graphene happens, the sensitivity to other gases should be affected significantly, which may prevent it from being effective gas sensors.

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