Materials Science & Engineering B 229 (2018) 193–200

Contents lists available at ScienceDirect

Materials Science & Engineering B

journal homepage: www.elsevier.com/locate/mseb

Investigation on adsorption properties of CO and NO gas molecules on aluminene nanosheet: A density functional application

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ARTICLE INFO

Keywords:
Aluminene
Nanosheet
Adsorption
Energy gap
Formation energy

ABSTRACT

The electronic properties of monolayer aluminene nanosheet and adsorption properties of CO and NO gas molecules on aluminene nanosheet are investigated using first-principles studies for the first time. The density of states spectrum gives a clear picture regarding the transfer of charge upon adsorption of CO and NO gas molecules on aluminene nanosheet. The adsorption properties of CO and NO molecules on aluminene base material are explored in terms of average energy gap variation, natural bond orbital, HOMO-LUMO gap and adsorption energy. The most prominent adsorption sites of CO and NO molecules on aluminene are studied at an atomistic level. The state-of-the-art of aluminene base material gives the information regarding the development of chemical nanosensor. The findings of the present work suggest the use of monolayer aluminene nanosheet for the detection of CO and NO gas molecules.

1. Introduction

The requirement for highly selective, sensitive, low power consuming, cost-effective, portable and stable chemical nanosensors motivated the research community for the development of gas/vapor sensing material. The significant feature of base material to be utilized for gas detection is its high surface-to-volume ratio. Moreover, monolayer nanostructures facilitate the adsorption of toxic gas/vapor molecules. This property strongly supports the adsorption of various gases on nanostructures resulting in high sensitive sensor performance [1]. Among various forms of nanostructure, two-dimensional (2D) nanostructures best suits for gas sensing applications owing to good chemical and thermal stabilities, large surface-to-volume ratio and tunable electronic properties [2].

The monolayer 2D material with single element leads to a variety of applications. For instance, graphene is a planar honeycomb monolayer of carbon element [3]. Apart from carbon, the other elements from group-IV such as germanium, silicon and tin also exhibits honeycomb monolayer along with buckled structure namely germanene, silicene and stanene respectively. Next to group-IV, the group-V elements such as arsenic, phosphorus, bismuth and antimony can also exhibit a honeycomb monolayer structure, namely arsenene [4], [5]phosphorene , bismuthylene [6] and antimonene [7] respectively. Interestingly, group-V monolayer possesses two significant stable configurations, puckered and buckled. The experimental synthesis of phosphorene monolayer film is reported [8]. Recently, antimonene and arsenene thin films have also been confirmed experimentally [9,10]. In recent days, new 2D material from group-III, namely borophene, has been investigated theoretically [11] and experimentally [12]. Owing to their unique physical properties of borophene, the geometry structures are complex, such as striped, χ_3, β_{12} and 8-*Pmmn* borophene is found to be stable [13–15]. Moreover, most of the boron sheet shows metallic, but striped boron sheet revealed direction-dependent Dirac cones, which depends upon hydrogenation. In addition, 8-*Pmmn* borophene, due to the intrinsic band structure exhibits Dirac cone. Moreover, the previous reports reveals that in low-dimensional materials such as silicene, phosphorene, antimonene, graphene, graphyne and MoS_2 nanostructures [16–27], the electronic, mechanical and adsorption properties can be fine-tuned, which is suitable for various applications. The novel properties of borophene motivated us to explore the electronic properties of other group-III elements, namely aluminum. From the literatures, it is known that very few works have been reported on aluminene, a two-dimensional aluminum sheet [28].

Yuan and coworkers [29] have reported the stability, thermodynamic and electronic properties of aluminene using density functional theory (DFT) studies. Kamal et al. [28] studied the stability, electronic and vibrational properties of monolayer structures from group-III elements such as Al, B, In and Ga using first-principles studies. In our previous works, detection of alcohol molecules on both borophene and borophane monolayer nanosheets are investigated using DFT method [11,15]. Moreover, there are no works reported based on aluminene monolayer for the detection of CO and NO gas. Furthermore,

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https://doi.org/10.1016/j.mseb.2017.12.015
Received 10 July 2017; Received in revised form 9 December 2017; Accepted 18 December 2017

the few layers nanomaterial such as germanene, silicene with functionalization of hydrogen exhibits good sensitivity towards different gases and volatile organic compounds (VOCs) [30,31]. We have studied the adsorption of NO_2 gas on germanene nanosheet [32]. In the present work, the adsorption properties of CO and NO gases on aluminene monolayer sheets are studied for their possible application as nanosensors and results are reported.

2. Computational methods

All calculations in this present work were carried out with the help of locally modified version [33] of Gaussian 09 package [34], utilizing the ultrafine Lebedev grid, which is the best collinear-solution to Kohn-Sham equations (using the keyword STABLE = OPT). The monolayer of aluminene nanosheet is optimized successfully using Gaussian 09 package [34]. The periodic boundary conditions (PBC) algorithm [35] has been used to calculate solid-state lattice constant of aluminene nanosheet. The adsorption properties of different toxic gases such as CO and NO on aluminene nanosheet are also studied using this package. In the present study, refined structure relaxation was performed utilizing density functional theory (DFT) method with the PBE0 [15] exchange-correlation functional combined with 6-311G* basis set [36]. To study the adsorption properties of CO and NO gases on aluminene nanosheet, selection of suitable basis set is one of the significant criteria. Piazza and coworkers [37] have chosen the same basis set 6-311 G* to relax group-III boron in the form of planar hexagonal B_{36} monolayer nanosheets. Moreover, PBE0/6-311G* basis set provides optimum output with a pseudo potential approximation for group-III elements [38,39]. The highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and density of states (DOS) spectrum of aluminene nanosheet were estimated using Gauss Sum 3.0 package [40]. In addition, IOP(5/98 = 1), IOP(5/103 = 10) and IOP(5/33 = 1) keywords have been used for the selection of k-points to compute the HOMO-LUMO gap of aluminene nanostructures. In order to represent the 2D Aluminene system, we used super cell geometry of 5 × 5 along with a vacuum of 16 Å in the direction normal to the plane of single layers so that the interaction among two neighboring unit cells in the arrangement of periodicity is negligible. A self-consistent energy and force convergence limit is adjusted to 10^{-10} Ry and 10^{-3} Ry/Bohr respectively, during the adsorption studies of CO and NO gas molecules on aluminene nanosheet.

3. Results and discussion

3.1. Structures of aluminene nanosheet

The aluminene nanosheet exhibits buckled nanostructures, including anisotropic corrugation with a honeycomb structure. Each honeycomb unit consists of two equivalents Al atoms in the aluminene nanosheet, where the adjacent row Al atoms are crumpled one after another along the zigzag direction [28]. The buckled aluminene nanosheet belongs to group-III monolayer material. The optimized lattice constant of buckled aluminene nanosheet is a = b = 2.751 with space group of *P-3m1*, which confirms the hexagonal crystal structure. The buckling height is found to be around 2.46 Å, which is in good agreement with the reported value of buckled aluminene [29]. The present study explores the formation energy, HOMO-LUMO gap, dipole moment, point group, and density of states spectrum of aluminene nanosheet in order to confirm both the structural stability and electronic properties of aluminene base material. Fig. 1 represents the schematic diagram of aluminene nanosheet base material with periodic boundary condition (PBC). The electronic and adsorption properties of CO and NO on aluminene nanosheet are studied and the results are discussed.

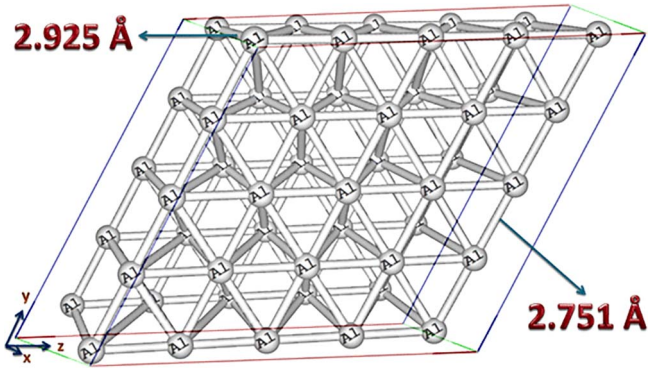

Fig. 1. Schematic diagram of isolated aluminene nanosheet with periodic boundary condition.

3.2. Structural stability and electronic properties of aluminene nanosheets

The structural stability of isolated aluminene nanosheet can be calculated in terms of formation energy [41] as shown in Eq. (1):

$$E_{form} = 1/n\,[E_{total} - nE(Al)] \quad (1)$$

where E_{total} represents the total energy of aluminene nanosheet, *E (Al)* refers the energy of isolated Al atom and *n* is the total number of atoms in aluminene nanosheet. Furthermore, we have also calculated the phonon density of states to confirm the stability of aluminene nanosheet. Moreover, the stability of 2D aluminene base material is a critical thing for experimental fabrication. Hence, to confirm the kinetic stability of proposed aluminene nanosheet, we performed phonon dispersion calculations for its geometric stability. Figs. S1–S5 represents the full phonon dispersion and phonon density of states of isolated aluminene nanosheet along with adsorbed CO and NO gas molecules. In order to reconfirm the structural stability of aluminene nanosheet upon adsorption of gas molecules, full phonon dispersion and phonon density of states are calculated. Moreover, the phonon dispersion as well as phonon density of states spectrum for the aluminene nanosheet base material clearly indicates that there are no imaginary frequency noticed. In addition, upon adsorption of CO and NO gas molecules, no imaginary frequency is found, which indicates the dynamic stability of the aluminene base material. Besides, to further strengthen our findings regarding the structural stability of aluminene nanosheet, Junhui Yuan et al. [29] have carried out the phonon dispersion calculation for two different aluminene nanostructures. The authors inferred that for two aluminene structures, no imaginary frequencies are noticed and also exhibits linear dispersion along the gamma point. Thus, the structural rigidity and geometrical stability is confirmed with the phonon dispersion spectrum. The formation energy, point group and dipole moment of aluminene nanosheet are tabulated in Table 1. The formation energy of isolated aluminene nanosheet is found to be −1.72 eV, which confirms the stability of aluminene nanosheet. The dipole moment (DM) gives the insights on the distribution of charge along aluminene nanosheet. The DM value of pristine aluminene nanosheet is recorded to be zero Debye, which shows the homogeneous distribution of charges across aluminene nanosheet and supports the adsorption properties of CO and NO gas molecules on the base material. Furthermore, the homogeneous distribution of charge on aluminene leads to easy transfer of electrons between CO and NO molecules and aluminene base

Table 1
Dipole moment, point group and formation energy of aluminene nanosheet.

Nanostructure	Formation energy (eV)	Dipole moment (DM) Debye	Space Group
Isolated aluminene nanosheet	−1.72	0.00	P-3m1 (1 6 4)