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Full Length Article

Theoretical study of the structural and electronic properties of novel stanene-based buckled nanotubes and their adsorption behaviors

Amirali Abbasi[a,b,c,*], Jaber Jahanbin Sardroodi[a,b,c], Alireza Rastkar Ebrahimzadeh[a,b,d], Mina Yaghoobi[a,b,d]

[a] Molecular Simulation Laboratory (MSL), Azarbaijan Shahid Madani University, Tabriz, Iran
[b] Computational Nanomaterials Research Group (CNRG), Azarbaijan Shahid Madani University, Tabriz, Iran
[c] Department of Chemistry, Faculty of Basic Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran
[d] Department of Physics, Faculty of Basic Sciences, Azarbaijan Shahid Madani University, Tabriz, Iran

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ABSTRACT

Density functional theory calculations were performed to investigate the geometrical, electronic and adsorption properties of stanene based nanotubes in order to fully exploit the gas sensing capability of these nanotubes. The strain energy, structural parameters and electronic properties of stanene-based nanotubes with armchair and zigzag chirality with various diameters were examined in detail. The results show that, these nanotubes have a buckled structure, in which the tin atoms were arranged in chair-like honeycomb configuration. Calculated strain energy for considered nanotubes are relatively small compared to some other nanotubes pointed to flexibility of stanene mono layer. It was found that the strain energies for (4, 0), (5, 0) and (6, 0) nanotubes have negative values, indicating their stability with respect to stanene nanosheet. The band structure calculations reveal that the armchair nanotubes are semiconductors with two maximums with nearly same energies in valence band. However, the zigzag ones show both conductor and semiconductor behaviors by direct band gap in Γ point. Also the spatial distribution of molecular orbitals in valence band maximums and conduction band minimums were presented and discussed. Moreover, the adsorption behaviors of (6, 6) and (8, 8) nanotubes as chemical O_3 detection device were investigated in detail. We found that O_3 molecule dissociates into O_2 over the considered nanotubes, being an effective strategy to help in the reduction of the concentration of these harmful pollutants in the environment. The results also suggest that O_3 dissociation over the (6, 6) nanotube is more favorable in energy than that on the (8, 8) nanotube. The results present a great potential of stanene based nanotube for application as a highly sensitive ozone gas sensor.

1. Introduction

Following the discovery of carbon nanotubes in 1991 [1], trying to explore and synthesis of different types of nanotubes and study their properties have been demonstrated to be of eminent importance in different fields of science and technology [2–5]. In the past decades, various researchers show that the properties of these one-dimensional nanostructures are different from their corresponding bulk materials, and in many cases depend on their chirality. For example, the armchair carbon nanotubes are conductor while the zigzag ones act as both conductor and semiconductor [6]. Exciting properties of these materials make them promising for next generation nanodevices especially in nanoelectronics field [7–10]. Despite the nanotubes formed from group IV elements except for tin, especially carbon and silicon nanotubes, which have been widely attracted attentions, the nanotubes of tin have not been investigated so far.

Stanene is a group IV graphene-like nano material constructed from tin atoms in a buckled configuration, which first predicted theoretically [11,12], and then synthesized by Zhu et al. [13]. Some unique properties of stanene such as the large-gap two-dimensional quantum spin Hall states, topological superconductivity and the near-room-temperature quantum anomalous Hall effect, have been presented by the recently published articles, which make it attractive for study. Recently, a huge surge of interest has arisen in the investigation of adsorption behaviors of graphene and graphene like two-dimensional materials. The study

* Corresponding author at: Molecular Simulation Laboratory (MSL), Azarbaijan Shahid Madani University, Tabriz, Iran.
E-mail address: a_abbasi@azaruniv.edu (A. Abbasi).

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of the adsorption properties of different materials applied as chemical gas sensing devices is currently focused on the fabrication of new sensing materials with high performance. In this regard, Zhang et al. examined the sensing capabilities of various TiO_2 and carbon based nanostructures using DFT computations [14–16]. The adsorption of ozone molecule on graphene has been investigated by combined theoretical and experimental study [17]. The interaction of ozone molecule with carbon nanotubes has been studied experimentally [18–22] and theoretically [23–27]. Experimental studies have exhibited that ozone-adsorbed CNTs possess surface-bound functional groups such as C═O, C═C and C—O, and a heat treatment ($T \gg > 473$ K) of the ozone-adsorbed CNT causes releasing of CO_2 and CO in the environment [18]. Based on theoretical studies, it was found that the adsorption energy of O_3 molecule on CNT is 0.2–0.3 eV depending on the diameter and chirality [23,28,29]. According to the theoretical study of Park et al. [30], the surface of graphene has smaller reactivity than that of CNTs. Therefore, the interaction of O_3 with CNTs is strongly favored rather than graphene surface. Understanding on the ozone interaction with stanene nanotubes is not established, so far. Based on these findings, we have studied the interaction of O_3 molecule with stanene nanotubes.

O_3 molecule is a well-known air pollutant, which has detrimental impacts on respiratory tissues and ocular mucosa. The main target of tropospheric ozone in the human body is the lung, making harmful effects on body performance. Also, the injurious impacts of O_3 molecule on the eyes and the nervous system have been addressed in detail [31]. Due to the important role of O_3 from the atmospheric protection and toxicology point of view, O_3 removal by efficient adsorbents would be necessary. Therefore, it is of eminent importance to make efforts in the design and development of novel stanene based nanotube sensors.

In this work, the nanotubes formed from stanene were studied by the help of density functional theory, DFT, method. The considered nanotubes have both armchair and zigzag chirality with the diameters in the range of 9.45–37.73 Å and 4.48-21.37 Å, respectively. The computed properties included optimized geometrical structures, strain energies and electronic properties of the considered nanotubes. In this paper, we have also performed a set of systematic density functional theory (DFT) calculations to examine the interaction of ozone molecule with (6, 6) and (8, 8) stanene based nanotubes and identify the chemisorption binding of O_3 molecule to the substrate. The main aim of this study is to examine the structural and electronic properties of novel stanene based nanotubes and discover the excellent sensing properties of these nanomaterials for harmful ozone gas detection. Fig. 1 shows a schematic representation of a stanene based nanotube for sensing of ozone molecule in the environment.

2. Computational details

The considered stanene based nanotubes, SnNTs, can be obtained by rolling up stanene mono layers and labeled by (n, m) same as carbon nanotubes [32]. In this research, we performed our calculations for armchair (n, n), a-SnNTs, and zigzag (n, 0), z-SnNTs, nanotubes, in which n belongs to {4, . . ., 10, 12, 15}. The structural models of the considered nanotubes have been made by the help of Graphical Display Interface for Structures, GDIS [33]. We used DFT in the framework of conjugated gradient algorithm. Our DFT computations were carried out by SIESTA suite of computer codes [34]. The Generalized gradients approximation, GGA, parameterized by Pedrew-Burke-Ernzerhof, PBE, have been used for the exchange correlation functional [35]. We used the Trouiller-Martins norm-conserving pseudopotential [36] for core electrons and DZP basis sets for valence atoms.

Table 1
Calculated values for diameter (D), buckling parameter (B), unit cell length (L), strain energy (E_{str}), energy band gap (E_g), and energy differences between two maximums in valence band (ΔE_V) of a-SnNTs.

(n, n)	D (Å)	B (Å)	L (Å)	E_{str} (eV)	E_g (eV)	ΔE_V (eV)
(4, 4)	9.45	0.96	4.63	0.010	0.45	−0.203
(5, 5)	12.24	0.91	4.64	0.007	0.42	−0.008
(6, 6)	14.58	0.91	4.64	0.005	0.33	0.041
(7, 7)	17.30	0.90	4.65	0.004	0.28	0.084
(8, 8)	19.72	0.90	4.65	0.003	0.24	0.120
(9, 9)	22.39	0.89	4.65	0.002	0.21	0.144
(10, 10)	24.82	0.89	4.65	0.004	0.18	0.244
(12, 12)	29.98	0.89	4.65	0.004	0.15	0.201
(15, 15)	37.73	0.89	4.65	0.003	0.12	0.233

In order to obtain the optimized configuration, the unit cells of considered nanotubes were relaxed in axial direction until the stress components were less than 1 GPa. Also, the atomic positions in the unit cell were optimized until the atomic forces were less than 0.02 eV/Å. We used 50 k-points sampling along the tube axis according to Monkhorst-Pack approach for calculation the total energy and band structure [37]. The open-source program XCrysDen [38] was employed for visualizing data such as molecular orbitals and other figures. We have also calculated the adsorption properties of both (6, 6) and (8, 8) stanene based nanotubes including the analysis of the adsorption energies and projected density of states. Our total energy calculations were performed using the open source package for material eXplorer (OPENMX3.8) [39]. We found that the O_3 molecule coordinates to the (6, 6) and (8, 8) nanotube in a bridge geometry, leading to the dissociation of O_3 molecule over the nanotube. Gas-phase O_3 molecule has a bent geometrical structure with calculated O-O bond length of 1.278 Å and O—O—O bond angle of 117°, based on GGA functional, in accordance with previously reported theoretical and experimental results [40]. We used the term desorption energy (E_{ad}) to describe the binding of the O_3 molecule to the stanene based nanotubes. The adsorption energies are obtained using

$$E_{ad} = E_{(composite + adsorbate)} - E_{composite} - E_{adsorbate} \quad (1)$$

Here, $E_{(\text{ substrate + adsorbate })}$ is the total energy of the nanotube with O_3 molecule on its surface, $E_{substrate}$ is the energy of the stanene based nanotube without O_3 molecule, and $E_{adsorbate}$ represents the energy of an isolated O_3 molecule at its equilibrium structure. By this definition, a negative adsorption energy value represents that the adsorption process is more energetically favorable.

3. Results and discussion

3.1. Geometrical structure and strain energy

At the first, the optimized geometrical structures for a-SnNTs and z-SnNTs with various diameters were obtained. The optimized structure of (6, 6) and (12, 0) SnNTs were represented in Fig. 2(a) and (b), respectively. These figures show that the Sn atoms were positioned on two curvature layers because of the buckled honeycomb arrangement of Sn atoms. The radial distance between these two atomic curvatures is known as buckling parameter, B. The results show that for a-SnNT, B parameter decreases from 0.96 Å by increasing the nanotube diameter and converges to the value of 0.89 Å. However, for z-SnNTs, B parameter increases from 1.29–1.53 Å for n = 4 to n = 6, then decreases by increasing diameter until 0.90 Å for n = 15. These high values for B in small diameter z-SnNTs, probably arise from more disturbance in chair conformation of Sn cyclohexane-like rings. Tables 1 and 2 summarize the B parameter for the considered nanotubes.