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Full Length Article

High Selective Gas Detection for small molecules based on Germanium selenide monolayer

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ABSTRACT

Predictive calculations based on density functional theory (DFT) are used here to study the electronic and optical properties of GeSe monolayer after adsorbing gas molecules (O_2, NH_3, SO_2, H_2, CO_2, H_2S, NO_2, CH_4, H_2O, NO, CO). Our results reveal that for all the gas molecules considered, only NH_3 is adsorbed on GeSe monolayer by physisorption. Whereas SO_2 and NO_2 are chemisorbed on GeSe monolayer with strong adsorption energies. In addition, the adsorption of O_2, NO and NO_2 distinctly enhances the optical absorbance and broaden the absorbance range of GeSe monolayer in visible light region. Also, it is found that the adsorption of H_2S, NO and NH_3 can reduce the work function of the GeSe monolayer. The results indicate that GeSe monolayer is not only a promising candidate for the sensing, capture, and storage of NH_3, but also an anticipated disposable gas sensor or metal-free catalyst for detecting and catalyzing SO_2 and NO_2. Furthermore, it has excellent potential to be applied to optical sensors, solar cells, nanoelectronics or optoelectronics devices.

1. Introduction

The two-dimensional (2D) materials have attracted enormous attention in recent years, owing to its fascinating mechanical and electronic properties [1,2]. The most famous one, graphene, was found to have many promising applications in nanoelectronics and optoelectronics, such as integrated circuits, transistors, supercapacitors [3], transparent conducting electrodes [4], gas storage materials, and gas sensors [3,5]. However, the gapless nature of graphene impedes the way of its practical applications [1,6]. Thus, the exploration of other 2D materials is still to be continued [7]. During this process, black phosphorus, also named phosphorene, has been isolated successfully in experiment [8], which possesses a sizable direct band gap [9], high mobility, highly on/off ratios, anisotropic electric conductance, and optical responses [10,11]. However, the main disadvantage of phosphorene is that it is unstable even in air [12,13].

Recently, a new 2D semiconducting material, Germanium selenide (GeSe) is found possessing an analogue structure with black phosphorous but exhibiting better stability [14]. The GeSe is already widely used in nanoscale devices because of its high stability, flexibility, earth abundance, high efficiency and many properties similar to the lead chalcogenides [15]. With the development of exfoliating technology, it can expect that GeSe monolayer also can be exfoliated from layered compound in the future and widely used in fields of nanomechanics and optoelectronics [15,16]. Specially, GeSe monolayer is interested for photodetector and consumer-touch sensors [15,17].

In the processes of industrial monitoring, medical treatment, crop cultivation, and environmental protection [18], sensing small gas molecules, or immediately catalyzing pollution gas is a crucial step. 2D materials, such as graphene, phosphorene, have great potential to be gas sensors, which have previously demonstrated experimentally and theoretically [19,20]. Additionally, optical gas sensor as a branch of sensor has been researched in the past decades [19]. A wide variety of articles have been published in this field based on 2D materials. Importantly, fermi level, carrier density, and optical properties of 2D materials can be modified by adsorbing small gas molecules [18]. Although there have been some researches about GeSe monolayer, systematic analyzing of GeSe

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monolayer adsorbing gas molecules remain poorly explored [21]. So it is meaningful to study the adsorption behavior of different gases adsorbed on the GeSe monolayer [22].

In this work, predictive calculations based on DFT are used to study the adsorption behavior of small molecules (O_2, NH_3, SO_2, NO_2, CH_4, NO, H_2S, H_2O, H_2, CO, CO_2) on GeSe monolayer [23]. We are focusing on the geometry structure, electronic, and optical properties of GeSe monolayer without and with gas molecules adsorption. The results show that NH_3 is physisorbed on GeSe monolayer with moderate adsorption energy, while SO_2 and NO_2 are chemisorbed on GeSe monolayer. In addition, GeSe monolayer exhibits extremely strong optical absorbance in the visible light range. And then, this tendency could be enhanced after the adsorption of NO_2, O_2, or NO molecules [24], and the work function of GeSe monolayer reduces after the adsorption of H_2S, NO, and NH_3 molecules [25].

2. Computational method

The system consisting of a $3 \times 3 \times 1$ supercell of GeSe monolayer, the lattice constant is a = 4.27 Å and b = 3.93 Å, which are in good agreement with previous reports [15,17]. A vacuum space of 20 Å is placed to avoid interaction between the adjacent layers in the direction perpendicular to the infinite plane of GeSe monolayer [26]. In this work, the first-principles computations of structural and electronic properties are based on DFT as implemented in the $DMol^3$ package [18]. The optical properties calculations are performed by CASTEP package [27]. All electronic energy of exchange correlation is treated through generalized gradient approximation (GGA) with PBE exchange-correlation function [28]. The dispersion corrected (DFT-D) proposed by Grimme has been employed in order to obtain a better understanding for the noncovalent chemical functionalization of GeSe monolayer by gas molecules adsorption. The double numerical atomic orbital plus polarization (DNP) is utilized as the basis set with the global orbital cut-off of 5.0 Å to ensure the high computational quality. The k-point is set to $16 \times 16 \times 1$ for structural optimizations and $20 \times 20 \times 1$ for the electronic properties calculations, and the smearing value is 0.005 Ha (1 Ha = 27.2114 eV). The k-point is set to $7 \times 7 \times 1$ in calculating the optical properties. The energy cut-off is set to 400 eV. In this work, non-spin-polarized calculation is used for the adsorption of H_2, CO_2, NH_3, CO, H_2S, CH_4, SO_2, and H_2O, and spin-polarized calculation is used for NO_2, O_2, and NO.

In order to evaluate the stability of the adsorption of gas molecules on GeSe monolayer, the adsorption energy (E_a) is defined as:

$$E_a = E_{GeSe+gas} - E_{GeSe} - E_{gas}$$

where $E_{GeSe+gas}$, E_{GeSe} and E_{gas} are the total energies of gas molecule adsorbed GeSe monolayer, GeSe monolayer, and gas molecule, respectively [29].

3. Results and discussion

Firstly, four typical anchoring positions for the gas molecules (O_2, NH_3, SO_2, NO_2, CH_4, NO, H_2S, H_2O, H_2, CO, CO_2) on the GeSe monolayer, including G site (on top of a Ge atom), S site (on top of a Se atom), C site (on top of puckered quadrilateral center), and B site (on top of a Ge-Se bond) [30,31], as shown in Fig. 1, are considered to identify the most favorable adsorption configuration. For all the gas molecules studied, gas molecule is initially placed at four typical different positions above GeSe monolayer mentioned before with different orientations, Herein, we take the NO_2 gas molecule as an example, three initial molecular orientations are examined at each site, one with NO_2 plane parallel to GeSe monolayer, and two with NO_2 plane perpendicular to it, with N atom or O atom pointing to GeSe surface, respectively [32].

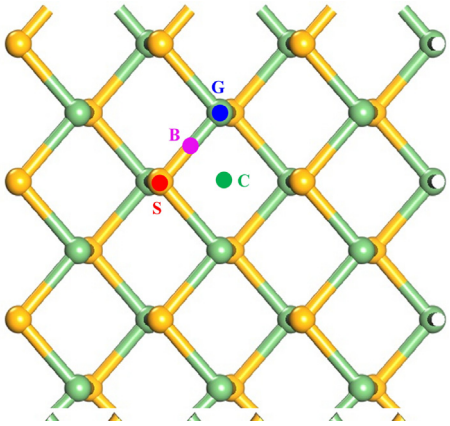

Fig. 1. Schematic view of G site, S site, C site and B site on GeSe monolayer.

Table 1
Adsorption Energy (E_a), the Nearest Distance (d) between Gas Molecule and GeSe monolayer and the Charge Transfer (ΔQ) between Gas Molecule to GeSe monolayer. A positive ΔQ indicates a transfer of electrons from the gas molecules to GeSe monolayer.

Gas molecule	E_a (eV)	d (Å)	ΔQ (e)	style
H_2	−0.053	2.996	−0.024	acceptor
CO	−0.087	3.504	0.007	donor
NO	−0.123	3.152	−0.041	acceptor
CO_2	−0.150	3.375	−0.015	acceptor
CH_4	−0.159	3.118	−0.057	acceptor
O_2	−0.201	2.933	−0.112	acceptor
H_2S	−0.208	3.404	0.048	donor
H_2O	−0.225	2.695	−0.011	acceptor
NH_3	−0.415	2.515	0.156	donor
SO_2	−0.490	2.855	−0.198	acceptor
NO_2	−0.677	2.287	−0.295	acceptor

We perform the geometric optimization of small gas molecules adsorbed on GeSe monolayer systems by DFT method. After full relaxation, the most stable adsorption configurations of small gases molecule adsorbed on pristine GeSe substrates are selected as shown in Fig. 2. The values of adsorption energy (E_a), nearest distance (d) (defined as nearest two atoms center-to-center distance between gas molecule and GeSe monolayer system) and charge transfer (ΔQ) for the optimized adsorption with stable site are generalized in Table 1.

From the most energetically stable configurations in Fig. 2, we find that O_2, SO_2, NO, H_2 molecules prefer to adsorb on G site, and NO_2, CH_4, CO molecules tend to be adsorbed on C site. In addition, NH_3, CO_2 molecules bind with S site and H_2O, H_2S are preferably adsorbed at the B site. After the adsorption of O_2, SO_2, NO_2, CH_4, NO, H_2O, H_2, and CO_2 gas molecules on pristine GeSe monolayer, the target gas molecules serve as acceptor, while the NH_3, H_2S, CO gas molecules play the part of donor. Compared with the negligible change in bond length and angle of most molecules, especially, the N—O bond of NO_2 have elongated by 0.025 Å and the O—N—O angle is shortened by 8.186°. Moreover, as shown in Table 1, the adsorption energy of NO_2 molecule on GeSe monolayer is calculated to be −0.677 eV and the value of charge transfer from GeSe monolayer to NO_2 is 0.295 e, both of them are the largest among these different gas adsorption systems. Furthermore, the adsorbed NO_2 molecule has the smallest distance with GeSe monolayer, the obtained d is calculated to be 2.287 Å which is very close to the Ge-N bond lengths 1.95 Å [33,34]. Obviously, GeSe monolayer has serious structure deformation after NO_2 adsorption which indicates that the interaction between them is greatly strong. In the other words,