Modulating the electronic and magnetic structures of P-doped graphene by molecule doping

# Modulating the electronic and magnetic structures of P-doped graphene by molecule doping

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## Abstract

The adsorption of gas molecules on P-doped graphene (PG) was theoretically studied using density-functional theory in order to find the possibility of modulating electronic and magnetic ordering of graphene. $H_2$, $H_2O$, $CO_2$, CO, $N_2$ and $NH_3$ molecules are physisorbed, while NO, $NO_2$, $SO_2$ and $O_2$ molecules are strongly chemisorbed on PG through the formation of P–X (X = O, N, S) bonds. P dopant introduces global spin polarization into graphene with order of 1.05 $\mu_B$. Chemisorption of $NO_2$ and $SO_2$ makes the spin polarization and projected density of states (PDOS) of molecules localized. NO also induces a partly localized spin state and $O_2$ an unpolarized system. Meanwhile, the systems of $NO_2$ and $O_2$ on PG are metallic, while NO and $SO_2$ on PG are half-metallic. Therefore, the properties of PG are strongly dependent on the types of molecules adsorbed, and the method of combining foreign atom doping followed by exposure to air is effective for the engineering of graphene.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

There is currently strong interest in graphene and graphene-based materials [1–4]. Among the many reasons for the renewed interest is the observation that the transport properties of carbon nanostructures (such as nanotube bundles or 'buckypaper'), exhibit large changes upon exposure to several gases [2, 3]. This observation may open two ways to apply graphene materials: first, the production of gas sensors with high sensitivity and fast response time [5, 6]; second, the potential modulation of the electronic and magnetic properties of graphene by gas doping [7–10].

It is well known that if a band gap and magnetic moment can be introduced into graphene, the applications of graphene should be extended much more widely in nanoelectronics and spintronics. Various methods for opening a gap or introducing spin polarization have been developed. In particular, chemical doping is a well known and widely used method of manipulating the electronic and magnetic properties of graphene. For example, different atoms such as boron, nitrogen [11–13], phosphorus [14], sulfur [15], transition metals [16] and boron clusters [17] can substitute carbon atoms in graphene or single-walled carbon nanotubes (SWCNTs), and then change the electronic and magnetic properties dramatically. Meanwhile, foreign gas molecules can also induce different electronic and magnetic properties of graphene through charge transfer and their intrinsic magnetic properties [7–10]. However, it has been shown that most gases are physisorbed on pristine graphene [18, 19], indicating that the effect of gas molecules such as water and ammonia [9] on the electronic structure of graphene is not stable.

We can imagine easily that the presence of gas molecules is expected to impact significantly on the properties of doped graphene in actual operating conditions and practical applications. Therefore, how the gas molecules affect the doped graphene materials is worth exploring more. For example, the unpolarized S-doped graphene (SG) [15] can be magnetic after $NO_2$ adsorption [6], which is important for its extended applications. Thus, adsorbed atoms or molecules can change the electronic properties [6, 20] and introduce

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spin polarization [21], including the complicated Kondo effect. Besides, the effect of $O_2$ on the electronic properties of carbon-doped boron nitride nanotubes [20] gives us some clues that combining 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.

Very recently, P-doped SWCNTs were synthesized using the chemical vapor deposition (CVD) method, and the calculation showed the localization of spin polarization [14]. Previous studies of SG and P-doped graphene (PG) have concluded that the PG could be quite a lot more reactive [22], indicating that its properties can be more potentially affected by foreign gas molecules. Therefore, considering the wide usage of P-doping in the semiconductor industry [23, 24], we chose PG as our object to study the influence of gas adsorption on doped graphene from first principles.

We find that NO, $NO_2$, $SO_2$ and $O_2$ molecules are strongly chemisorbed on P-doped graphene, via the formation of P–X (X = O, N, S) bonds. Furthermore, the distributions of spin density and projected density of states (PDOS) of impurities show that the spin states in PG and NO–PG systems are over the entire supercell, while the spin states in $NO_2$–PG and $SO_2$–PG systems are very localized. $O_2$–PG is not polarized. In the end, the analysis of the density of states (DOS) shows that the electronic properties are expected to be changed when the gas molecules are adsorbed on the PG: $NO_2$–PG and $O_2$–PG systems are metallic, while NO and $SO_2$ induce a band gap only for minority spin states (half-metallicity).

## 2. Computational details

We perform density-functional theory (DFT) calculations using the Perdew–Burke–Ernzerhof (PBE) [25] approximation to the exchange–correlation potential [26]. Spin polarization is allowed in all calculations. The system is modeled as a $4 \times 4$ supercell of graphene (32 C atoms) with a P atom substituting a C atom and a single molecule adsorbed onto it. With this model, the concentration of P dopant is about 3%. In the direction normal to the surface, the supercell extends for 15 Å. The same model has been used successfully in [19]. A larger model with $6 \times 6$ graphene was also tested, and there was no obvious difference found. A plane-wave basis set up to a kinetic energy cutoff of 25 Ryd for the wavefunction and of 200 Ryd for the charge density is used. The Brillouin zone is sampled using a $5 \times 5 \times 1$ Monkhorst–Pack [27] grid and Methfessel–Paxton [28] smearing of 0.01 Ryd. A $15 \times 15 \times 1$ Monkhorst–Pack grid and the tetrahedron method [29] are used for the calculation of DOS, and simple Gaussian broadening with a width of 0.01 Ryd for the calculation of PDOS. Atomic positions are optimized until the maximum force on any atom is less than 0.001 au. We have tested all these parameters, and found they are good for a strict energy-convergence criterion. All calculations are performed using the Quantum-ESPRESSO package [30]. It is worth noting that the van der Waals interaction is not considered within the GGA approximation in DFT, but it should give reasonable results for the adsorption energies/geometries and the electronic structures of graphene with adsorbates.
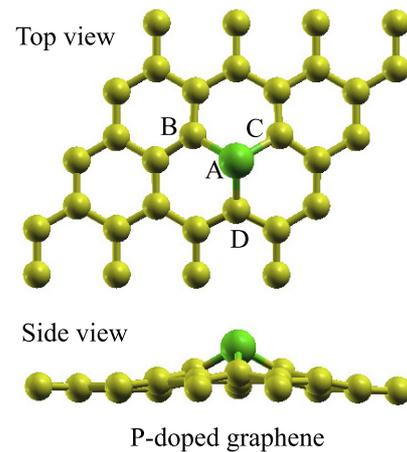


**Figure 1.** The most stable relaxed structures of PG. The P atom is labelled A.

The adsorption energy is defined as the difference between the system with a bound gas molecule and the sum of the energy of the isolated molecule and of the PG or pristine graphene layer. In order to minimize systematic errors, the same supercells and $k$-point grids are used for all calculations.

The distance from the adsorbate to the graphene surface is calculated from the atom of the molecule nearest to the graphene layer and the carbon atoms of the graphene sheet or the P atom of the doped graphene layer.

For the case of pristine graphene, three adsorption sites are considered: on top of C atom (T); the center of a carbon hexagon (C); the bridge site of a C–C bond (B). For these sites, several configurations with different orientations of the molecules as discussed in [19] are calculated. In all cases, the molecules are found physisorbed at the ground states, and some metastable chemisorbed configurations are also found but with very high energies, which is in agreement with the previous results [18, 19]. In this paper, we are concerned only about the results of gas adsorption on PG.

## 3. Results and discussion

When one P atom replaces a C atom in the graphene plane, as shown in figure 1, the geometric structure of PG undergoes a significant rearrangement, due to the much larger size of the P atom with respect to C. The P atom protrudes out of the graphene plane at a distance of 1.19 Å. The P–C bond length elongates to 1.765 Å from the ideal C–C bond length of 1.420 Å. This is associated with a distortion of hexagon structures adjacent to the P atom, which is similar to what is observed in Al-doped SWCNTs [31] or S-doped graphene [15, 22]. The formation energy of PG is found to be 2.17 eV according to the definition in [22], indicating possible synthesis of PG.

We look for the adsorption of a single gas molecule on the top of the P atom of PG, starting from the same adsorption sites mentioned above as the initial configurations. After relaxation, we find that $H_2$, $H_2O$, $CO_2$, CO, $N_2$ and $NH_3$ are physisorbed, by the large distances from the graphene plane, as shown in table 1. By contrast, $O_2$, NO, $NO_2$ and
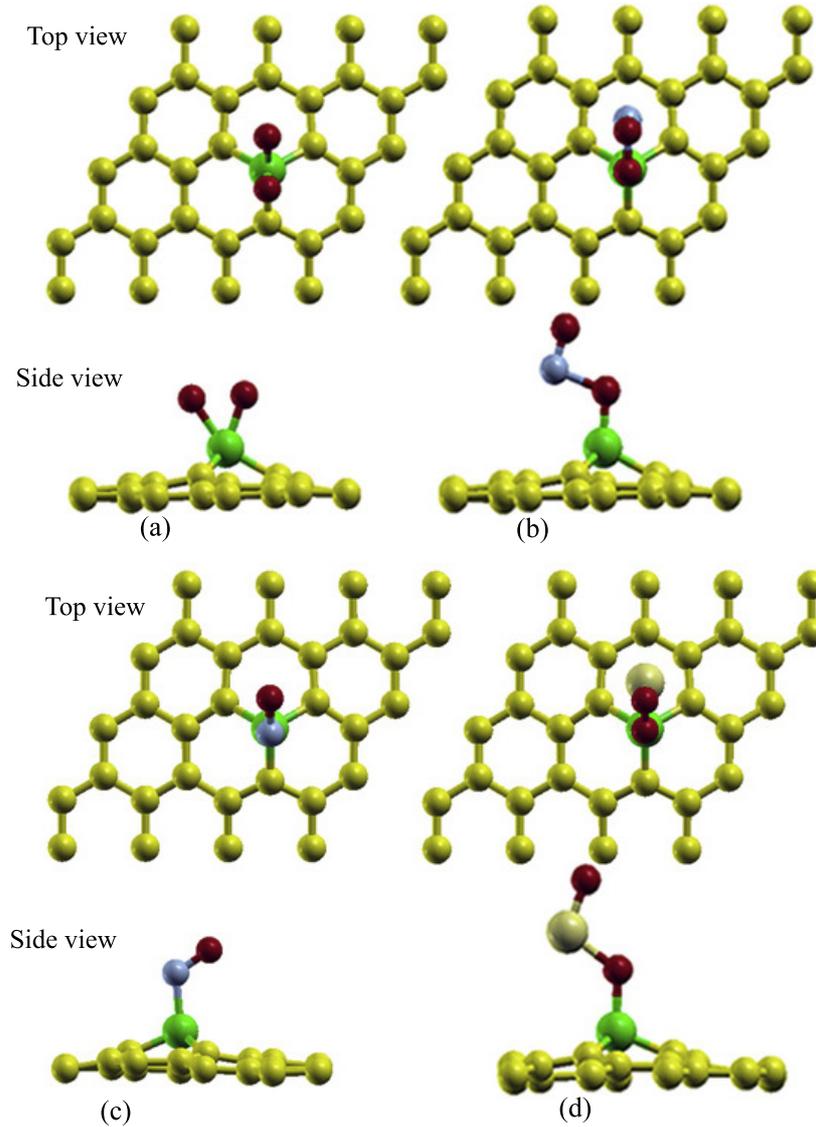
**Figure 2.** The most stable relaxed structures of $O_2$ on PG (a) and $NO_2$ with O downwards (D) on PG (b), NO with N downwards (U) on PG (c), and $SO_2$ with O upwards (D) on PG (d), respectively.

**Table 1.** The most stable configurations of physisorption of gas molecules on P-doped graphene. Adsorption energy ($E_a$ (eV)), equilibrium molecule–graphene distance ($d$ (Å)).

|       | $H_2$   | $H_2O$  | $N_2$   | $CO_2$  | CO      | $NH_3$  |
|-------|---------|---------|---------|---------|---------|---------|
| $E_a$ | −0.0143 | −0.0469 | −0.0091 | −0.0107 | −0.0685 | −0.0146 |
| $d$   | 3.3625  | 3.4650  | 4.2252  | 4.0019  | 4.3139  | 4.5685  |

SO$_2$ are found chemisorbed through the formation of P–X (X = O, N, S) bonds. The most stable relaxed configurations of them are shown in figure 2. The adsorption of these gas molecules causes a structure change in the PG, resulting in shorter P–C bonds. The P–C bond lengths change from $l_{AB} = l_{AC} = l_{AD} = 1.765$ Å for PG without adsorbed molecules, to $l_{AB} = l_{AC} = 1.744$ Å, $l_{AD} = 1.756$ Å for $O_2$ adsorption; $l_{AB} = l_{AC} = 1.732$ Å, $l_{AD} = 1.730$ Å for $NO_2$ adsorption; $l_{AB} = l_{AC} = 1.709$ Å, $l_{AD} = 1.704$ Å for NO adsorption; $l_{AB} = l_{AC} = 1.697$ Å and $l_{AD} = 1.695$ Å for $SO_2$ adsorption

**Table 2.** Results of the most stable configurations of $O_2$, $NO_2$, NO and $SO_2$ molecules on the PG surface. Adsorption energy ($E_a$), the bond length of P–X (X = O, N, S) ($d$), magnetic moments ($M_B$) and Löwdin charge [32] transfers from PG to gas molecules $c$ are shown.

|              | $O_2$   | $NO_2$  | NO      | $SO_2$  |
|--------------|---------|---------|---------|---------|
| $E_a$ (eV)   | −1.0895 | −1.8875 | −0.5093 | −0.3216 |
| $d$ (Å)      | 1.6279  | 1.5364  | 1.8074  | 1.6580  |
| $M_B$ ($\mu_B$) | 0.00 | 0.58    | 2.00    | 0.96    |
| $c$ (e$^-$)  | 0.8181  | 0.6198  | 0.4995  | 0.5007  |

(A, B, C, D denote the different atoms, as shown in figure 1). More specifically, for adsorption of $O_2$, two bonds of P–O are formed, as shown in figure 2(a), and the distance between two O atoms is 1.560 Å in this case. Adsorption energies and bond lengths are shown in table 2, indicating that the $O_2$, NO, $NO_2$ and $SO_2$ are chemisorbed with a sizable adsorption energy and a short bond length of P–X.
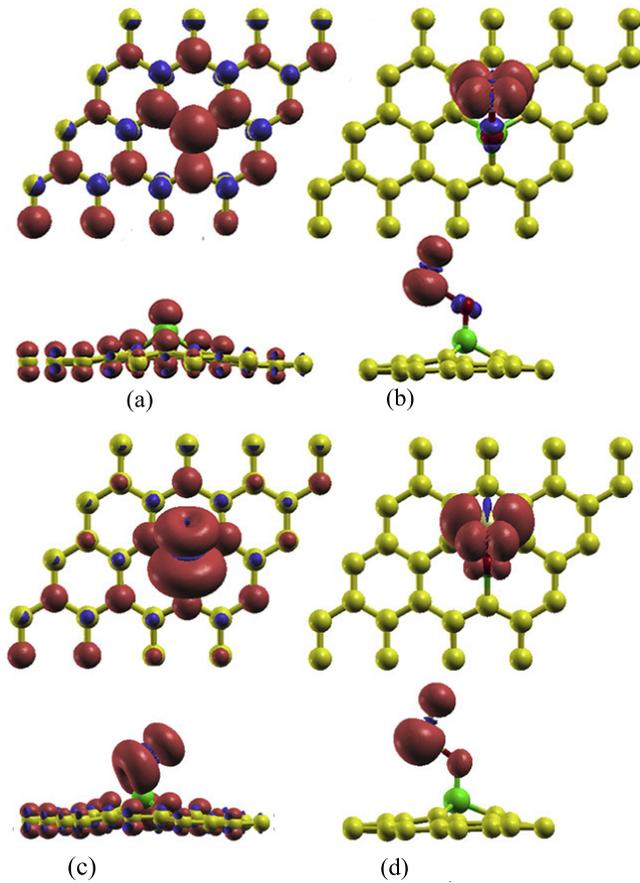
**Figure 4.** The DOSs of the most stable configurations of PG (a), the NO$_2$–PG system (b), the NO–PG system (c), the SO$_2$–PG system (d), (e) and the O$_2$–PG system (f). The scale of the axes between the small panel and the big panel is equal. The solid line refers to DOS of spin-up and the dotted line to spin-down for the adsorption of the molecule system.



**Figure 3.** Spin density in PG (a), in NO$_2$ on PG (b), in NO on PG (c) and in SO$_2$ on PG (d). The isovalues are $\pm 0.002$ au.

P atom doping introduces spin polarization into graphene with magnetic moment of 1.05 $\mu_B$. It is interesting to find a metastable configuration of PG with all atoms in graphene including P in the same plane, whose energy is 1.4 eV higher than that of the stable one. But it should be noticed that there is only a very low energy barrier (about 0.01 eV) from this 'flat' configuration to the stable one according to the climbing-image nudged elastic band (CI-NEB) calculation, and it is very easy to overcome this barrier to reach the stable configuration. No magnetization appears in this metastable configuration. Therefore, the local curvature induced by the P atom plays an important role in the generation of magnetization. Furthermore, the spin state of PG is distributed over the whole supercell and the direction of the spin state between the nearest two carbon atoms is opposite, as shown in figure 3(a), which is different from the local spin distribution in P-doped SWCNTs [14]. We also tested the spin distribution of a larger supercell of 6 × 6 graphene, and the same distribution is found. But it is noticed that the spin density around the P atom is much larger than that around other carbon atoms, which indicates that the spin state has a character of partial localization.

After adsorption of gas molecules, the character of spin polarization changes dramatically. The spin polarization disappears with chemisorption of O$_2$. It is clear that for the P atom, five covalent bonds are formed in this configuration, with
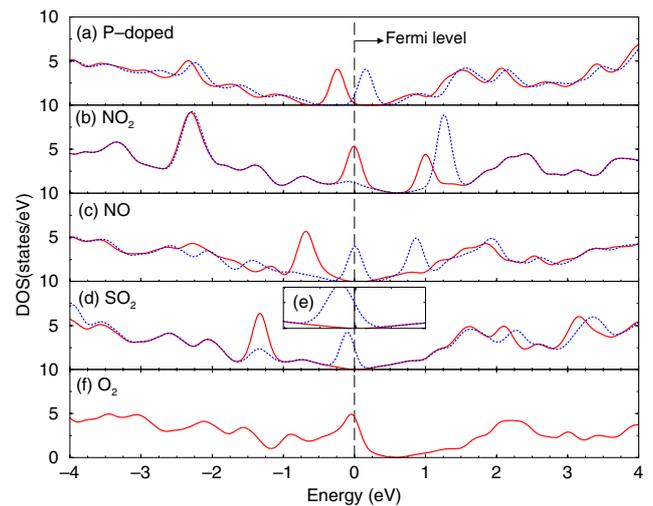
three P–C bonds and two P–O bonds, equaling five valence electrons of P element. Therefore, there is no unpaired electron left, giving rise to no magnetization. For adsorption of NO$_2$, NO and SO$_2$, the spin polarization remains with magnetic moments of 0.58, 2.00 and 0.96 $\mu_B$, respectively. The spin states of these systems are shown in figures 3(b)–(d). It is shown that the spin is distributed in the gas molecules for adsorption of NO$_2$ and SO$_2$, indicating a strong localization. For adsorption of NO on PG, the spin distribution is similar to PG without gas adsorption, which is partly localized. The chemisorption makes these systems good materials in spintronics with their localized magnetization, which is one of the typical characteristics of the Kondo effect.

To further investigate the changes of electronic structure caused by the adsorption of a single molecule on PG, the DOSs for PG and after the adsorption of NO$_2$, NO, SO$_2$ and O$_2$ are calculated. As shown in figure 4(a), P-doping introduces spin polarization due to the unbonded electrons of the P atom added to the system and the PG system behaves as a metal. For the configurations of PG with the most stable chemisorbed NO$_2$, NO, SO$_2$ and O$_2$, the DOSs change much, as shown in figures 4(b)–(f). For NO$_2$ on PG, the DOS of spin-up electrons increases greatly around the Fermi level, and decreases at a position of around 0.5 eV above the Fermi energy for both spin-up and spin-down electrons. NO$_2$–PG is also a metallic system, as in figure 4(b). Interestingly, for NO and SO$_2$ adsorption, as in figures 4(c)–(e), respectively, the DOSs of spin-up and spin-down show different properties. There is a sharp peak for spin-down electrons, but a band gap for the spin-up electrons. For the spin-up electrons of NO and SO$_2$ adsorption, the band gaps are 0.25 eV and 0.18 eV, respectively. These systems are much like the 'half-metals' [33]. For the O$_2$–PG system, it is unpolarized and behaves as a metallic system. It is clear that the DOS increases greatly around
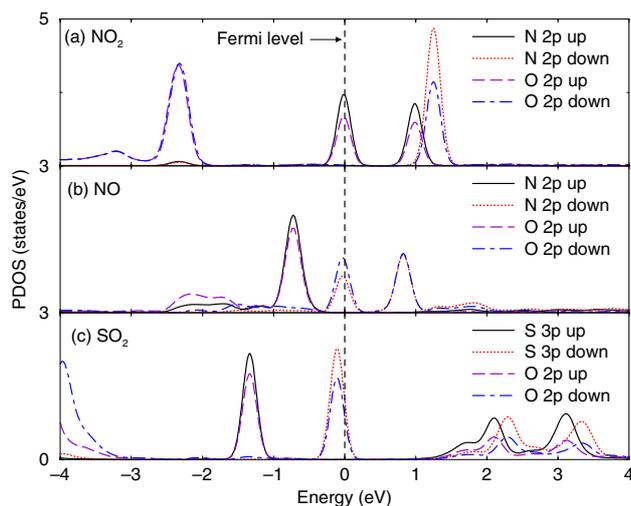
**Figure 5.** The PDOSs of gas molecules of the most stable configurations of the $NO_2$–PG system (a), the NO–PG system (b) and the $SO_2$–PG system (c). Up represents spin-up, down represents spin-down.

the Fermi level. All the properties above show that the chemisorbed molecules of NO, $NO_2$, $SO_2$ and $O_2$ on the PG surface will change the electronic and magnetic properties of the doped graphene layer. The large charge transfer shown in table 2 is one of the main mechanisms to induce these changes. Furthermore, considering that the Löwdin charge does not satisfy any sum rules, the spilling parameter [34] is calculated. The spilling parameter is a measure of how well the occupied electron manifold superposes to the one spanned by the atomic wavefunctions used to build the PDOS. The smaller it is, the better is the superposition. In all cases, the spilling parameters are less than 0.01, which means most of the Hamiltonian eigenstates (at least 99%) are included in the subspace spanned by the atomic basis.

In order to understand the localization induced by the impurities, analyses of the PDOS of the adsorbed molecules are performed. In figure 5, the PDOS of $NO_2$, NO and $SO_2$ is shown. It is very clear that there is a PDOS peak at the position of the Fermi level for every molecule. For the PDOS of $NO_2$ and $SO_2$, the PDOS peak at the Fermi level is very isolated, as shown in figures 5(a) and (c), where the DOS of electrons with different spin polarized directions is totally different, indicating the localized spin polarization. This is also in agreement with the spin densities in figures 3(b) and (d), which may point to the possible Kondo effect in the system. For the PDOS of NO molecule, three peaks are very close and all around the Fermi level, as shown in figure 5(b). The isolated NO molecule has isolated energy levels and after adsorption, the bound levels of NO molecule are moved to around the Fermi level due to the charge transfer between the NO molecule and PG. This phenomenon is very interesting, and it tells us the possible NO-induced quasibound states in PG by the coupling of these states with the electronic states of PG. They are the acceptor levels produced by NO and are similar to impurity-induced quasibound states in carbon nanotubes [35]. Therefore, the conductivity of the system should be changed dramatically due to the existence of these quasibound states.

These changes of electronic and magnetic properties are very useful. On the one hand, by detecting the change of conductivity of P-doped graphene systems before and after adsorption of $NO_2$, NO, and $SO_2$, the presence of these toxic gases can be detected sensitively. On the other hand, combining P-doping and gas-doping should be a good path to modulate the electronic and magnetic properties of graphene.

## 4. Conclusion

In conclusion, the adsorption of gas molecules ($H_2$, $H_2O$, $O_2$, $CO_2$, CO, $NO_2$, NO, $SO_2$, $NH_3$, $N_2$) on PG is investigated using first principles calculation. $O_2$, NO, $NO_2$ and $SO_2$ molecules are strongly chemisorbed onto the P-doped graphene, forming P–X (X = O, N, S) bonds with large adsorption energy; other molecules are physisorbed. In the chemisorption, remarkable changes of electronic and magnetic properties are induced by the adsorption. Adsorption of $O_2$ on PG makes the spin polarization of PG disappear; adsorption of $NO_2$ and $SO_2$ induces a strong localized distribution of spin density, which makes $NO_2$–PG and $SO_2$–PG good materials as candidates for Kondo impurities. Adsorption of NO also induces a large magnetic moment of 2.0 $\mu_B$, which is partly localized. Finally, it is interesting to notice that the systems of $O_2$–PG and $NO_2$–PG are metallic, and NO–PG and $SO_2$–PG are half-metallic, which is also very useful in the field of electronics and spintronics.

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