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Adsorption of CO molecules on doped graphene: A first-principles study

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As a typical kinds of toxic gases, CO plays an important role in environmental monitoring, control of chemical processes, space missions, agricultural and medical applications. Graphene is considered a potential candidate of gases sensor, so the adsorption of CO molecules on various graphene, including pristine graphene, Nitrogen-doped graphene (N-doped graphene) and Aluminum-doped graphene (Al-doped graphene), are studied by using first-principles calculations. The optimal configurations, adsorption energies, charge transfer, and electronic properties including band structures, density of states and differential charge density are obtained. The adsorption energies of CO molecules on pristine graphene and N-doped graphene are −0.01 eV, and −0.03 eV, respectively. In comparison, the adsorption energy of CO on Al-doped graphene is much larger, −2.69 eV. Our results also show that there occurs a large amount of charge transfer between CO molecules and graphene sheet after the adsorption, which suggests Al-doped graphene is more sensitive to the adsorption of CO than pristine graphene and N-doped graphene. Therefore, the sensitivity of gases on graphene can be drastically improved by introducing the suitable dopants. [http://dx.doi.org/10.1063/1.4942491]

I. INTRODUCTION

Because solid-state gas sensors have high sensitivity, wide range of applications and low cost,[1] a new generation of gas sensors has been demonstrated using carbon nanotubes (CNTs) and semiconductor nanowires in the past few years.[2] CNTs seems likely to be a great nanoscale sensor because of its fast response time and high sensitivity at room temperature.[3,4] However, there is a desire for more sensitive gas sensors in environmental monitoring, control of chemical processes, space missions, agricultural and medical applications.[5,6]

Similar to the good sensor properties of CNTs, graphene, a single atomic layer of graphite, is considered to be an excellent sensor material due to its special properties such as the two dimensional structure maximizing the interaction of absorbates on the layer, low Johnson noise, and few crystal defects.[7] A graphene sample has been reported to be used as a very sensitive gas sensor with the possibility of detecting NO_2 molecules,[8] which has encouraged the theoretical examination of the sensing properties of graphene.

It was demonstrated that donor or acceptor molecules on graphene can significantly change the electronic properties, by using first-principles methods.[9] And when gases molecules adsorbed on graphene sheet, there appears changes in the resistivity, which makes it possible for graphene to be a solid-state sensor to detect the individual gas from others. As we all know that the charge transfer

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between the gases molecules and graphene sheet relates to the orientation of the gases molecules with respect to the graphene sheet, and has nothing to do with the adsorption site.[10] Considering the above situation, we studied the different sites and orientations of CO molecules to find out the most optimal adsorption configuration.

Most of the previous work focused on pristine graphene, and predicted relatively low adsorption energies in comparison with the essential requirement of gas sensing applications.[10–12] It was reported that the detectable range and sensitivity of the single wall carbon nanotubes (SWCNTs) could be widened and improved through doping technology.[4,13,14] SWCNT coated with Pb nanoparticles has high sensitivity to H_2,[14] and SnO_2/SWCNTs hybrid material shows an enhanced sensitivity to NO_2.[14–16] Therefore, in order to improve the sensitivity for gases in graphene, doping is a kind of good methods. In this work, we report a first-principles simulation of the interactions between CO molecules and various graphene sheets. The graphene doped by nitrogen or aluminum atom has one more or one less outer electron than pristine graphene, respectively, which could represent the most widely used n-type and p-type doping methods. Meanwhile, structurally perfect graphene is also studied for comparison.

II. MODELING AND COMPUTATIONAL DETAILS

All the density functional theory (DFT) calculations were performed using VASP with the projector augmented wave (PAW) basis sets and periodic boundary conditions.[17] The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional is used, and the plane-wave cutoff energy is set as 500 eV throughout the calculations.

Each simulated system consists of a 4×4 graphene supercell (32 C atoms) with a doped atom substituting a C atom and a single CO molecule adsorbed onto it. The corresponding dopant concentration is about 3.1 %. In the direction normal to the graphene surface, the supercell extended for 15 Å in order to avoid the interference between adjacent graphene layers. In the geometrical structure optimization and self-consistent calculation, the Brillouin zone is sampled using a $5 \times 5 \times 1$ Monkhorst-Pack k-point grid and Methfessel-Paxton smearing of 0.05 eV, which is tested to give converged results for all the properties calculated. For the Energy band calculation, we use an $11 \times 11 \times 1$ Monkhorst-Pack grid and a Gaussian smearing of 0.05 eV. Atomic positions are optimized until the maximum force on any ion is less than 0.001 eV/Å for all systems.

In order to calculate the adsorption energy, we have to obtain the total energy of an isolated CO molecule. We construct a cubic supercell of length 10 Å with a single CO molecule inside.[18] And we have implemented the spin-polarized DFT calculation with the same force and energy convergence precision to the adsorption systems, and only the Gamma point is sampled in its Brillouin zone.

The adsorption energy E_{ad} of CO on graphene was calculated as Equ. (1),

$$E_{\mathrm{ad}} = E_{\mathrm{CO+graphene}} - E_{\mathrm{graphene}} - E_{\mathrm{CO}} \tag{1}$$

where $E_{\mathrm{CO+graphene}}$ and E_{CO} are the total energies of the adsorbed system, isolated graphene and CO molecule, respectively. And it is a physical quantity reflecting the adsorption strength. In this definition, the adsorption energy is generally negative, and adsorption is unstable when we get the positive values. The greater the absolute value of adsorption energy is, the more stable the system will be. Naturally, the smaller ones can testify the instability of the adsorption systems.[19–21]

Charge transfer $\triangle Q$ between CO and graphene are calculated based on the Bader charge analysis.[22] By using this method, the charge of each atom in the simulated system can be calculated, and the total system charge can also be gotten through charge accumulation. For the system of gas molecules adsorbed on pristine graphene, $\triangle Q$ can be calculated as the charge variation of gas molecules before and after the adsorption.[23,24]

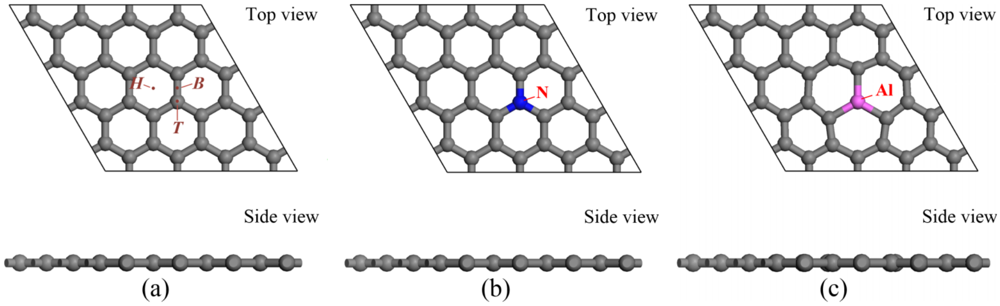

FIG. 1. Top views and side views of different graphene models after full relaxation: (a) pristine graphene. There are three different adsorption sites: *T*, *B*, and *H* which stand for the position above the carbon atom, above the carbon-carbon bonding, and above the center of the hexagonal ring of graphene, respectively; (b) N-doped graphene; (c) Al-doped graphene.

III. RESULTS AND DISCUSSIONS

As for the doped graphene layer alone, both N-doped graphene and Al-doped graphene retain the planar form of pristine graphene after full relaxation. And their corresponding models are shown in Fig. 1. Compared with the carbon-carbon bond length of 1.43 Å in pristine graphene, which is consistent with the experimental value. The carbon-nitrogen atom distance is found to be 1.41 Å for N-doped graphene, and the carbon-aluminum atom distance 1.71 Å for Al-doped graphene, which are in agreement with previous theoretical work in Al-doped SWCNTs and Al-doped graphene.[25–27] Compared with N-doped graphene, Al-doped graphene has more energy loss and larger formation energy.[28]

For the adsorption systems, the possible adsorption sites of CO molecule on graphene are shown as in the top view of Fig. 1(a). They are top, hollow, and bridge sites, namely, the tops of a carbon atom (*T*), the center of a carbon hexagon (*H*), and the center of a carbon-carbon bond (*B*), respectively.[8] For each adsorption position above, three different orientations of CO molecule on graphene were all examined to find the optimal adsorption configuration. Two with the molecule perpendicular to graphene surface, with the O atom above the C atom and the other way around, and one parallel to the surface.

Fig. 2 gives the most stable configurations after full relaxation of CO adsorption on pristine graphene, N-doped graphene and Al-doped graphene, respectively. The gray, red, pink and blue spheres are denoted as C, O, Al, and N atoms, respectively. It can be found from Figs. 2(a) and 2(b) that the pristine graphene and N-doped graphene have almost no change after CO molecule adsorption. While in Fig. 2(c), the adsorption of CO causes a structure change in Al-doped graphene dramatically, where the Al atom protrudes out of the graphene plane with an elevation of about

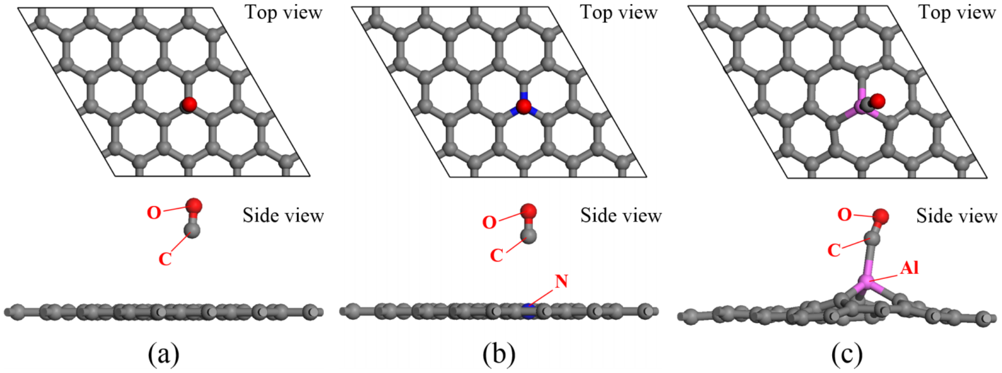

FIG. 2. Top views and side views of most stable configurations of (a) pristine graphene, (b) N-doped graphene and (c) Al-doped graphene after CO molecule adsorbed on the top site of C (N or Al) atom with O upwards.

TABLE I. Calculation results of the most stable adsorption configurations.

Adsorption system	E_{ad} (eV)	D (Å)	ΔQ (e)	C-O (Å)[a]	C-C, C-N or C-Al (Å)[b]
CO on pristine graphene	−0.0102	3.8561	−0.0011	1.1432	1.4253, 1.4253, 1.4252
CO on N-doped graphene	−0.0261	3.5540	−0.0027	1.1430	1.4140, 1.4139, 1.4139
CO on Al-doped graphene	−2.6928	2.0623	0.2346	1.1501	1.8774 ,1.8702, 1.8784

[a] C-O bond length of CO molecule.

[b] Chemical bond length of C-C, C-N, and C-Al in the corresponding graphene sheets of adsorption systems.

1.38Å. The adjacent C atoms also protrude in varying degrees, which is agreement with other similar studies.[27,28]

More calculation results of the most stable adsorbed systems were given in Table I, where D denotes equilibrium graphene-CO distance for the first three systems. For the adsorption of CO on pristine graphene and N-doped graphene, the small adsorption energies, large CO-graphene distances and little charge transfers indicate no binding between CO and graphene other than chemisorption. Al-doped graphene can adsorb the CO molecule with rather large adsorption energy of

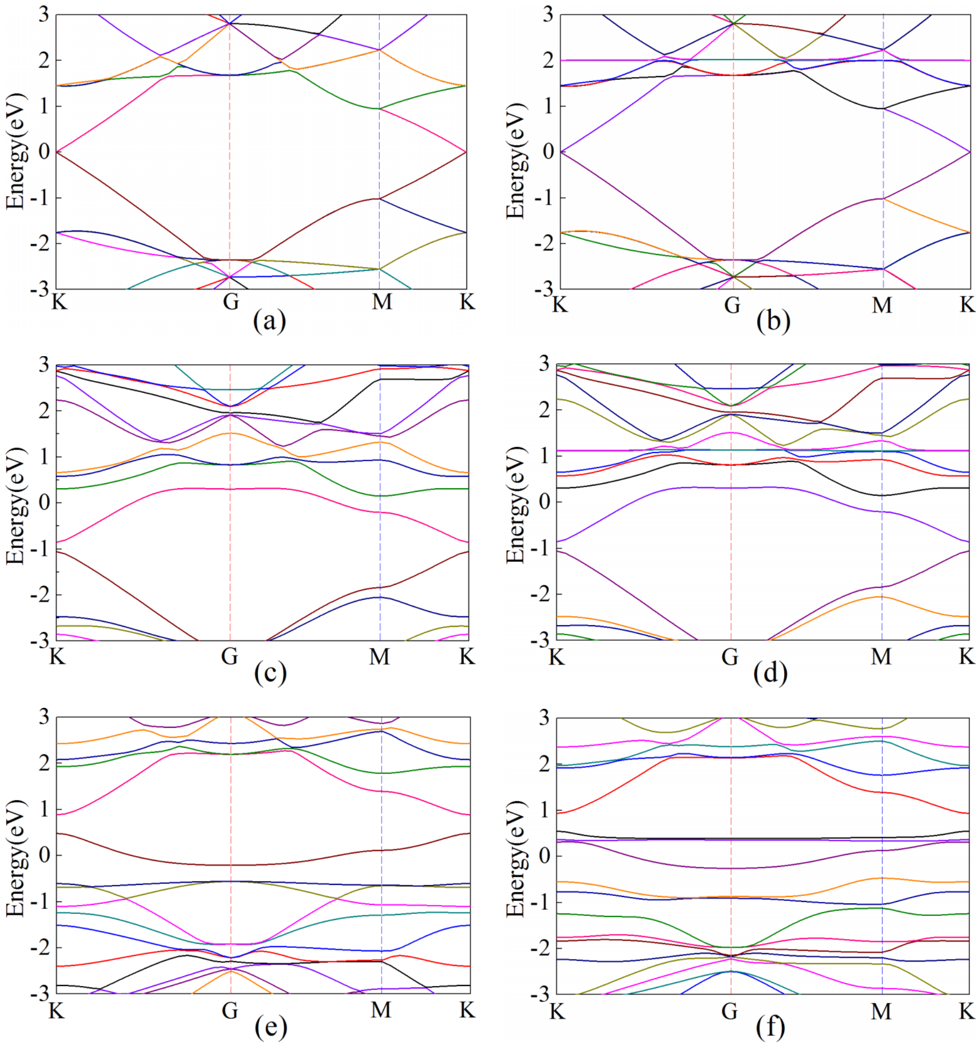

FIG. 3. Energy band diagrams of different systems, (a) Pristine graphene; (b) System of CO adsorbed on pristine graphene; (c) N-doped graphene; (d) System of CO adsorbed on N-doped graphene; (e) Al-doped graphene; (f) System of CO adsorbed on Al-doped graphene.

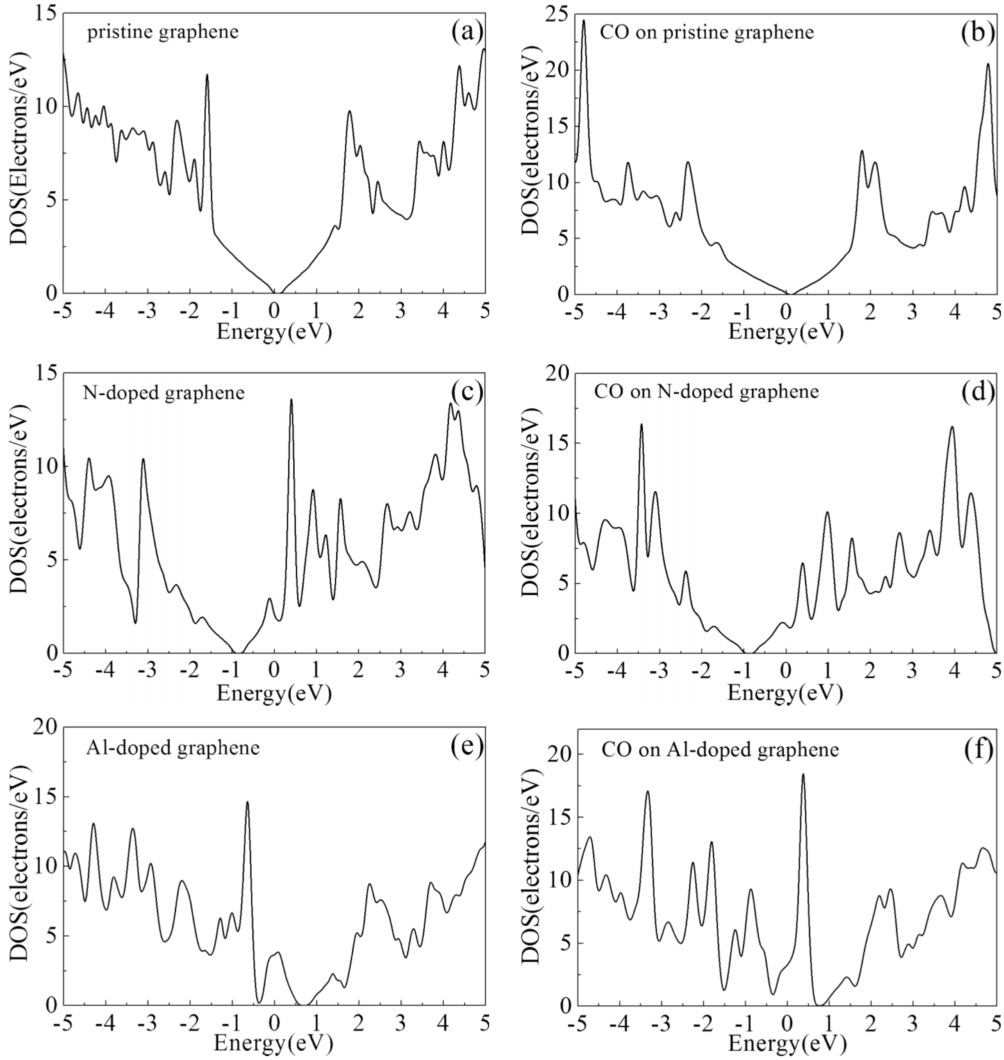

FIG. 4. Density of states (DOS) of different systems, (a) Pristine graphene; (b) System of CO adsorbed on pristine graphene; (c) N-doped graphene; (d) System of CO adsorbed on N-doped graphene; (e) Al-doped graphene; (f) System of CO adsorbed on Al-doped graphene.

−2.69 eV, and the distance is found to be about 2.06Å, which can show that Al-doped graphene is sensitive to CO molecule to some extent. The results are consistent with those reported in other studies.[29] And the charge transfer between CO molecule and Al-doped graphene is about 0.2346 e, which is larger than that of other reports. This difference may be caused by the different dopant concentration[7]

To further study the effects of adsorbed CO molecules on the electronic properties of graphene, the band structures, electronic density of states (DOS) and charge density difference are calculated for the systems with and without the adsorption. Fig. 3 gives the energy band diagrams of different systems, respectively. K, G and M are the high symmetric k points of the Brillouin zone corresponding to the systems above.

In Fig. 3(a), the band gap is close to zero, which proves that the algorithm for computing of graphene adsorption system in this paper is appropriate. After CO adsorption, the band structure is almost the same to that of pristine graphene at the vicinity of the Fermi level (the Fermi level is set at 0eV) in Fig. 3(b). It implies that pristine graphene is not sensitive to CO molecules. In Fig. 3(c), the N-doped graphene has a band gap of about 0.23 eV, which demonstrates that the algorithm in present work is appropriate.[30] And Fig. 3(d) gives that the Fermi level elevated to the conduction band on account of the alternative doping of nitrogen atom, which is due to the fact that a nitrogen atom has one more electron than a carbon atom. Therefore, the nitrogen atom acts as an n-type dopant. Though there appears a flat band at the level of about 1.2 eV in Fig. 3(d), the band structure near the Fermi level is almost not changed. As shown in Fig. 3(e), there appears a band gap of about 0.38 eV after full relaxation, which is in agreement with the conclusion that had been demonstrated.[30] Fig. 3(f) shows the Fermi level moved into the valence band because the valence electrons of the introduced Al atom are one less than C atom, which indicates Al atom can act as a p-type dopant. By doping an Al atom, impurity levels are introduced in the graphene band, which enhance the interaction between graphene and CO. The emergence of a few flat bands around the Fermi level in Fig. 3(f) can verify this point. The results here are consistent with the first part analysis in this article.

The total DOS curves of the various systems are given in Fig. 4. The analysis from the DOS closing to the Fermi level could give consistent results with the band structures shown in Fig. 3. The DOS of adsorption system of CO on pristine graphene in Fig. 4(b) has no distinct change near the Fermi level from that of pristine graphene in Fig. 4(a), although tow great peaks appear at the level of −4.78 eV and 4.82 eV after CO adsorption, it is far away from the Fermi level. So CO adsorption does not change the electronic properties of pristine graphene, and this result also illustrates pristine graphene is not sensitive to CO molecule. As shown in Fig. 4(c), the Fermi level rises into the conduction band obviously and there appears a band gap of about 0.202 eV, consistent with the results in band structures. Comparing Fig. 4(d) with Fig. 4(c), there is still no obvious changes near the Fermi level of the DOS curves.

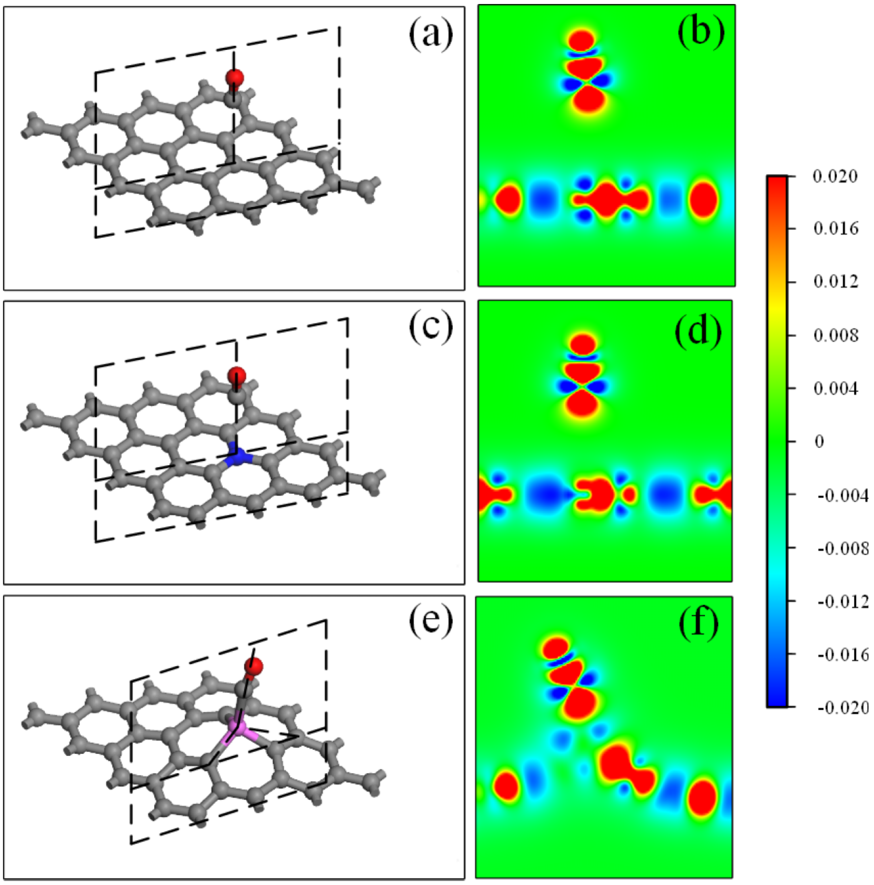

FIG. 5. Section plane and section view of charge density difference for CO molecule on pristine and doped graphene: (a) and (b), pristine graphene; (c) and (d), N-doped graphene; (e) and (f), Al-doped graphene. The black dashed line stand for the section plane. The red (blue) distribution corresponds to charge accumulation (depletion).

In Fig. 4(e), when doping an Al atom instead of a C atom in graphene, the relatively high DOS peak in a certain range near the Fermi level appears just below the Fermi level, and the energy of graphene is also reduced. This indicates that the doping Al atom induces shallow acceptor states in graphene like B atom in SWCNs,[25] thus enhancing its extrinsic conductivity. However, when the CO molecule is adsorbed on the Al-doped graphene, there appears a peak close to the Fermi level. This shows that the CO adsorption largely affects the electrical conductivity of Al-doped graphene, which means that Al-doped graphene is likely to become an important candidate for gas sensor in the future.

The differential charge density of different systems are shown in Fig. 5. The charge density difference was calculated as Equ. (2),

$$\Delta\rho = \rho_{(\mathrm{CO+graphene})\mathrm{sc}} - \rho_{(\mathrm{CO+graphene})\mathrm{nsc}} \tag{2}$$

where $\rho_{(\mathrm{CO+graphene})\mathrm{sc}}$ and $\rho_{(\mathrm{CO+graphene})\mathrm{nsc}}$ are the total charge density of the adsorbed system after and before self-consistent.

Fig. 5(a), 5(c), and 5(e) give the cross sections at which the charge transfer is calculated, while Fig. 5(b), 5(d), and 5(f) give the charge transfer between the systems before and after adsorption. The red and the blue in Fig. 5(b), 5(d), and 5(f) represent the positive and negative, respectively. Fig. 5(f) shows that a significant amount of electron transfer occurred between the CO molecules and Al-doped graphene, which indicates the interaction between CO molecule and graphene doped with Al atom is much stronger than that of CO adsorbed on pristine graphene or N-doped graphene. Also, the calculated adsorption energy has similar results with the electron transfer. From Fig. 5, one can hardly see any electron transfer from CO molecule to graphene or from graphene to CO molecule, which indicates that the adsorption of CO molecules on pristine graphene and N-doped graphene is physical adsorption, while the adsorption of CO molecules on Al-doped graphene is likely to be chemical adsorption.

IV. SUMMARY

In this article, the adsorption of CO molecules on pristine graphene, N-doped graphene, and Al-doped graphene was investigated based on the first-principle theory, including different sites and orientations. The calculation results show that the most stable adsorption configuration is the top of a carbon (nitrogen or aluminum) atom of graphene sheets. After full relaxation the configurations of pristine graphene and N-doped system have almost no change, while the adsorption of CO molecule causes a structure change in Al-doped system dramatically, where the Al atom protrudes out of the graphene plane with an elevation of about 1.38Å, and the adjacent C atoms with Al are also protrude in varying degrees. Our study of band structure, DOS, and differential charge density show that the adsorption of Al-doped system is significantly different from pristine and N-doped system. All these findings suggest pristine graphene can only physisorb CO molecules, the interaction between CO and N-doped graphene has certain enhancement, but still belongs to physical adsorption. Al-doped graphene is strongly reactive to CO molecule, and may be a good candidate for sensing CO gas.

COMPETING INTERESTS

The authors declare that they have no competing interests.

AUTHORS' CONTRIBUTIONS

The analysis of the simulation results was mainly carried out by WW and YC. The simulations were mainly conducted by YZ and CS. All authors read and approved the final manuscript. All authors read and approved the final manuscript.

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