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A first-principles study of gas adsorption on monolayer AlN sheet

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ABSTRACT

The monolayer AlN is one of graphene-like 2D material. On the basis of density functional theory (DFT) calculations, the adsorption of CO_2, CO, H_2, N_2, CH_4, O_2 and NO on the monolayer AlN was investigated. Due to the dipole moment of the Al-N bond, the gas molecules can be adsorbed directly on the AlN sheet. This avoids the problem about formation of metal clusters using metal decorated carbon nanostructures as gas storage materials. Among all the gas molecules, only CO_2 on the AlN sheet has strong interaction with adsorption energy of 0.91 eV. While other gas molecules bind to the AlN sheet much weakly with the adsorption energy being less than 0.5 eV. Due to the charge transfer between gas molecules and the AlN sheet, the AlN sheet can be used to gas sensors for CO_2, CO, H_2, O_2 and NO. Moreover, the AlN sheet can be taken potential applications as sorbent materials for CO_2 separation and capture from gas mixture.

1. Introduction

Since the successful synthesis of graphene and the subsequent discovery of its high conductivity and carrier mobility at room temperature, graphene has captured enormous experimental and theoretical interests [1,2]. Due to its high surface area and high electron mobility, the graphene has been used as energy storage material and gas sensor [3–6]. However, the weak interaction between gas molecules and the pristine graphene limits its immediate potential. Introducing defects and single metal atoms embedded in graphene are effective ways of enhancing the interaction between gas molecules and graphene [7–9]. However, it is technically not easy to introduce defects or heteroatoms to graphene due to the high formation energy of such doped graphene [10], thus hampering the potential use of graphene. Metal decorated graphene can capture gas molecules with large uptake capacities [11,12]. But the obstacle about the formation of the metal cluster should be solved [13].

Recently, two-dimensional materials become a hot topic due to their interesting properties and promising potential applications in electronic and optoelectronic devices [14–17]. Among these, aluminum nitride nanosheet (AlN) has been extensively studied by both experiments and theoretical simulations due to its novel properties [18–26]. The results show that AlN sheet endows confinement effects in their electronic, magnetic, and optical properties [27–31]. Different from the four coordination in bulk, the Al and N atoms in AlN sheet are all threefold-coordinated with dangling bonds, and can serve as active sites for gas adsorption [32,33]. Unlike nonpolar bond in graphene, owing to the charge transfer from Al to N, the Al-N bond in AlN sheet has dipole moment, which also plays an important role in the adsorption of gas molecules and the AlN sheet.

In this work, we carried out DFT computations to explore the adsorption behavior of the common gas molecules including CO_2, CO, H_2, N_2, CH_4, O_2 and NO on AlN monolayer. The results showed that the adsorption of CO_2 on AlN sheet is highly preferred over other gas molecules. Moreover, it can be used as gas sensors for the CO_2, CO, H_2, O_2, and NO.

2. Computational method

The first-principles calculations are performed based on the DFT with a generalized gradient approximation (GGA) in the Perdew-

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Burke-Ernzerhof (PBE) [34] form implemented in the Vienna ab initio simulation package (VASP) code [35–37]. A kinetic energy cutoff of the plane-wave basis set was used to be 500 eV. A k-point sampling of 5 × 5 × 1 Monkhorst-Pack grids [38] in the first Brillouin zone of the 4 × 4 supercell is used in the calculation. The convergence criteria of total energy and Hellmann-Feynman force were set as 10^{-4} eV and 0.01 eV/Å, respectively. Since the van der Waals (vdW) interaction plays a crucial role in the adsorption of gas molecules on the substrate, the vdW correction was taken into account in our calculations through employing DFT-D2 method of Grimme [39]. By means of Bader analysis [40], charge transfer between the AlN sheet and the gas molecule is obtained. It should be pointed out that although different methods besides Bader analysis may give rise to different values in determining the electronic charge transfer, the direction and order of magnitude should be the same.

3. Results and discussion

The AlN sheet has typical graphene-like structure. The optimized length of Al-N bond is 1.80 Å, which is consistent with the findings in recent studies [27,41–43]. Our discussion begins with adsorption different gas molecules, i.e., CO_2, H_2, CO, O_2, NO, N_2, CH_4 on the AlN sheet. As shown in Fig. 1, there are four different adsorption sites, which are the hollow center of the Al-N hexagon (H), the bridge of Al-N bond (B), the top of the Al atoms (T1) and the top of the N atoms (T2). Moreover, several typical orientations of gas molecule with respective to the AlN surface are considered. The gas molecule is initially placed with its center of mass exactly located at these sites. For each site, configurations with different molecular orientations are then examined. Take CO_2 as an example, CO_2 molecule is initially placed either parallel or vertically to the surface of AlN sheet for all the possible adsorption sites. For all the gas molecule/AlN systems, the adsorption energy is defined as

$$E_a = E_{gas} + E_{AlN} - E_{gas/AlN} \quad (1)$$

where E_{gas}, E_{AlN}, and $E_{gas/AlN}$ are the energies of the isolated gas molecule, AlN sheet and the gas molecule/AlN system. By this definition, the larger E_a, the stronger the interaction between the gas molecule and the AlN sheet. A negative value of E_a indicates that the adsorption is endothermic.

The most stable adsorption configurations of different gas molecules on the AlN sheet are shown in Fig. 2. The other possible adsorption configurations for all the gas molecules are given in Fig. S1-Fig. S5. The adsorption energy, the charge transfer for the adsorption of gas molecules on AlN sheet, and the distance between the AlN sheet and the nearest atom of the gas molecule are summarized in Table 1. We see that except for the N_2 and CH_4 with the negative adsorption energies, all the other molecules can be adsorbed on the AlN sheet. The distance between N_2 (CH_4) and AlN sheet is 3.279 Å (3.212 Å), which is larger than 3 Å. This suggests that the N_2 and CH_4 molecules can't be adsorbed on the AlN sheet. Therefore, we next only study the adsorption of CO_2, H_2, CO, O_2, and NO on the AlN sheet. We also calculated the adsorption energy with

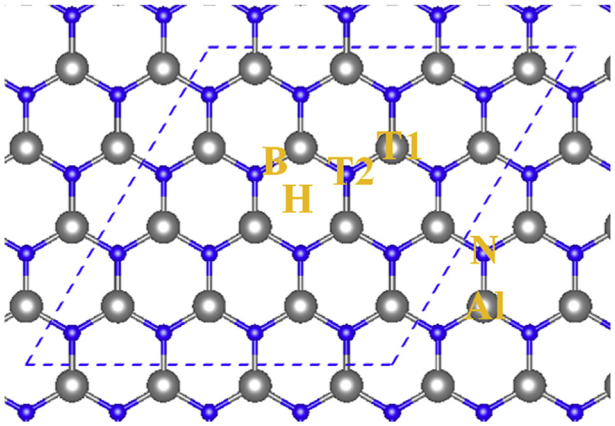

Fig. 1. The optimized atomic structures of monolayer AlN and four possible adsorption sites.

Table 1
The distance between the AlN sheet and the nearest atom of the gas molecule, the adsorption energy, the charge transfer from AlN sheet to various gas molecules and the band gap of different systems.

	CO_2	H_2	CO	O_2	NO	N_2	CH_4
d (Å)	1.436	2.688	2.222	2.482	2.141	3.279	3.212
E_a(eV)(GGA + vdW)	0.91	0.07	0.14	0.19	0.45	−0.08	−0.03
E_a(eV)(GGA)	0.68	0.02	0.03	0.10	0.29	−0.16	−0.17
Bader charge (*e*)	0.66	−0.20	0.15	0.17	0.30		
Band gap (eV)	2.95	0	2.65	0.54	1.04		

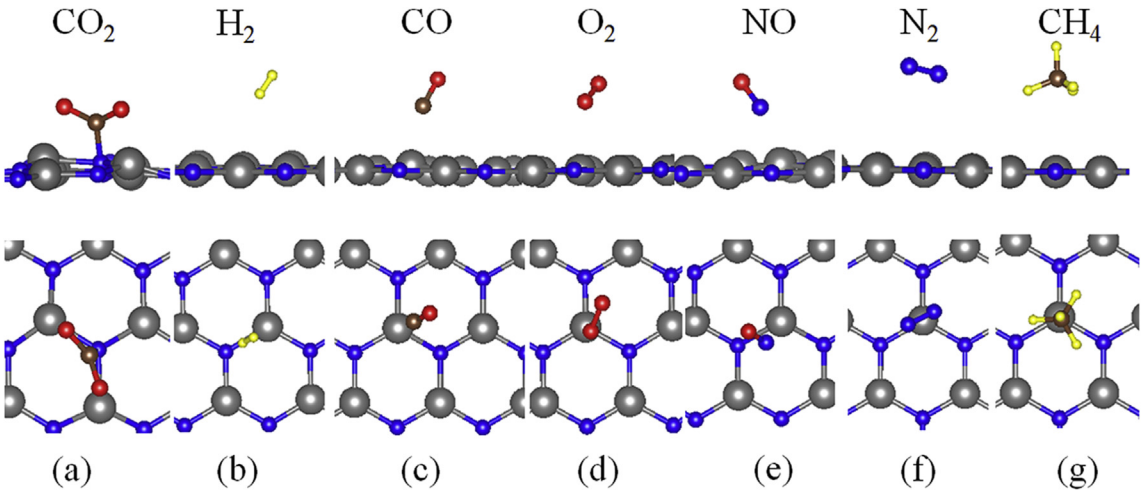

Fig. 2. Side and top views of the most stable configurations of molecules adsorbed on the AlN sheet, including (a) CO_2 on T2 site, (b) H_2 on B site, (c) CO on T1 site, (d) O_2 on T1 site, (e) NO on B site, (f) N_2 on T1 site, and (g) CH_4 on T1 site, respectively.