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Detection of nucleobases using 2D germanane nanosheet: A first-principles study

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ABSTRACT

The electronic properties and geometric stability of germanane nanosheet is explored using first-principle studies. The germanane nanosheet exhibits semiconducting properties and stability of germanane sheet is ensured with formation energy. The adsorption behavior of deoxyribo nucleic acid (DNA)/ribo nucleic acid (RNA) nucleobases on monolayer germanane nanosheet have been investigated using density functional theory with van der Waals dispersion correction. The adsorption of nucleobases is found to be physisorbed on germanane nanosheet with the van der Waals type of interaction. The order of adsorption of nucleobases with germanane nanosheet is known to be C > G > A > T > U. We observed the changes in the energy band structure and the density of states variation due to the adsorption of nucleobases on germanane nanosheet. Our results confirm that apart from graphene, germanane monolayer can be used to detect nucleotides in the field of biotechnology and medical science.

1. Introduction

The human genome sequencing has been carried out for past two decades; from the previous literatures, it is known that only 1.5% of the human genome codes for amino acids. Moreover, around 98.5% is the junk DNA. Besides, the substantial part of so-called junk DNA encodes to non-coding RNA [1]. Furthermore, messenger RNA (mRNA), ribosomal RNA and transfer RNA (tRNA) were identified with the advancement of new methods, making it possible to depict the different types of RNA. A biosensor is required for the assessment of DNA/RNA molecules. The interaction of DNA/RNA molecules in the base material should produce the change in the signal. The advancement in nanoscience led to the development of nano biosensors that detect at the level of the single molecular cell. The adsorption properties of nucleobases on to the substrate depend on the different morphology of the base material such as quantum dots, nanoparticles, nanowire, carbon nanotube, nanoribbon, nanosheet for bio sensing applications. Thus, the sensing platform for nano biosensor plays an important role in sequence detection of nucleic acid. The adsorption properties of DNA/RNA bases on MoS_2 and Li-doped MoS_2 nanosheet is studied by Miesam Sadeghi et al. [2]. Moreover, many researches have been carried out in the adsorption of nucleobases. K. Hammami et al. have reported about the interaction of adenosine monophosphate with biomimetic apatite substrate [3]. The adsorption of cytosine on aluminium and gallium doped graphenes using density functional theory (DFT) is carried out by Ali Shokuhi Rad and co-workers [4]. B. Pathak et al. have studied the DNA sequencing through the double functionalized nanopore embedded electrodes. The study shows that the current signal differs by one order of magnitude for four different nucleic acid bases, which the DNA sequence can be carried out by the variation in the electrical signal [5]. The DNA nucleobases, aromatic acids and heterocyclic compounds adsorption on silicene and germanene monolayers is reported by Tanveer Hussain et al. [6]. The authors report that pristine germanene and silicene monolayers can be used for detecting biomolecules. Haiying He et al. reported about the DNA sequencing through the functionalized nanopore embedded electrodes. The report suggests that hydrogen bonds formed between the target bases and molecular probe stabilize the scanned DNA from thermal fluctuations [7]. Saikat Mukhopadhyay et al. have studied the nucleobase physisorption on boron nitride nanotubes [8]. The report shows that the binding of nucleobases on boron nitride nanotube forms the order G > A ≈ C ≈ T ≈ U. Seung Kyu Min et al. studied the DNA sequencing based on graphene nanochannel device in which the conductance change is noticed upon passage of DNA strand through graphene nanoribbon [9]. Jun-Ho Lee et al. [10] demonstrated the adsorption of DNA nucleobases on to the boron nitride and graphene nanosheets using different exchange-correlation functional. Moreover, we have reported the adsorption behavior of NO_2, CO and NO gas

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molecules on to the germanene nanosheet [11,12]. Also the adsorption characteristics of alcohol and aldehyde molecules on germanene nanosheet are studied and the findings show that the adsorption of alcohol is more favorable rather than aldehyde molecules [13]. Among the different two-dimensional (2D) materials, germanene holds promising characteristics due to its fascinating properties such as its spin-orbital coupling effects and tunable electronic properties. Moreover, Satoshi Endo et al. [14] have synthesized germanene sheet on Al (1 1 1) by Ge deposition near at ambient condition. Also the authors report the strong hybridization between Al (1 1 1) substrate and Ge layer. Besides, Ya-ping Wang and co-workers [15] have studied the opening of band gap in germanene by organic molecule adsorption such as acetone, ammonia, benzene, methane, toluene. The study revealed that the band gap varies from 3.9 to 81.9 meV. Elisabeth Bianco et al. [16] synthesized hydrogen-termination germanium (germanane-GeH) from topochemical deintercalation of $CaGe_2$. The authors reports that GeH is stable up to 75 °C. Nevertheless, the surface modification leads to enhanced adsorption properties of biomolecules on to the germanane sheet material. In addition, R.H. Scheicher group extensively studied the DNA adsorption and sequencing on the monolayer materials and through the nanopores [17–22]. Moreover, the previously published reports by R. H. Scheicher group gives detailed insights in the DNA sequencing. The unique aspect of the present work is to use the germanane nanosheet as a base material for the adsorption of nucleobases. Further, the present report demonstrates the possible application of DNA sequencing using germanane nanosheet base material.

2. Computational details

The ab initio calculation on the electronic properties and geometrical optimization of germanane nanosheet is performed with the help of density functional theory (DFT) technique facilitated with SIESTA package [23]. The local structural optimization of germanane nano-material was performed through generalized gradient approximation (GGA) with van der Waals dispersion correction along with Perdew, Burke, Ernzerhof (PBE) exchange–correlation functional [24–26]. Further, the adsorption behavior of nucleobases namely, adenine, cytosine, guanine, thymine and uracil on germanane nanosheet are investigated through SIESTA package. Zhao et al. [27] investigated the optical, structural and transport properties with defects in germanane nanoribbons using GGA/PBE exchange correlation functional, which strengthens and validates the present study. The Troullier norm-conserving pseudopotential [28] is utilized for core-valence interaction. The grid mesh cutoff is set to 500 eV for geometrical optimization of germanane nanosheet. The complete optimization of germanane nanosheet was performed with conjugated gradient (CG) algorithm and double-zeta-polarization (DZP) [29,30] until the Hellmann-Feynman force is converged to 0.03 eV/Å. Besides, the Brillouin zone integration of germanane is sampled with $(18 \times 18 \times 1)$ Γ-centered Monkhorst-pack k-grid [31]. The energy band gap, density-of-states, charge density including the electron localization function of germanane nanosheet were calculated with the help of SIESTA code. The transfer of charge is investigated with Bader-atoms-in-molecule (BAIM) analysis [32].

3. Results and discussion

3.1. Structure of germanane base material

The structure of germanane resembles a buckled structure. The neighboring rows of Ge atoms are furrowed in up and down directions. Thus, the germanium atoms are passivated with H atoms in the up and down directions giving rise to formation of germanane nanostructure. Fig. 1 represents germanane nanosheet, which is used as a base material to identify the sequence of nucleobases. Hence, germanane sheet can be used as a biosensor. Initially, to study the stable structure of germanane nanosheet, the formation energy is used to ensure its stability.

The formation energy of germanane nanosheet is calculated from the equation given below,

$$E_{form} = (1/n)[E(HGe) - xE(Ge) - yE(H)]$$

where E (HGe) represents the total energy of germanane nanosheet. E(Ge) and E(H) infers the energy of isolated germanene and hydrogen atom, respectively. n is the total number of atoms in germanene material. The formation energy of germanane nanosheet is calculated to be -3.89 eV. The negative value of formation energy authenticates the stability of germanane nanosheet. Moreover, the atomic energies of the elements are taken into count for the calculation of formation energy. Also the formation energies of germanane nanosheet are compared with the previous reports and are found to be in agreement. Table 1 illustrates the formation energy of germanane from the previously available reports.

Moreover, the formation energy decreases by an amount of 0.573 eV for germanane compared with bare germanene due to passivation of dangling bonds with hydrogen atoms. However, germanane nanosheet is stable in its structure, which can be used as a base substrate material to identify the nucleobase sequence. Fig. 2 illustrates the energy band structure and density of states (DOS) spectrum of germanane nanosheet. Upon hydrogenation of germanene nanosheet, the band gap widens due to sp^3 hybridization in the germanane nanostructure. The energy band gap of germanane nanosheet is calculated to be 1.91 eV along the gamma point, which possesses semiconducting nature, one of the feasible conditions for biosensor. Also, Jun Zhao et al. [27] calculated the band gap of zig-zag germanane nanoribbion to be 1. 47 eV at Γ-point.

Moreover, depending upon edge structure of germanane nanosheet such as zig-zag or arm chair structure, the band gap can be fine-tuned [27]. In the present work, zig-zag germanane nanosheet is used as a base substrate material for the detection of nucleobases. Moreover, the DOS spectrum shows more peak maxima along the virtual orbital (conduction band). The more peak maxima refer the easy electronic transfer between nucleobases and the base material germanane. Thus, the band structure and DOS spectrum illustrate the semiconducting nature of germanane nanosheet, which can be utilized to adsorb the nucleobases namely, adenine (A), cytosine (C), guanine (G), thymine (T) and uracil (U).

3.2. Adsorption of nucleobases on germanane nanosheet surfaces

The adsorption characteristics of nucleobases on germanane nanosheet are discussed in terms of energetics, charge transfer and band gap variation. In the current work, for each complex system, i.e. the adsorption of nucleobases on germanane nanosheet, the minimum energy configuration has been chosen from the global minima position. In order to map the global minima positions for each nucleobases on to the germanane nanosheet, we have studied the distance between germanane nanosheet and nucleobase as illustrated by R. G Amorim and R. H Scheicher group [17,20]. The plot of distance versus binding energy between germanane nanosheet and all nucleobases are presented in Fig. S1 in the supplementary information. (Kindly refer supplementary information for global minima positions). Furthermore, the vibrational analysis is also carried out for germanane sheet and upon adsorption of nucleobases on germanane nanosheet. There are no imaginary frequencies noticed upon adsorption of nucleobases on to the