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# Adsorption of H<sub>2</sub>S molecules on non-carbonic and decorated carbonic graphenes: A van der Waals density functional study



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## ABSTRACT

The adsorption of hydrogen sulfide (H<sub>2</sub>S) molecules on non-carbonic (B, Al, and Ga nitride) graphene was studied using a *first-principles* van der Waals density functional (vdW-DF) method. For the adsorption of a single molecule, we determined the most stable configurations, equilibrium geometries, adsorption energies, and electronic properties by approaching the molecule on the surface of non-carbonic graphenes at different possible sites. The Ga nitride (GaN) graphene was more capable of H<sub>2</sub>S molecule adsorption than the other graphenes due to the higher binding energy value and shorter bonding distance between the H<sub>2</sub>S molecule and the graphene surface. Electron transfer calculations confirmed that the electronic properties of GaN graphene changes significantly compared to other graphenes after H<sub>2</sub>S molecule adsorption. The density of states results indicated a stronger physical hybridization between H<sub>2</sub>S and GaN graphene. Furthermore, co-adsorption of two H<sub>2</sub>S molecules on the GaN graphene as a single-layer/bi-layer of adsorbed molecules was examined. Finally, Al and Ga metal atoms decorated on carbonic graphene (Al- and Ga-cargraph) to investigate H<sub>2</sub>S adsorption. The adsorption of H<sub>2</sub>S on Al- and Ga-cargraph was weaker than that on the non-carbonic graphenes. Therefore, based on the obtained results, GaN graphene is promising for uses in gas sensor devices for detect H<sub>2</sub>S.

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## 1. Introduction

Gas and liquid fuels contain sulfur-containing molecules that are challenging and expensive to completely remove before fuel combustion [1]. In addition, many industrial plants, including natural gas processing, petroleum refining, petrochemical plants, Kraft mills, coke ovens and coal gasifiers, produce significant amounts of H<sub>2</sub>S. Much research has focused on the removal of H<sub>2</sub>S from industrial sources; due to environmental concerns, many methods, such as chemical absorption by special adsorbents, have been investigated [2]. Sulfur is a ubiquitous poison that can act as a catalyst poison in both its oxidized and reduced forms (e.g., SO<sub>2</sub>, SO<sub>3</sub>, H<sub>2</sub>S, CO<sub>2</sub>) due to its capability to adsorb strongly onto metals and metal oxides. Moreover, sulfur is harmful to human health. For hydrocarbon fuels, direct removal of sulfur compounds using a generable adsorbent is an attractive means of achieving required low sulfur levels. Due to its toxic and corrosive nature, H<sub>2</sub>S must be safely removed from the gases produced in gasification or combustion processes. Thus, the development of a suitable adsorbent for an

adsorbing desulfurization process has attracted major attention from researchers during the last two decades [3]. However, hydrogen sulfide (H<sub>2</sub>S) is extremely hazardous at a concentration range of 10–30 to 1000–2000 ppm. Exposure to a concentration of only 300 ppm for 30 min can be fatal, and thus the H<sub>2</sub>S concentration must be dramatically reduced to the lower limit of toxicity (i.e., at least 10 ppm) [4–10].

New nanomaterial and graphene sheets represent the “third wave” of nanomaterial research, following earlier studies of nanoparticles/fullerenes and nanowires/nanotubes [11]. In 2004, a group of physicists from Manchester University, UK, directed by Novoselov et al., used a very diverse and, at first look, even naive approach to obtain graphene and lead a revolt in this field [12]. They started with three-dimensional graphite and removed a single sheet (a monolayer of atoms) using a technique called micro-mechanical cleavage. Graphenes have attracted vast attention due to their interesting physical properties, such as unusual quantum Hall effects and massless Dirac fermions, which are credited to the special linear behavior of electronic bands near the Fermi level in the *K* (or *K'*) point of the Brillouin zone [13].

Boron nitride (BN), aluminum nitride (AlN) and gallium nitride (GaN) graphenes are wide band gap III–V compounds with

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remarkable physical properties and chemical stabilities. Hexagonal BN, AlN, and GaN are composed of alternating boron, aluminum, gallium and nitrogen atoms in a honeycomb arrangement consisting of sp<sup>2</sup>-bonded two-dimensional (2D) layers. Within each layer of hexagonal lattices, B, Al, Ga and N atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals (vdW) forces, as in graphite [14]. In this group of graphenes, domains are easily formed in the basal plane of graphene due to phase separation. *First-principles* calculations have demonstrated that the band gap of graphene can be opened effectively around *K* (or *K'*) points by introducing small B, Al, and GaN domains. In addition, random doping with B, Al, and Ga or N enables the opening of a small gap in the Dirac points, although the Fermi level is not modulated.

This group of graphenes has large capacities as H<sub>2</sub>S adsorbents. The adsorption mechanisms of hydrogen sulfide on non-carbonic graphenes sides can be evaluated by quantum mechanical calculations based on density functional theory (DFT) calculations.

However, due to the challenges involved in planning experiments to explore the interfacial interaction mechanisms involved in these systems and interfaces, molecular mechanics (MM), molecular dynamics (MD) and *ab initio* quantum mechanical methods have also been used. *Ab initio* quantum mechanics is characterized as Hartree–Fock (H–F) and DFT calculations. Although *ab initio* quantum mechanical calculations afford supplementary accurate consequences than other classical systems, DFT can be successfully applied from small to extended systems [15]. DFT is a valuable tool that can readily accommodate the periodic boundary conditions necessary to model a graphene sheet and can, in principle, calculate the adsorption properties of an arbitrary molecule.

However, the reliability of the results obtained with the most widely used exchange–correlation DFT functionals, i.e., local density approximation (LDA) and generalized gradient approximation (GGA) is often inadequate. In exact, omission of nonlocal dispersion correlations can affect the calculated adsorption properties because the interaction of guest molecules with graphene involves a large component of London dispersive forces of non-local nature. Therefore, to obtain accurate adsorption properties, it is important to describe the vdW effects based on *first-principles* van der Waals density functional (vdW-DF) calculations [16,17].

There have been no published DFT-based analyses of the properties of the interaction between H<sub>2</sub>S and non-carbonic graphenes. In this paper, vdW-DF calculations within the PBE-GGA level of theory were conducted to investigate the adsorption properties of H<sub>2</sub>S on BN, AlN, and GaN graphenes. In addition, we decorated carbonic graphene with single Al and Ga metal atoms and investigated the adsorption behavior of the decorated graphene after H<sub>2</sub>S adsorption. The goals of this work were to analyze the structural and electronic properties of graphenes after H<sub>2</sub>S adsorption (H<sub>2</sub>S/graphene), determine the binding energies of H<sub>2</sub>S on graphene, and examine the influence of graphene type on the strength and stability of H<sub>2</sub>S/graphene bonds.

## 2. Computational method

The atomic geometry and electronic structure of H<sub>2</sub>S molecule adsorption on non-carbonic graphenes were calculated within the context of *ab initio* DFT [18,19] using the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) code [20,21]. We employed the GGA for the electronic exchange and correlation effects according to the Perdew–Burke–Ernzerhof (PBE) functional [22]. Furthermore, we have used the fully self-consistent implementation of vdW-DF at the GGA level of theory with the PBE exchange functional, which is favorable for calculating vdW interactions [23]. In all trials, a split-valence double- $\zeta$  basis set of localized numerical atomic orbitals was used, including

polarization functions (DZP) with an energy shift of 50 meV and a split norm of 0.25 [24,22,25,26]. A  $5 \times 5 \times 1$  Monkhorst–Pack lattice for *k*-point selection of the Brillouin zone was set, and the atomic situations were relaxed until the remaining forces on every atom were less than 0.03 eV/Å. An energy cutoff of 120 Ry for the lattice integration was selected to signify the charge density. The basis set superposition error (BSSE) was removed by adding ghost atoms to the calculation for graphene in the presence of adsorbate. Ghost atoms have normal basis functions but do not have a significant impact on the calculation, ensuring that similar degrees of freedom are presented to the wave functions in each calculation. A supercell composed of 50 atoms and a periodic boundary condition was applied to these graphenes. The blocks were parted from their periodic images normal to the surface with a vacuum gap of 20 Å, which was sufficient to eliminate slab–slab interactions. Both the adsorbent and adsorbate were allowed to relax through optimization calculations.

The binding energy of H<sub>2</sub>S-molecule adsorption on the graphene with BSSE corrections  $E_b(M_{BSSE})$  was calculated as follows:

$$E_b(M_{BSSE}) = E(\text{host}/M) - E(\text{host}_{\text{ghost}}/M) - E(\text{host}/M_{\text{ghost}}) \quad (1)$$

where  $E(\text{host}/M)$  is the total energy of the basic graphene (host material) interacting with the H<sub>2</sub>S molecule and the 'ghost' molecule or atom/host corresponds to an additional basis wave function centered at the position of the H<sub>2</sub>S or the graph without any atomic potential. Therefore, a negative binding energy indicates a stable adsorption structure.

## 3. Results and discussion

The accuracy of the method used in this work was first examined to describe the properties of the H<sub>2</sub>S molecule in the gas phase. The calculated bond length and angle of free H<sub>2</sub>S were 1.36 Å (1.35 Å) and 91.6° (90.5°), respectively, in good agreement with the experimental values listed in parentheses [27]. The optimized structure of the free H<sub>2</sub>S molecule in the gas phase is shown in Fig. 1.

In the optimized BN, AlN, and GaN graphene, the bond lengths of B–N, Al–N, and Ga–N were found to be approximately 1.45, 1.84 and 1.76 Å, respectively (Fig. 2). Charge analysis using the Mulliken method indicated that approximately 0.62, 0.91, and 0.92 electron charges are transferred from the boron, aluminum and gallium atoms to the adjacent nitrogen atoms, respectively. These findings indicate that the gallium atom is considerably positively charged, and the resulting empty local state can act as an electrophilic center. By relating the asymmetry of the charge density to the ionicity of the compound, we concluded that GaN and AlN graphenes have a higher ionicity than BN graphene. The calculated DOS plots

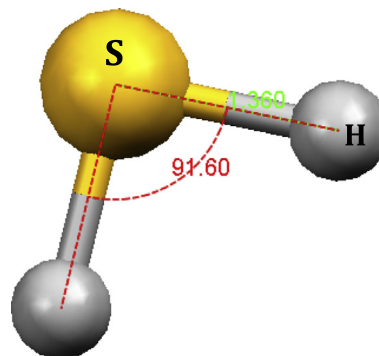
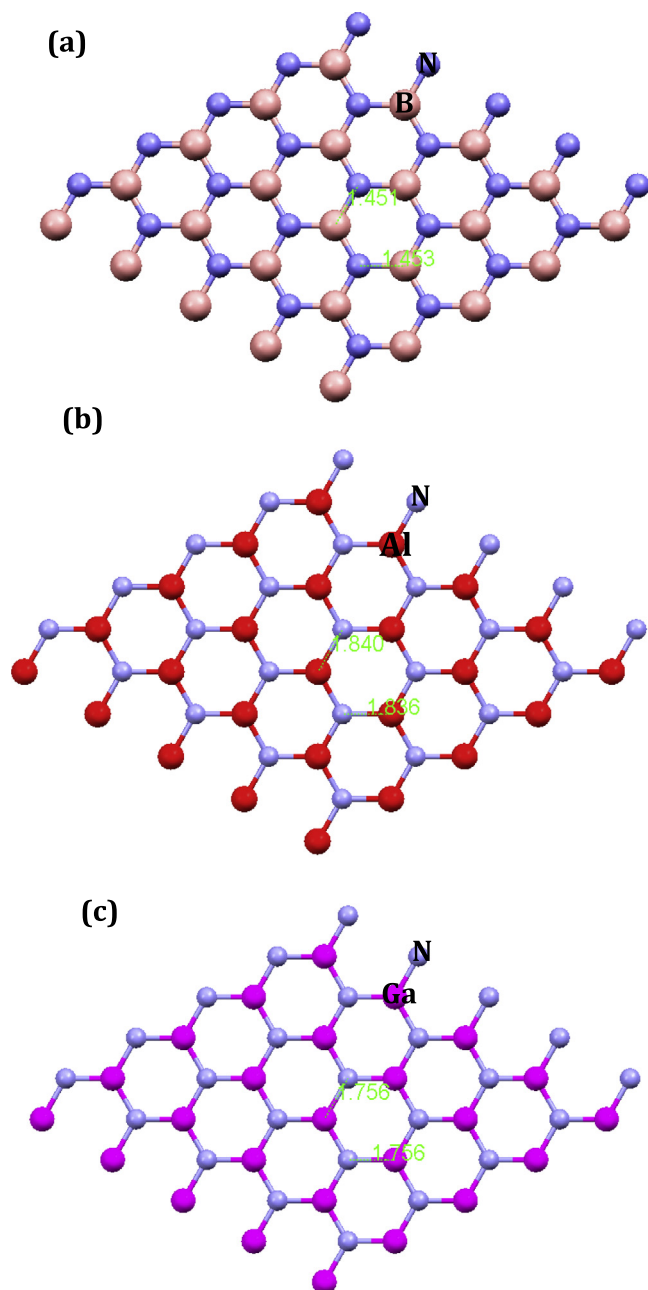


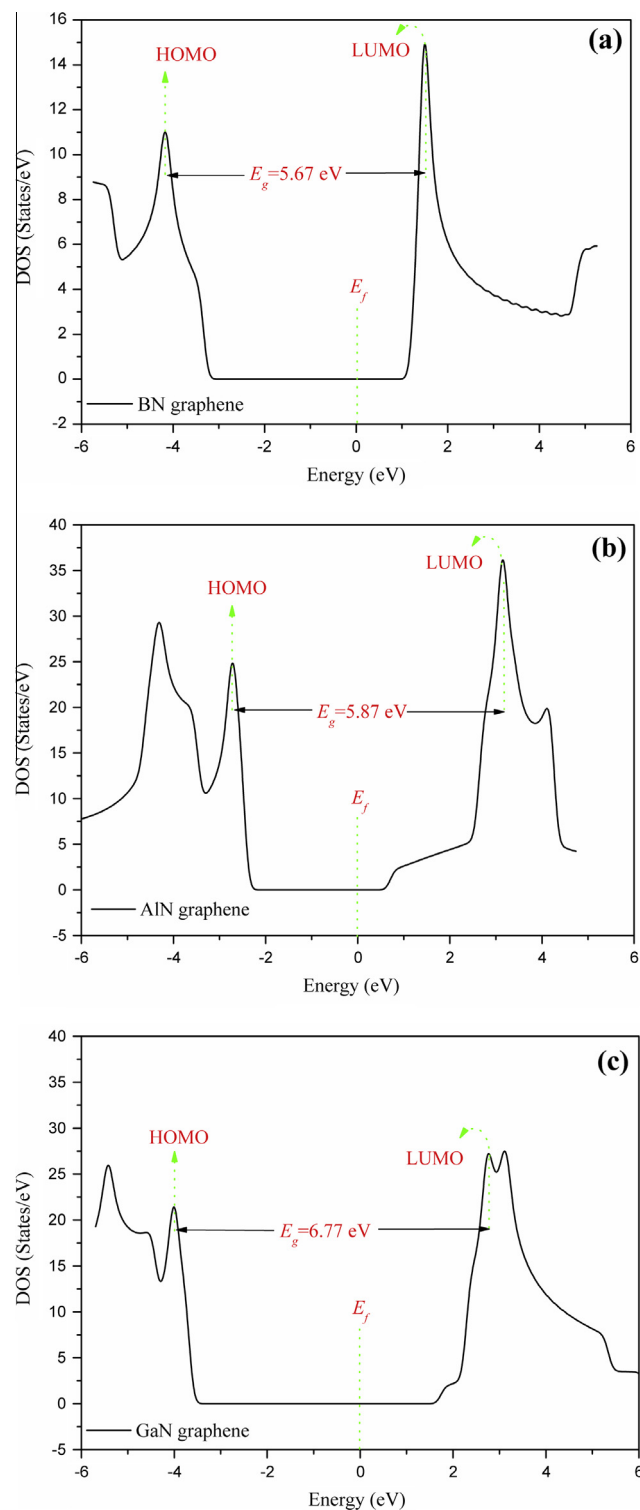
Fig. 1. The optimized structure of an individual H<sub>2</sub>S molecule (bonds in Å and degrees).



**Fig. 2.** Optimized structures of bare (a) BN graphene, (b) AlN graphene and (c) GaN graphene (bond length in Å).

(Fig. 3) revealed that the bare BN, AlN, and GaN graphenes might be semiconductors with a HOMO (the highest occupied molecular orbital)/LUMO (the lowest unoccupied molecular orbital) energy gap ( $E_g$ ) of 5.67, 5.87, and 6.77 eV, respectively. It is noteworthy to mention that  $E_g$  is the energy range in the insulator and semiconductor molecules at which no electron states can exist. In addition, the DOS analysis demonstrated that the Fermi level energies ( $E_f$ ) of BN, AlN, and GaN graphene are equal to  $-4.26$ ,  $-3.74$  and  $-1.31$  eV, respectively. These results are in agreement with values reported in the literatures [28,29].

To consider the favorability of H<sub>2</sub>S adsorption on the non-carbonic graphene, we first computed the adsorption of H<sub>2</sub>S on the BN graphene sheet (BN/H<sub>2</sub>S). H<sub>2</sub>S molecules were initially placed at different positions and orientations above the graphene surface. Various configurations of the triangular-shaped H<sub>2</sub>S molecule

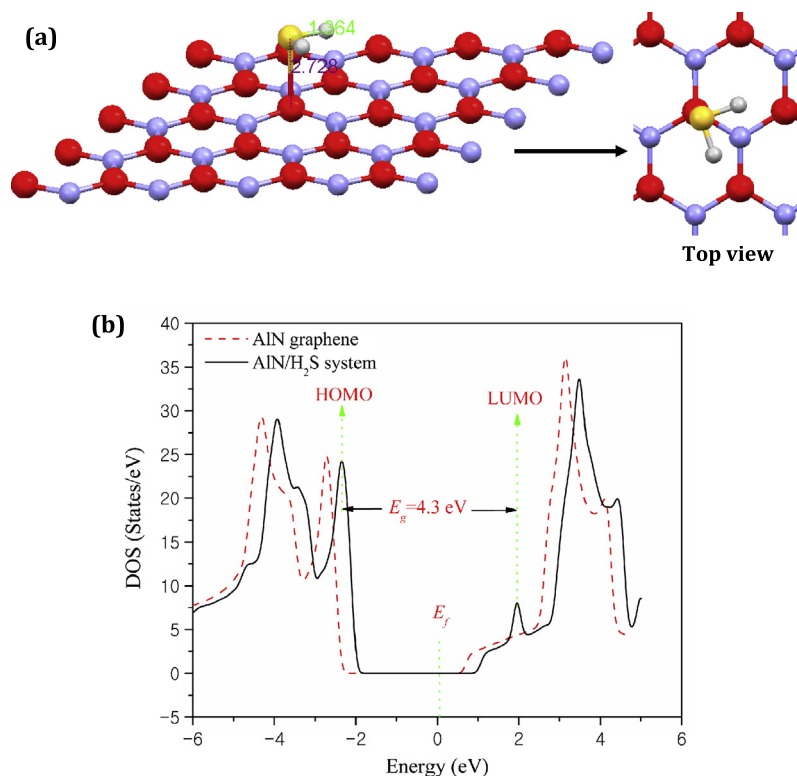


**Fig. 3.** Calculated DOS for bare (a) BN graphene, (b) AlN graphene and (c) GaN graphene. The Fermi level was set to zero.

adsorbed onto the BN graphene surface, including individual sulfur or hydrogen atoms of  $\text{H}_2\text{S}$  that were perpendicularly close to the surface on the bridge and hollow sites, and on the top sites of the B and N atoms were investigated. We investigated twelve possible adsorption configurations on the graphene surface to find the energetically favorable configuration. The optimized structure of the most favorable configuration for the BN/ $\text{H}_2\text{S}$  system is shown







**Fig. 5.** (a) Optimized structure, geometric parameters and (b) DOS plot for the AlN/H<sub>2</sub>S system (bond distances in Å). The Fermi level was set to zero.

(from  $E_f = -3.74$  eV for the AlN graphene to  $E_f = -4.01$  eV for the AlN/H<sub>2</sub>S system). This significant difference in the Fermi level energy confirms a charge transfer from the H<sub>2</sub>S molecule to AlN graphene in the adsorption process. Meanwhile, the energy gap decreases from 5.87 eV for bare AlN graphene to 4.30 eV for the AlN/H<sub>2</sub>S system. Thus, in agreement with the above mentioned results, H<sub>2</sub>S molecules can also be adsorbed onto AlN graphene surfaces via physical interactions.

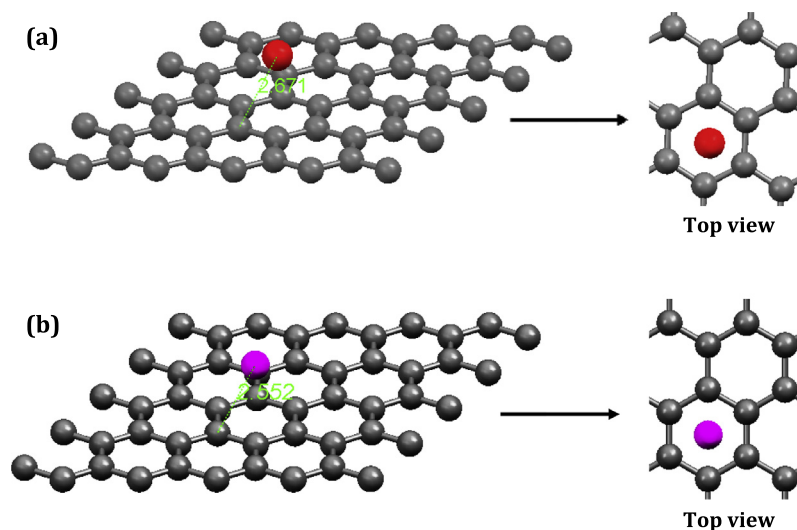
To evaluate the interaction between the H<sub>2</sub>S molecule and GaN graphene, we first calculated the binding energies of the adsorbed systems. For this purpose, as in previous sections, we identified the stable GaN/H<sub>2</sub>S adsorption geometry from twelve different initial geometrical configurations. After complete structural optimization of the selected systems, the H<sub>2</sub>S molecule was found to be adsorbed parallel onto the surface of GaN graphene, and the S atom of the molecule bound on the substrate above the Ga atom with a binding energy of approximately  $-0.33$  eV. In addition, we found that the equilibrium distance,  $d_{Ga-S}$ , was equal to 2.72 Å. Fig. 6(a) shows a schematic representation of the optimized geometric structure for the adsorption/interaction of the H<sub>2</sub>S molecule with GaN graphene at the most stable configuration. Furthermore, to elucidate the effects of H<sub>2</sub>S molecule adsorption on GaN graphene, we determined the charge transfer between them. Mulliken charge analysis revealed a 0.12 electron charge transfer from the H<sub>2</sub>S molecule to GaN graphene, compared to 0.01 and 0.06 electrons for the BN/H<sub>2</sub>S and AlN/H<sub>2</sub>S systems, respectively. These results indicate that the adsorption process is typical physisorption. To confirm the above findings, we also calculated the DOS of the GaN/H<sub>2</sub>S system at the most stable configuration, as illustrated in Fig. 6(b). The DOS of the GaN/H<sub>2</sub>S system increased by approximately 1.81 eV compared to the results obtained for the bare GaN graphene. These results demonstrate that the shift in the electronic energy spectra for the GaN/H<sub>2</sub>S system is larger than that for the AlN/H<sub>2</sub>S system (0.38 eV). Therefore, GaN graphene interacts more strongly with

the H<sub>2</sub>S molecule than AlN graphene. Moreover, the calculated  $E_f$  of the GaN/H<sub>2</sub>S system is  $-3.06$  eV, which is significantly greater than the values obtained for bare GaN graphene. In addition, the value of  $E_g$  in the GaN/H<sub>2</sub>S system (3.98 eV) is smaller than that in GaN graphene (6.77 eV). Previous studies [33,34] have indicated that an increase in changes of  $E_g$  during the adsorption process ( $\Delta E_g$ ) leads to higher electrical conductivity. Thus, GaN graphene can directly transform the presence of the H<sub>2</sub>S molecule into an electrical signal, and therefore GaN graphene has potential for use in a sensor device for the detection of H<sub>2</sub>S with high sensitivity due to the considerable change in  $E_g$ .

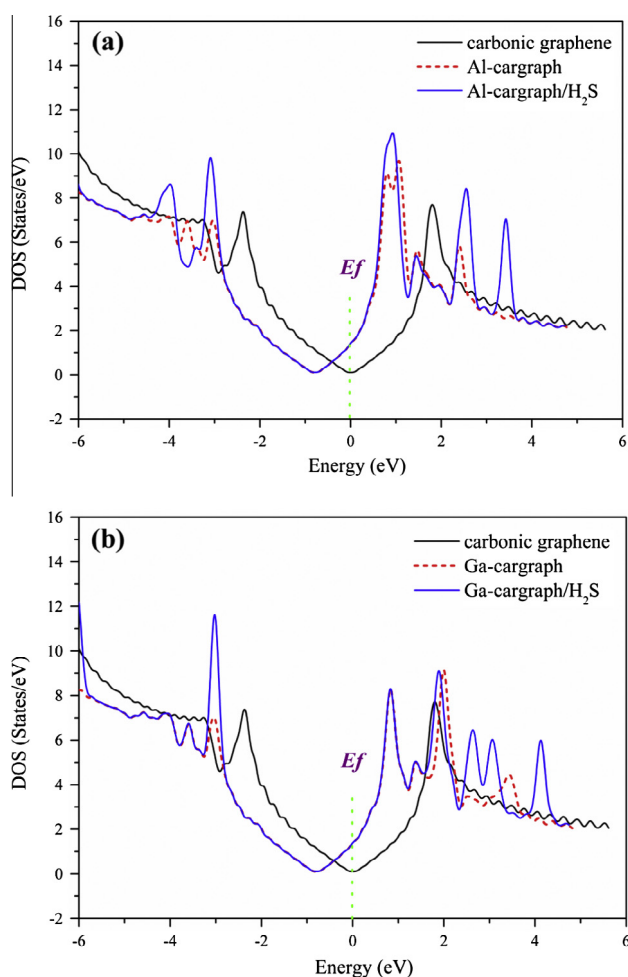
Furthermore, the co-adsorption of two H<sub>2</sub>S molecules on the surface of the GaN graphene was examined. For this propose, two strategies were selected for the approach of the H<sub>2</sub>S molecules to the surface of the substrate. In the first strategy, the adsorbed H<sub>2</sub>S molecules were positioned as a single layer on the active site of the substrate (single-layer GaN/H<sub>2</sub>S system). In the second strategy, the formation of additional layers around the GaN graphene was examined (bi-layer GaN/H<sub>2</sub>S system). The full structural optimization of the considered systems indicated that two H<sub>2</sub>S molecules prefer to be adsorbed on the GaN graphene surface according to the first strategy with adsorption energy of approximately  $-0.38$  eV per adsorbed molecule. The obtained binding energy for the bi-layer adsorbed molecules was approximately  $-0.19$  eV/H<sub>2</sub>S. The optimized structures of the single-layer and bi-layer GaN/H<sub>2</sub>S systems are illustrated in Fig. 7.

Finally, we decorated carbonic graphene with single Al and Ga metal atoms to identify a suitable adsorbent with lower production cost and higher sensitivity to H<sub>2</sub>S than other carbonic/non-carbonic graphenes. Three different adsorption sites for single-sided adsorption to carbonic graphene were considered: the hollow site (H1) above the center of the hexagon; the bridge site (B1) over a C–C bond; and the top site (T1) directly above a C atom. Our calculations



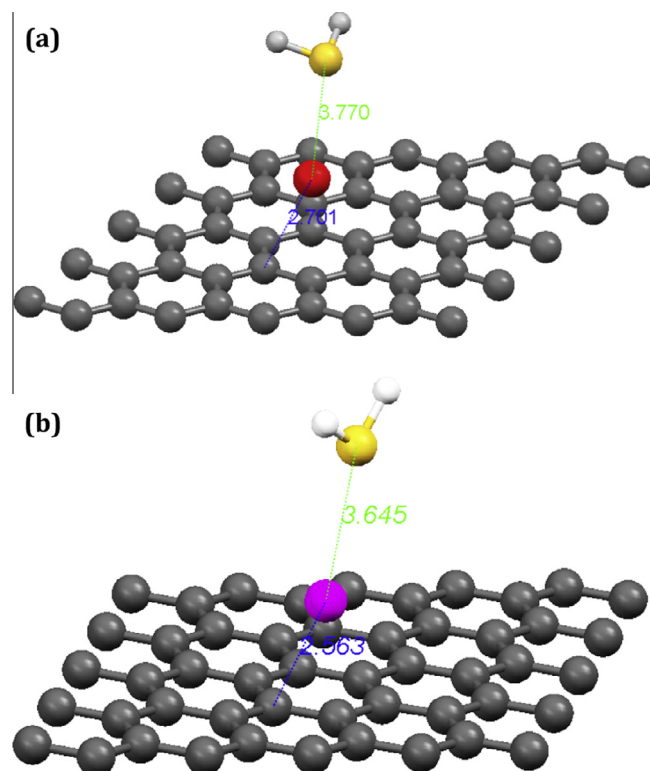


**Fig. 8.** Optimized structure and geometric parameters for the (a) Al-cargraph and (b) Ga-cargraph systems (bond distances in Å).



**Fig. 9.** Calculated DOS for (a) Al-cargraph and (b) Ga-cargraph with and without adsorbed  $\text{H}_2\text{S}$ . The Fermi level was set to zero.

occurred from H<sub>2</sub>S to the Al- and Ga-cargraph surfaces, respectively. These results demonstrate the low strength of the interaction between H<sub>2</sub>S and decorated carbonic graphenes.



**Fig. 10.** Optimized structure and geometric parameters for the (a) Al-cargraph/H<sub>2</sub>S and (b) Ga-cargraph/H<sub>2</sub>S systems (bond distances in Å).

## 4. Conclusion

In summary, the adsorptions of  $\text{H}_2\text{S}$  molecules on BN, AlN, and GaN graphenes were investigated by using a *first-principles* vdW-DF method. To identify the most favorable adsorption configuration,  $\text{H}_2\text{S}$  molecules were initially placed at twelve different positions above the graphene. Compared with carbonic graphene, the BN graphene system has a higher binding energy value and shorter binding distance due to the strong adsorption of the  $\text{H}_2\text{S}$  molecule. The interaction energy for the BN/ $\text{H}_2\text{S}$  system indicates that the  $\text{H}_2\text{S}$  molecule adsorbs onto the BN graphene surface via



van der Waals attraction. The following order of binding energies was observed for the H<sub>2</sub>S molecule and graphenes: GaN/H<sub>2</sub>S (−0.33 eV) > AlN/H<sub>2</sub>S (−0.30 eV) > BN/H<sub>2</sub>S (−0.18 eV) > H<sub>2</sub>S/graphene (−0.04 eV). In addition, the study of the electronic structure confirmed that the interaction between the H<sub>2</sub>S molecule and GaN graphene is stronger than that with the other selected graphenes. After a single molecule adsorption process, the HOMO/LUMO gap of the GaN graphene dramatically decreased from 6.77 to 3.98 eV, consequently enhancing electrical conductivity. Thus, GaN graphene might be a more sensitive sensor for H<sub>2</sub>S molecule detection than the other graphenes. Furthermore, co-adsorption of two H<sub>2</sub>S molecules on the GaN graphene as a single-layer/bi-layer of adsorbed molecules was investigated in the favorable position. Our *first-principles* results revealed that the second H<sub>2</sub>S molecule adsorbed on the graphene according to the first strategy. Finally, to select the best adsorbent graphene, Al or Ga atom were introduced and positioned on the surface of carbonic graphene. In these cases, a weak adsorption was observed due to the small binding energy and charge transfer in comparison with the BN/H<sub>2</sub>S system.

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