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Adsorption studies of trimethyl amine and n-butyl amine vapors on stanene nanotube molecular device – A first-principles study

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ABSTRACT

The stanene nanotube is designed and used for the detection of trimethyl amine (TMA) and n-butyl amine (n-BA) vapors, which is investigated using first-principles study. The electronic properties of bare stanene nanotube and the adsorption properties of TMA and n-BA molecules are studied using density functional theory with non-equilibrium Green's function. Moreover, the device density of states shows the shift in the peak maxima upon adsorption of TMA and n-BA molecules on to the stanene nanotube. The variation in the flow of electron is noticed upon adsorption of TMA and n-BA molecules in the transmission spectrum of stanene nanotube. I-V characteristics clearly confirm the variation in the current upon adsorption of TMA and n-BA molecules. The findings of the study clearly suggest that the stanene nanotube molecular device can be used for the detection of trace levels of TMA and n-BA molecules present in the atmosphere.

1. Introduction

In recent days, researchers have focused on two-dimensional (2D) group IV elements viz., silicene, germanene and stanene for their application in chemical nanosensors [1–3]. The tuneable properties of monolayer 2D materials lead to their likely utilization in energy generation, conversion and development of future electronic devices. Thus, two-dimensional nanomaterial is a present pursuit among research community [4,5]. The most widely considered 2D nanomaterial is graphene, whose Fermi velocity is in correspondence with the velocity of light [6]. Moreover, similar to graphene, silicene, germanane and stanene have buckled honeycomb geometry with large spin-orbit coupling strength, which tends to widen their band gap for the possible applications in nanosensors. Besides, stannum, germanium and silicon will not exhibit the layered structure like graphite. The single layer nanostructure of stannum, germanium and silicon namely stanene, germanene and silicene have been proposed in theory and recently synthesized experimentally [6]. Nevertheless, the modern evolution in the nanomaterial synthesis leads to the synthesis of stanene [3], germanene [7] and silicene [8]. The other group-IV two-dimensional nanostructures also have high carrier mobility similar to graphene [9]. In addition, many of the two-dimensional materials possess semi-metallic nature with insufficient band gap energy, which restricts its use in the fabrication of field effect transistors (FETs). Stanene holds a low-buckled honeycomb nanostructure that exhibits the stable structure. The buckled structure of stanene arose due to the weakening of $\pi - \pi$ bonding among tin atoms and extends to the overlapping of π and σ orbitals, which guides to a stable structure. Furthermore, the computational studies confirm the zero band gap of stanene without spin-orbital-coupling (SOC) effect, whereas in the presence of SOC effects, the band gap energy of stanene opens up to 0.1 eV [10].

The volatile organic vapor (VOCs) like trimethyl amine (TMA) is emitted by industries, decay of animal and plant residues. Furthermore, the physisorbed vapor molecules expeditiously modify the electronic properties, carrier density and the Fermi level shifting in 2D nanomaterial improving their sensing capability [11]. The adsorption properties of silicene, germanene and graphene layers have been studied and used as gas/vapor sensors [12–15]. Owing to the widening of band gap in monolayer 2D materials, the monolayer of graphane, silicane and stanane are well considered in the development of chemical sensors. [16]. The advantage of using 2D monolayer as chemical sensor is it can be used as a simple two-probe device, where the change in resistance can be measured. The variation in the resistance is directly proportional to the concentration of the target vapor. Besides, the electron transfer between the monolayer base materials with the target vapor takes place easily. The prime objective of using monolayer base materials is the enhanced adsorption and desorption of vapor molecules during oxidation and reduction process. Moreover, the adsorption and

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desorption process changes the band gap resulting in the variation of electrical resistance of 2D-base material, which can be used for vapor sensing. Also the baseline resistance of monolayer base material can be easily attained. These are the reasons behind the selection of monolayer materials for the development of chemical sensors. Liu and co-workers [17] reported about the electronic properties of stanene and inferred that a band gap is noticed at the Dirac point when SOC effects are taken into account. Liu et al. [16] studied about the 2D-stanane material, which possess high carrier mobility, strain-tuneable electronic structure and obtrusive light adsorption. Chen et al. [18] observed the dumbbell stanane, which exhibits a quantum spin Hall Effect that can be used in quantum computation and spintronics. Zhou et al. [19] studied the adsorption properties of hazardous molecules such as CO, CO_2, SO_2, H_2S on stanene sheet using DFT calculations. Using first-principles calculations, Chen et al. [20] investigated the adsorption of toxic molecules on monolayer stanene. In our previous work, we have reported the adsorption properties of a hydroxyl functional group of alcohol such as methanol, ethanol and 1-propanol on hydrogen functionalized stanene sheet called stanane [21]. In order to check the presence of trace levels of TMA and n-BA, the development of solid-state gas sensor is required. The inspiration behind the proposed work is to develop a prominent chemical sensor to detect the presence of trimethyl amine (TMA) and n-butyl amine (n-BA) using stanene nanotube. Based on the previously published articles, the tuneable electronic properties of stanene nanosheet initiated the present work to investigate the adsorption properties of VOCs such as TMA and n-BA vapors on stanane nanotube device.

2. Computational details

The electronic properties of stanene nanotube device are investigated using density functional theory technique in combination with non-equilibrium Green's functional method (NEGF) executed on TranSIESTA module included in the SIESTA package [22]. The optimization of stanene nanotube is carried out by decreasing the atomic forces on the Sn-atoms to below 0.05 eV/Å. The calculation process is carried out using generalized-gradient-approximation (GGA) along with suitable Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional in order to study the electron-electron interactions [23,24]. The Brillouin zones of stanene nanotube are sampled by $8 \times 8 \times 10$ k points. The super cell of stanene nanotube is $1 \times 1 \times 5$. The electronic wave functions of stanene nanotube are studied in terms of the basis set that depends on the numerical orbitals. The double zeta polarization (DZP) basis set is utilized in the present work while optimizing the stanene nanotube [25]. The adsorption properties of TMA and n-BA molecules on stanene nanotube device are also studied using SIESTA package. Moreover, to prevent the interaction of periodic images in stanene nanotube, the vacuum padding of 10 Å along x and y axes is used. Besides, the atoms in stanene nanotube are allowed to transfer freely to their positions until the convergence force is attained below 0.05 eV/Å.

3. Results and discussion

3.1. Structure of stanene nanosheet molecular device

The stanene nanosheet, which comprises of a single hexagonal layer of tin atoms are enfolded to make it as a stanene nanotube that extends along the z-direction with the supercell size of $1 \times 1 \times 5$. Fig. 1 (a) represents the schematic diagram of isolated stanene nanotube molecular device. The stability of the optimized stanene nanotube can be explored with the help of formation energy. The formation energy of stanene nanotube is calculated using the equation.,

$$E_{form} = 1/n[E(Sn\text{-}NT) - nE(Sn)]$$

where E(Sn-NT) is the energy of stanene nanotube, E(Sn) is the energy of isolated tin atom and n denotes the number of tin atoms in the stanene nanotube. The calculated formation energy for the stanene nanotube is observed to be −3.78 eV which confirms the stability of the stanene molecular device. The two ends of the stanene nanotube are considered as left and right electrodes. The bias voltage of 0 V to 1 V is applied along the scattering region of the isolated stanene nanotube. Moreover, the designed stanene nanotube is used as the base material for the detection of TMA and n-BA vapors. The adsorption of trimethyl amine on stanene nanotube is referred as position P and n-butyl amine adsorbed on stanene nanotube is named as position Q as shown in Fig. 1(b) and (c) respectively. Initially, in order to optimize the adsorption sites of TMA and n-BA on stanene nanotube, various adsorption possibilities are studied. Further, the optimized global minima positions of TMA and n-BA adsorbed on stanene nanotube are considered in the present study. Usually, the semiconductor material is required for chemical sensor. The band gap of stanene nanotube is found to be around 0.128 eV, which is noticed from the energy band structure diagram as shown in Fig. 2. Along the Γ-point the energy band gap is observed to be 0.128 eV. Upon adsorption and desorption of TMA and n-BA molecules the change in the band gap of stanene nanotube is noticed. Moreover, the density of states diagram as shown in Fig. 3, illustrates that peak maxima in the conduction band. In general, the peak maxima in various energy levels along the conduction band support the possible application of stanene nanotube as a base material for chemical nanosensor. Furthermore, the electronic transition between TMA and n-BA with stanene nanotube are facilitated by the numerous peaks in the conduction band of stanene nanotube. Besides, the variation in the bias voltage has its effect on transmission of charge and density-of-states along stanene nanotube. The variation in the current along the stanene nanotube upon adsorption of TMA and n-BA leads to the conclusion of stanene nanotube as a chemical sensor. (*The atomic coordinates of the stanene nanotube is included in the supplementary information for the readers to carry out future studies*).

The adsorption energy E_{ads} of TMA and n-BA molecules can be calculated using the formula

$$E_{ads} = E_{complex} - (E_{stanene} + E_{TMA/n\text{-}BA})$$

where $E_{complex}$ is the energy for the stanene nanotube with TMA and n-BA, $E_{stanene}$ is the energy of isolated stanene nanotube and $E_{TMA/n\text{-}BA}$ are the energy of TMA and n-BA. When the molecules get desorbed from the stanene nanotube, the system is exothermic. The adsorption of TMA and n-BA leads to a decrease in the residual forces on the surface of the stanene nanotube. Thus, it leads to the decrease in the surface energy of the adsorbent. Furthermore, the charge transfer between the stanene nanotube and TMA and n-BA molecules are estimated through natural bond orbital (NBO) analysis. Moreover, a charge transfer of 0.049 e and 0.117 e is observed for the positions P and Q respectively. Table 1 represents the adsorption energy and charge transfer upon adsorption of TMA and n-BA molecules on stanene nanosheets.

3.2. Density of states of stanene nanotube upon adsorption of TMA and n-BA molecules

The density of states enables us to measure the distribution of charge as a function of energy and provides an insight on the transport phenomena and electronic properties of stanene nanotube [26–29]. The density of charge for various energy intervals of stanene nanotube molecular device for various bias voltages is envi-