

Gas adsorption on graphene doped with B, N, Al, and S: A theoretical study

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(Received 19 June 2009; accepted 16 November 2009; published online 8 December 2009)

The adsorption of several common gas molecules over boron-, nitrogen-, aluminum-, and sulfur-doped graphene was theoretically studied using density-functional theory. B- and N-doped graphene retain a planar form, while Al and S atoms protrude out of the graphene layer. We find that only NO and NO₂ bind to B-doped graphene, while only NO₂ binds to S-doped graphene. Al-doped graphene is much more reactive and binds many more gases, including O₂. We suggest that B- and S-doped graphene could be a good sensor for polluting gases such as NO and NO₂. © 2009 American Institute of Physics. [doi:10.1063/1.3272008]

Graphene is an interesting candidate for usage as a gas sensor, having a two-dimensional character (thus maximizing the interaction of adsorbates on the layer), few crystal defects,^{1–4} low Johnson noise.^{1–5} Recently, ultrahigh sensitivity of graphene to individual NO₂ molecules was experimentally demonstrated⁶ and theoretically explained⁷ as a direct doping effect of NO₂ molecules on graphene. Other experiments⁸ and calculations,^{9,10} however, show that NO₂ is physisorbed on pristine graphene and that room-temperature sensitivity to gas adsorption is related to the presence of impurities.^{8,11,12} This suggests that doping with impurities may allow to tune the properties and the chemical sensitivity of carbon nanostructures.^{13–15} Physisorption can create change in the conduction, but the effect of chemisorption upon conduction should be more visible and more thermally stable than the effect of physisorption. This chemisorption can be enhanced by the dopants. Impurities like B, N, Al, and S in either graphene or single-walled carbon nanotubes (SWCNT) have been studied, either theoretically^{14,16,17} or experimentally,^{18–20} but there are just a few studies on gas adsorption on doped graphene.^{14,21}

In this letter, we perform a systematic theoretical study of the ability of graphene, doped with different substitutional impurities (B, N, Al, and S), to chemically bind many common or polluting gases: H₂, H₂O, O₂, CO₂, CO, NO₂, NO, SO₂, NH₃, and N₂. We perform density-functional theory calculations using the Perdew–Burke–Ernzerhof²² generalized gradient approximation (GGA) to the exchange-correlation potential, including spin polarization in all calculations. The system is modeled as a 4×4 supercell of graphene (32 C atoms) with a single doping atom substituting a C atom and a single molecule adsorbed onto it. The corresponding dopant concentration is 3.125%. A larger 6×6 supercell (72 C atoms) gives the same qualitative results, with structural parameters within 0.02 Å from the results of the smaller supercell. In the direction normal to the surface, the supercell extends for 15 Å. Ultrasoft pseudopotentials²³ with a plane-wave basis set up to a kinetic energy cutoff of 25 Ry for the wave functions, of 200 Ry for the charge density, are used. The Brillouin zone is sampled using

a 5×5×1 Monkhorst–Pack²⁴ **k**-point grid and Methfessel–Paxton²⁵ smearing of 0.01 Ry. A 15×15×1 Monkhorst–Pack grid is used for the calculation of charge density and density of states (DOS). Atomic positions are optimized until the maximum force on any atom is less than 0.001 a.u. The adsorption energy, E_a , is defined as the difference between the energy of the system with a bound gas molecule and the sum of the energy of the isolated molecule and of the doped graphene layer. To minimize systematic errors, the same supercells and **k**-point grids are used for all calculations. The usage of GGA, and 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. All calculations are performed using the QUANTUM ESPRESSO package.²⁶

Let us consider first the doped graphene layer alone. Both boron-doped graphene (BG) and nitrogen-doped graphene (NG) retain the planar form of undoped graphene [see Fig. 1(a)]. The carbon-dopant atom distance is found to be $d_{(B-C)}=1.48$ Å for BG, $d_{(N-C)}=1.41$ Å for NG (to be compared with $d_{(C-C)}=1.42$ Å in pristine graphene). These results are in agreement with previous theoretical work in B- and N-doped SWCNTs.²⁷ In aluminum-doped graphene (AG) as well as in sulfur-doped graphene (SG), the dopant atom protrudes instead out of the plane, at a distance d from the plane of $d=1.43$ Å for Al, $d=1.10$ Å for S [see Fig. 1(b)]. The carbon-dopant atom distance is $d_{(Al-C)}=1.85$ Å in AG, $d_{(S-C)}=1.74$ Å in SG. Previous results¹⁴ for AG assumed a planar configuration with $d_{(Al-C)}=1.63$ Å, which we find to be metastable and 2.35 eV higher in energy than the stable configuration. This behavior is not unexpected and can be tracked to the longer covalent Al–C and S–C bond lengths with respect to C–C, B–C, and N–C bond lengths. The Al–C bond length in AG is close to the value $d_{(Al-C)}=1.886$ Å found in Al-doped SWCNT,²⁸ the S–C bond length is comparable to that of dimethyl disulphide and ethylmethyl sulphide (average bond length 1.82 Å).²⁹ The consequences on gas adsorption are important: the local curvature induced by Al doping tends to increase the local reactivity.²⁹

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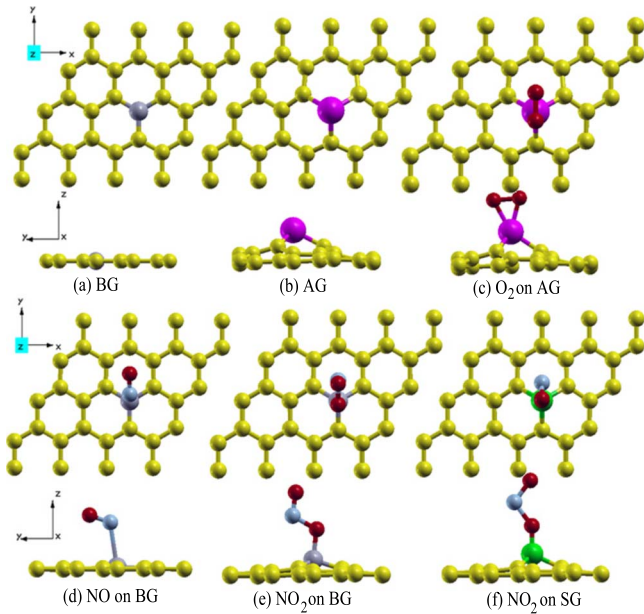


FIG. 1. (Color online) The most stable configurations of BG (a), AG (b), AG with adsorbed O₂ (c), BG with adsorbed NO (d), BG with adsorbed NO₂ (e), and SG with adsorbed NO₂ (f). The coordinate axis are shown at the left of the panel.

We then look for the adsorption of a single gas molecule on the top of substituted atom of doped graphene, starting from different dopant atom-molecule distances and from different orientations of the molecule. Results are collected in Table I. In most cases one finds small adsorption energies and large molecule-graphene distances, pointing to no binding other than physisorption. For BG, however, NO and NO₂ bind with a significant ($E_a \sim 0.3$ eV) adsorption energy. The corresponding atomic structures are shown in Fig. 1(d) and 1(e). For NG, the largest binding energies ($E_a \sim 0.2$ eV) are found with NO₂, SO₂, and O₂, but the corresponding dopant atom-molecule distances are rather large ($d > 3$ Å), suggesting that a true chemical bond is not formed. SG can only bind the NO₂ molecule, with a rather large adsorption energy $E_a = -0.83$ eV, in a configuration that is similar to that of NO₂ on BG [see Fig. 1(f)]. Finally, AG is very reactive and binds all molecules except H₂, via the formation of strong Al-X ($X=O, N, C$) bonds, of length $d_{Al-X} \sim 2$ Å or less. Here, we only show the ground-state configuration of O₂ on AG [Fig. 1(c)], in which both O atoms bind to Al.

Our results for BG are somewhat different from the theoretical results of Ref. 13, obtained within the local-density approximation (LDA). In Ref. 13 B-doped CNT are found to bind H₂O, CO, and NH₃; N-doped CNT binds NO₂ as well.

TABLE I. Adsorption energy E_a (eV) and shortest molecule-doping atom distance for the most stable configurations of gas molecules on B-, N-, Al-, and S-doped graphene.

		NO	NO ₂	NH ₃	CO	CO ₂	H ₂ O	SO ₂	O ₂	H ₂	N ₂
B-doped	E_a	-0.341	-0.325	-0.016	-0.019	-0.007	-0.040	-0.030	-0.01	-0.014	-0.004
	d	2.38	1.56	3.37	3.81	3.57	3.73	3.63	3.45	3.22	4.11
N-doped	E_a	-0.093	-0.260	-0.015	-0.013	-0.025	-0.060	-0.189	-0.149	-0.008	0.017
	d	3.56	3.03	3.49	3.89	3.27	3.47	3.21	3.30	3.22	4.02
Al-doped	E_a	-1.351	-2.476	-1.374	-0.662	-0.218	-0.809	-1.538	-1.661	-0.013	-0.202
	d	1.90	1.79	2.03	2.05	2.10	1.99	1.79	1.88	2.92	1.98
S-doped	E_a	-0.122	-0.831	-0.003	-0.006	-0.004	-0.019	-0.092	-0.034	-0.006	-0.0001
	d	2.89	1.47	4.03	4.15	3.60	3.88	3.224	3.45	3.60	4.20

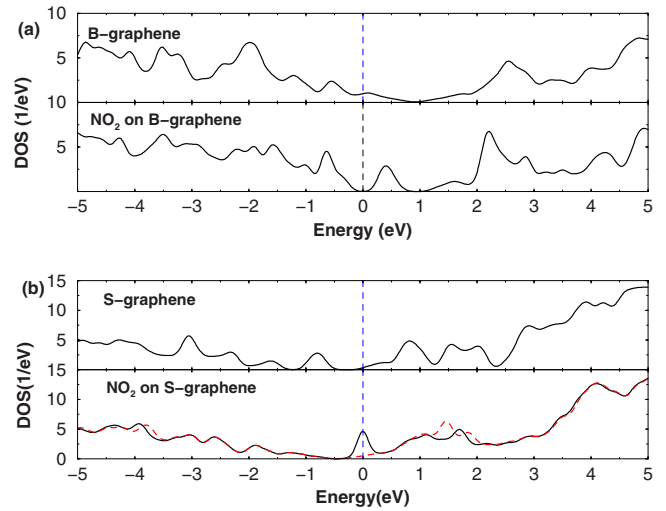


FIG. 2. (Color online) The DOS for (a) NO₂ on BG, and (b) NO₂ on SG. Solid line is the DOS of majority spin and dashed line is minority spin. The vertical dashed lines represent the Fermi level of the system, which is set to zero here.

A possible reason for this difference is the effect of the curvature of CNT, making it more reactive than graphene. It should also be mentioned that LDA tends to overestimate binding energies. Our results for AG also differ from those of Ref. 14 for CO on AG. In this case, the difference is obviously due to the different ground state assumed for AG in absence of gas.

Let us focus on the results of NO₂ on BG and on SG. The boron atom protrudes out of the plane, at a distance $d=0.77$ Å, when it binds to one O atom of the NO₂ molecule with a bond length $d_{(B-O)}=1.56$ Å. The C—B bond length expands to $d_{(B-C)}=1.56$ Å, while the O—N bond on the side of the B atom expands to $d_{(N-O)}=1.42$ Å, from 1.22 Å of the isolated molecule. Interestingly, in SG the S atom moves closer to the graphene plane, at $d=0.93$ Å, and the C—S bond length shortens to $d_{(S-C)}=1.69$ Å, after NO₂ adsorption. The S—O bond length is $d_{(S-O)}=1.47$ Å, and the longer N—O bond in the molecule extends to $d_{(N-O)}=1.57$ Å.

To better understand the change in the electronic structure caused by gas adsorption, the electronic DOS are calculated for NO₂ on BG and on SG. Before adsorption, BG is obviously metallic, having an unpaired electron. The adsorption produces the disappearance of spin polarization and the opening of a bandgap with width of ~ 0.6 eV, as shown in Fig. 2(a). Adsorption of NO₂ on SG introduces spin polar-

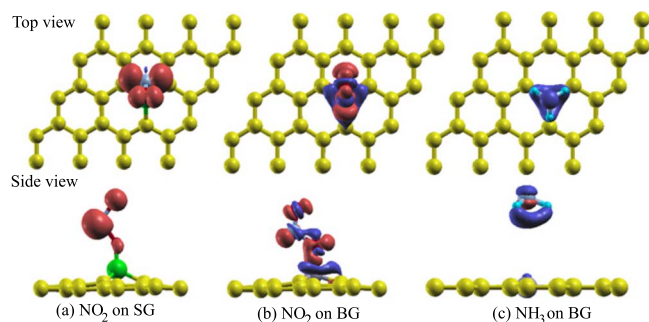


FIG. 3. (Color online) (a) Spin density of NO_2 on SG with isovalue of ± 0.002 a.u. (b) Isosurface plot of the electron charge density difference for NO_2 on BG, and for (c) NH_3 on BG. Isovalues: 0.005 a.u. and -0.005 a.u.

ization in the system, with a magnetic moment of $0.74 \mu_B$. The distribution of spin density is shown in Fig. 3(a), which shows that the magnetization is mainly located on the NO_2 molecule. The DOS at the Fermi level actually increases upon adsorption, as visible in Fig. 2(b). An isosurface three-dimensional contour plot of the electron charge density difference (i.e., the electron charge density of the molecule-doped graphene system, minus the electron charge density of the isolated molecule and of the doped graphene, calculated with the same atomic positions of molecule-doped graphene) for NO_2 on BG [Fig. 3(b)], clearly shows charge density piling between the O atom of NO_2 and the B atom of the BG, indicating the orbital hybridization between NO_2 and BG. Such a bonding charge is completely absent for physisorbed gases, for instance NH_3 on BG [Fig. 3(c)]. Finally, the analysis of Löwdin³⁰ charges shows that there is a charge transfer of about $0.35 e^-$ from BG to NO_2 , of about $0.76 e^-$ from SG to NO_2 , indicating that NO_2 works as an acceptor. Such a large charge transfer is expected to induce sizable changes on the conductivity of the system.

In summary, first-principle calculations show that graphene doped with different impurities exhibits different behavior when exposed to common and polluting gas molecules. Al-doped graphene is strongly reactive and thus presumably not suitable for usage as a gas sensor. N-doped graphene is possibly not reactive enough, while B-doped and S-doped graphene are able to chemically bind NO_2 and possibly NO as well. The change in the electronic structure produced by absorption and by orbital hybridization are expected to produce a large change of conductivity, making it possible their usage as sensor for important polluting gases such as NO and NO_2 in air.

This work is supported by the National Natural Science Foundation of China under Grant Nos. 10734140 and 60621003, the National Basic Research Program of China (973 Program) under Grant No. 2007CB815105, and the National High-Tech ICF Committee in China. P.G. acknowledges support from Progetto Regionale NANOCAT. All

calculations are supported by the Research Center of Supercomputing Application, NUDT.

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