Physics Letters A 382 (2018) 334–338

Contents lists available at ScienceDirect

Physics Letters A

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Lithium-functionalized germanene: A promising media for CO_2 capture

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ARTICLE INFO

Article history:
Received 5 September 2017
Received in revised form 16 November 2017
Accepted 18 November 2017
Available online 22 November 2017
Communicated by R. Wu

Keywords:
Germanene
Functionalization
CO_2
Capture
DFT

ABSTRACT

Density functional theory (DFT) is employed to investigate the interactions of CO_2 gas molecules with pristine and lithium-functionalized germanene. It is discovered that although a single CO_2 molecule is weakly physisorbed on pristine germanene, a significant improvement on its adsorption energy is found by utilizing Li-functionalized germanene as the adsorbent. Excitingly, the moderate adsorption energy at high CO_2 coverage secures an easy release step. Moreover, the structure of Li-functionalized germanene can be fully recovered after removal of CO_2 gas molecules. Our results suggest that Li-functionalized germanene show promise for CO_2 sensing and capture with a storage capacity of 12.57 mol/kg.

1. Introduction

The climate change created by greenhouse emissions is one of the biggest issues mankind faces today. Carbon dioxide (CO_2) is the main anthropogenic greenhouse gases. Hence, the development of technology for CO_2 separation, capture, and storage has garnered huge interest [1,2]. The current industrial technology which is based on chilled ammonia suffers from toxicity, solvent loss, low energy efficiency, and corrosion issues [3,4]. To overcome these problems, various materials such as metal-organic frameworks [5], boron nitride nanotubes [6], and carbon nanotubes [7] have been employed as effective sorbents for CO_2 capture. Nevertheless, their large adsorption energies lead to a difficult regeneration step [6]. Ergo, the selection of adsorbents with both high selectivity and an easy release step is a vital task for the development of CO_2 technology.

Since its discovery in 2004 [8], graphene has enticed a great deal of interest due to its outstanding properties. The potential application of graphene for gas sensing has been widely studied [9–12]. Although the physisorption of CO_2 on pristine graphene limits its potential for single molecule detection [9], its sensing capability can be improved by modifying the graphene [10–13]. Motivated by the successful detection of individual gas molecules by graphene, the sensing capability of other two-dimensional (2D) structures toward different polluting gasses have been explored [14]. Unlike flat graphene sheet, silicene and germanene have buckled honeycomb structures due to the partial sp^3 hybridization of Si and Ge atoms [15–19], making them chemically more reactive toward atoms and molecule adsorption compared to graphene [20–23]. Although N-based molecules are chemisorbed on silicene and germanene *via* strong covalent bonds, CO_2 is weakly physisorbed on silicene and germanene sheets [21,22, 24–28]. The electronic structures of silicene and germanene show strong modifications under Li decoration [29–32]. It was also stated that functionalization of Si atoms with Au (Li) improves the interaction between silicene and CO (CO_2) molecules [33,34]. Yuan et al. performed DFT calculations to investigate the stability, structural and electronic properties of saturated and half-saturated germanene with alkali metal atoms and found that the complete lithiated germanene has the highest stability among all the studied structures [35].

In this study, density functional theory (DFT) method is accepted to examine the CO_2 adsorption on germanene sheet functionalized by Li atoms.

2. Computational method

Calculations are performed using first-principle methods based on DFT implemented in Atomistix ToolKit (ATK) package [36]. The exchange-correlation functional is approximated by the Generalized Gradient Approximation of Perdew–Burke–Ernzerhof (GGA-PBE) with a double-ζ polarized basis set. To describe long-range van der Waals (vdW) interactions, the Grimme vdW correction (DFT-D2) [37] is also considered. The density mesh cut-off is set to

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https://doi.org/10.1016/j.physleta.2017.11.021
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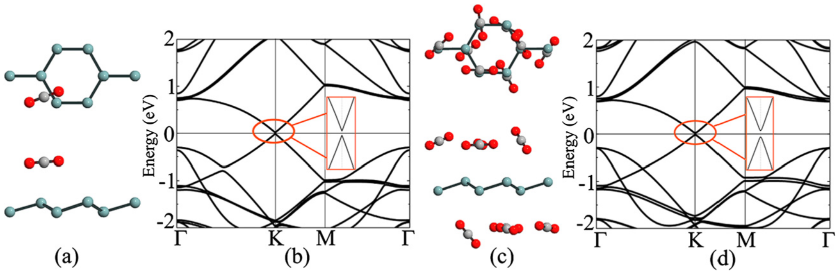

Fig. 1. The most stable adsorption configurations (top and side view) and their corresponding band structures for (a) and (b) one CO_2 (low coverage) (c) and (d) eight CO_2 (high coverage) on pristine germanene, respectively. The cyan, grey, and red balls represent Ge, C, and O atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

be 150 Ry. To avoid adjacent images interactions, a large vacuum space of 25 Å is considered in z-direction. Prior to the calculations; all the structures are fully relaxed using the conjugate gradient method up until the force on each atom is less than 0.01 eV/Å. For the germanene unit cell, the first Brillouin zones are sampled using $11 \times 11 \times 1$ and $21 \times 21 \times 1$ k-points for optimization and calculations, respectively. Moreover, first-principles molecular dynamics (MD) calculation are performed under NVT conditions where the number of atoms (N), the volume (V), and the temperature (T) are conserved. The temperature is controlled by the sampling of the canonical ensembles using algorithm of Nosé Hoover [38]. The MD simulation time is 1.5 ps with a time step of 1.0 fs.

3. Results and discussions

We first discuss the adsorption behavior of CO_2 gas molecules on the pristine germanene sheet. To this end, an individual CO_2 is initially placed on a germanene sheet at four different positions including valley (the Ge atom in the lower sublattice), hill (the Ge atom in the upper sublattice), bridge (the Ge–Ge bond), and hollow (the center of a hexagon ring) sites with two different molecular orientations, parallel and perpendicular to the surface. We use the notation $Ge_8(CO_2)_n$ to distinguish between the various numbers of CO_2 molecules, n, in a 2×2 supercell of germanene (adopted from Ref. [34]). The adsorption behavior of molecule on germanene is investigated after full relaxation. The structural stability can be addressed using adsorption energy (E_{ad}) which is

$$E_{ad} = [E_{Germanene+\mathrm{CO_2}} - E_{Germanene} - n \times E_{\mathrm{CO_2}}]/n \tag{1}$$

Here, $E_{Germanene+\mathrm{CO_2}}$, $E_{Germanene}$, and $E_{\mathrm{CO_2}}$ denote the total energies of the germanene–CO_2 system, pristine germanene, and the isolated CO_2 molecule, respectively. Based on the definition, the negative E_{ad} represents the structural stability. Moreover, for a material to be suitable as a medium for CO_2 capture, relatively large amounts of adsorption energy and charge transfer are vital. Comparing the adsorption energies of different adsorption geometries, the horizontal alignment on top of the bridge site is found to be energetically more favorable, as shown in Fig. 1(a). The distance between CO_2 and the germanene sheet is 3.88 Å, showing weak vdW interactions. A small adsorption energy of −0.11 eV along with small charge transfer (calculated by Mulliken population analysis) of 0.04 e from the molecule to the germanene confirms this fact that CO_2 molecule is physisorbed on the germanene. Therefore, pristine germanene could not be an appropriate material for CO_2 capture because a minimum adsorption energy of −0.14 eV is required from an application point of view [39]. These results agree well with previous theoretical findings [21,28]. It should be noted that for the higher CO_2 coverage, the molecules are inclined with respect to the horizontal direction due to the repulsion between them, as shown in Fig. 1(c). The distances between CO_2 molecules and germanene are 3.51 to 3.97 Å. The average adsorption energy and charge transfer from each CO_2 to germanene are decreased to −0.09 eV and 0.02 e for high coverage, respectively. These small values limit the application of germanene as a potential media to capture CO_2. Pristine germanene is a zero-gap semiconductor. We found that the linear Dirac-like dispersion relation of germanene at K point remains almost unchanged upon physisorption of a single CO_2 gas molecule. A tiny band gap of 3 meV is opened at the Dirac point of germanene, as shown in Fig. 1(b). The change in the band structure of germanene is a little more pronounced at the high coverage of CO_2 where the band gap is enhanced to 44 meV, as illustrated in Fig. 1(d).

Lithium functionalization is expected to enhance the stability of CO_2 gas molecules on germanene nanosheet [35]. Similar to fully lithiated silicene [40] and graphene [41], lithium atoms occupy sites on top of the Ge atoms in the lower sublattice, which is in agreement with previous findings [35]. The optimized geometry of Li-functionalized germanene is presented in Fig. 2(a). The lattice distortion caused by lithium adsorption is noticeable. The buckling distance and Ge–Ge bond length are enlarged from 0.73 and 2.46 Å in pristine germanene to 1.23 and 2.55 Å in lithiated germanene, respectively. Furthermore, the minimum Ge–Li bond length is 2.55 Å. The bond strengths can be assessed on the basis of the adsorption energy of lithium atoms on the surface of germanene using following formula:

$$E_{ad} = [E_{Germanene+\mathrm{Li}} - E_{Germanene} - N_{\mathrm{Li}} \times E_{\mathrm{Li}}]/N_{\mathrm{Li}} \tag{2}$$

Here, $E_{Germanene+\mathrm{Li}}$ and E_{Li} are the total energies of the lithiated germanene system and the single Li atom, respectively. In addition, N_{Li} is the number of adsorbed Li atoms in the supercell. Adsorption energy of −1.01 eV/atom reflects the stability of fully lithiated germanene (Ge_8Li_8) and suggests the chemisorption of lithium atoms on the surface of germanene. However, the electronic total charge density indicates that there is a small electron orbital overlap between Li and Ge atoms, showing that a weak covalent bonding exists between Li and germanene, see Fig. 2(c). It is found that each Li atom (electronegativity of 1) donates 0.176 e to the more electronegative Ge atoms (electronegativity of 2); hence, the main character of the bonding between Ge–Li in this system is ionic. Consequently, the ionic interaction induced by large charge transfer between Li and Ge atoms is the reason of high stability of fully lithiated germanene. Upon complete lithiation, the band structure is transformed from a zero-gap semiconductor to an indirect semiconductor with 220 meV band gap, as shown in Fig. 2(b). Unlike pristine germanene, fully lithiated germanene does not have the linear dispersion at the K point.

Osborn et al. predicted an energy gap of 368 meV in fully lithiated silicene [40]. A Ge atom has a larger atomic radius in comparison with Si atom, giving rise to a decrease in the strength of covalent bonds in Ge–Li compared to Si–Li. Hence, larger energy band gap in fully lithiated silicene than that in germanene can be