Computational Materials Science 153 (2018) 126–133

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Electrical and mechanical properties of a fully hydrogenated two-dimensional polyaniline sheet

Meysam Bagheri Tagani

Department of Physics, Computational Nanophysics Laboratory (CNL), University of Guilan, Po Box: 41335-1914, Rasht, Iran

ARTICLE INFO

Keywords:
Polyaniline sheet
Density functional theory
Young modulus
Phonon modes

ABSTRACT

Two-dimensional (2D) polyaniline sheet has been recently synthesized and showed that it is a semiconductor with indirect band gap. In this research, we examine electrical and mechanical properties of a fully hydrogenated 2D polyaniline sheet C_3NH using density functional theory. Results show that the C_3NH sheet is an insulator with a band gap more than 5 eV. The sheet is quasi planner and dynamically stable confirmed by phonon band structure. Young modulus of the sheet is 275 N/m. Ab-initio molecular dynamics simulations show that the C_3NH sheet can be stable at 1000 K indicating a high melting point. Tensile strain reduces the band gap of the sheet and electron effective mass. In return, hole effective mass is strongly dependent on the strain direction so that strain along zigzag (armchair) increases (reduces) hole effective mass. Our findings show that C_3NH sheet is a promising candidate for electronic and optoelectronic applications and strain engineering can be used to tune its properties.

1. Introduction

Nowadays, synthesis and characterization of two-dimensional materials (2D) has attracted a lot of attention. The story of 2D materials begun after discovery of graphene at 2004 [1]. Graphene as a monolayer of carbon atoms has individual and different properties in comparison with prior materials. High carrier mobility and thermal conductivity, excellent mechanical ability, quantum hall effect, and linear band structure around Fermi level make it a fascinating material for scientists [2–5]. An atom thickness of graphene introduces it as a promising candidate for next-generation field effect transistor, however, absence of band gap is a great challenge in this field. Two strategies have been considered to solve the problem of band gap: creating a band gap in graphene structure or finding other 2D materials with intrinsic band gap. The former led to graphene nanoribbons [6,7], graphene antidote lattices [8,9], and mutilayer graphene sheets [10]. The later added silicene [11], germanene [12], phosphorene [13], stanene [14], and borophene [15] to 2D material family which some of them are semiconductor. In recent years a lot attention has been paid to 2D materials to investigate electrical, mechanical, and magnetic properties of them [16–22].

Mahmood et al. has recently synthesized a new 2D planner material from carbonized organic single crystal [23]. Two-dimensional polyaniline sheet with empirical formula of C_3N is an indirect semiconductor which has attracted a lot of attention because of its similarity with graphene. Indeed, C_3N can be considered as an improved version of nitrogenated holey two-dimensional structure with C_2N stoichiometry synthesized at 2015 [24]. Yang and coworkers has prepared C_3N sheet by polymerization of 2,3-diaminophenazine and showed that field-effect transistors made from C_3N display an on-off current ratio of 5.5×10^{10} [25]. Xu et al. showed that C_3N sheet is an excellent anode material for lithium-ion batteries [26]. C_3N sheets have also attracted attention from theoretical point of view [27–31]. It was shown that C_3N can be an excellent sensor for probing toxic gases like NO_2 and SO_2 [28]. Optical and mechanical properties of C_3N has been investigated in Ref. [29]. Bilayer C_3N shows anisotropic carrier mobility [30] and high thermal conductivity [31]. We studied C_3N nanoribbons and found that some of them can be half-metal [32].

Hydrogenation of single element 2D sheets can significantly change their electronic, mechanical and optical properties. Theoretical predictions showed that graphane, a fully hydrogenated graphene sheet, unlike graphene is a semiconductor [33]. Later, Elias et al. synthesized graphane and confirmed the theoretical predictions [34]. In this research, we study a fully hydrogenated 2D polyaniline sheet (C_3NH) with formula C_3NH_3 using ab initio calculations. Our investigation shows that just carbon atoms can host hydrogen and adding hydrogen atoms to nitrogen results in deformation of the structure. Phonon band structure shows the C_3NH is a stable and quasi 2D sheet. The electronic band gap of the sheet is about 5 eV and the sheet can be stable under uniaxial tensile strain as high as 10%. Ab-initio molecular dynamics simulations show that the structure is stable at 1000 K.

E-mail address: m_bagheri@guilan.ac.ir.

https://doi.org/10.1016/j.commatsci.2018.06.027
Received 1 May 2018; Received in revised form 9 June 2018; Accepted 18 June 2018
0927-0256/

2. Simulation details

In this paper we have used SIESTA package [35], which is based on density functional theory (DFT) and uses strictly localized basis sets, to study electronic properties of C_3NH sheet. Exchange-correlation functionals are described using GGA-PBE approximation and ultra-soft pseudopotentials are used for core electrons. Brillouin zone is meshed by $51 \times 31 \times 1$ K point sampling. Double zeta single polarized (DZP) basis set is chosen to describe valance electrons. All studied structures are carefully relaxed so that the maximum force which is applied on each atom is less than 0.001 eV/Å and stress on the cell is less than 0.001 GPa. Cutoff energy is set to 75 Ha and Van der Walls correction as Grimme DFT-D2 [36] is considered to describe interaction between hydrogen and carbon atoms. A 20 Å vacuum is set perpendicular to the sheet to prevent artifact interactions between the sheet and its image.

To investigate the mechanical properties of the sheet a supercell composed of 28 atoms is considered. Dynamical stability of the sheet is studied using phonon band structure for each strain. For phonon calculations, we have used a supercell composed of 420 atoms. Phonon calculation are very time consuming and needs huge CPUs, therefore, we have used DFT-tight binding method (DFTB) on the basis of Slater-Koster parameters [37] which is a very fast method and executable on laptop. The first Brillouin zone of the supercell is meshed by a $8 \times 8 \times 1$ k-point sampling and cutoff density is 40 Ha. Comparison between the phonon band structure obtained from DFTB and DFT for pristine C_3N shows that DFTB provides reliable results for phonon structure in C_3N and its derivatives.

Thermal stability of the structure is investigated using ab initio molecular dynamics (AIMD). A $4 \times 4 \times 1$ supercell is considered and Brillouin zone is meshed by a $3 \times 3 \times 1$ K-point sampling. The simulation is carried out in NVT ensemble with Nose-Hoover thermostat approach. The simulation is preformed for 3 ps with time step of 2 fs. Thermal stability of the sheet is studied at 300, 500, and 1000 K.

3. Results and discussions

Fig. 1 shows the structure of a polyaniline monolayer, C_3N, and two different hydrogenated polyaniline monolayer, C_3NH with hexagonal symmetry. Our investigation shows that just carbon atoms are enable to absorb hydrogen (see Fig. S1) and the structure is still quasi planner. Adding hydrogen atoms to nitrogen ones having three electrons for bonding disturbs the structure because of breaking C—N bonding. It is clear in Fig. S1 that there is no bonding between nitrogen and hydrogen and the distance between them is larger than 1.9 Å. We consider two different scenarios for hydrogenating the structure like graphane: hydrogen atoms are located at two different z planes as chair-like, Fig. 1b, or they are at the same plane as boat-like, Fig. 1c. To compare the stability of two different C_3NH structures the formation and binding energies of the structures are calculated as follows:

$$E_f = E_T(sheet) - \frac{1}{2}(N_N E(N_2) + N_H E(H_2)) - N_C E(C_g) \tag{1}$$

$$E_b = E_T(sheet) - (N_N E(N) + N_H E(H)) - N_C E(C) \tag{2}$$

where $N_N(N_H)$ is the number of nitrogen (hydrogen) atoms in the unit cell, and $E(N_2)(E(H_2))$ is total energy of nitrogen (hydrogen) molecule. N_C denotes the number of carbon atoms, and $E(C_g)$ is energy of each carbon atom in graphite. For binding energy calculation we have used ground state energy of isolated atoms obtained from spin-dependent calculations. Binding energy of chair-like structure is -5.473 eV/atom, while it is -5.128 eV/atom for boat-like structure. Formation energy of the chair-like structure is equal to -2.45 eV, while it is equal to 2.38 eV for the other structure. Therefore, we conclude that the structure with hydrogen atoms in opposite sides is energetically more favorable and we start to analyze this structure. Same trend is observed for graphane case but with lower energy difference between two different configurations [33].

C_3N has a hexagonal lattice with lattice constant of 4.87 Å and is composed of six carbon and two nitrogen atoms bonded together with sp^2 hybridization. C—N bond length is equal to 1.41 Å, and C—N bond length is 1.40 Å. These results are in consistent with perviously experimental and theoretical reports [25,29]. C3NH shows a hexagonal symmetry with lattice constant of 4.90 Å. Adding hydrogen does not disturb the lattice symmetry and increase of lattice constant is ignorable. However, bond length, angles and atom positions are significantly altered after hydrogenation. A transition from sp^2 to sp^3 is observed resulting in the increase of C—C and C—N bond length. C—C bond length is equal to 1.53 Å i.e. 8 percent increase, and C—N is equal to 1.46 Å i.e. 4 percent increase. C—H bond length is equal to 1.12 Å. The angle of C—N—C is equal to 110° indicating sp^3 hybridization. The obtained C—C bond length is equal to the graphane case [33]. The buckling between N atoms is equal to 0.45 Å and to 0.50 Å for carbon ones.

Electron and phonon band structure of C_3N and C_3NH is plotted in Fig. 2. C_3N is a semiconductor with indirect band gap of 0.39 eV. Top of valance band is located at M point and bottom of conduction band is located at Γ point. The calculated band gap is consistent with perviously theoretical and experimental reports [23,25,29]. Nitrogen and carbon atoms have equal participation at the top of valance band, but the bottom of conduction band is belonging to carbon atoms as shown in Fig. 3a. Our results reveal that C_3NH is an insulator with band gap of 5.53 eV which is 2 eV more than graphane case [33]. It is well-known that GGA-PBE functional underestimates the band gap, so we expect that calculations performed by hybrid functional like HSE06 or many-body perturbation theory like GW predict larger band gap. Maximum of valance band is located at $\Gamma-K$ direction and near K point. Hydrogenation strongly reduces the dispersion of valance band so electrons are completely localized. In addition, the Dirac cone observed in C_3N sheet at $E = -2$ eV is disappeared after hydrogenation. It is found that the nitrogen atoms have the dominant role at the creation of maximum of valance band, while the minimum of conduction band is related to hydrogen atoms as seen in Fig. 3b. Appearance of buckling, change of hybridization from sp^2 to sp^3, and increase of bond length between atoms are the main factors in the increase of band gap and localization of electrons in valance band. Dynamical stability of the structures is investigated by computing phonon band structure. Both structures are stable because there is no imaginary phonon mode. The phonon band structure obtained for C_3N in our work is similar to the one presented for the same structure based on DFT calculations, therefore, DFTB method used in this work can be considered as a suitable choice for computing phonon modes. Comparison between DFTB and DFT based phonon calculations are presented in Fig. S2 which shows reliable accuracy of DFTB method. Acoustic flexural mode with quadratic dispersion around Γ point is observed in C_3N sheet and crosses with other acoustic modes at K point. This mode is a characteristic of low dimensional crystals and indicates the motion of atoms toward out of the plane. This mode has a low energy because there are no atoms out of the plane. Several phonon bands cross each other at K point which is a property of hexagonal structures [38,39]. The flexural mode becomes linear like transverse and longitudinal acoustic modes in C_3NH because there are hydrogen atoms and some buckling in z direction. There are six degenerate phonon bands in energies more than 300 meV, shown by circle, which are absent in C_3N sheet. These modes are related to the motion of hydrogen atoms under condition that all carbon and nitrogen atoms are fixed. The different modes indicating the motion of hydrogen atoms are plotted in Fig. 4. To gain more insight about the bonding in $C3NH$, electron density and electron localization function (ELF) are presented in Fig. 5. It is clear that the electrons are distributed between carbon and nitrogen atoms showing a covalent bonding. However, the electron density is more on nitrogen atoms because they are more