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Mechanical behaviors and electronic characteristics on two-dimensional C_2N_3 and C_2N_3H: First principles calculations

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ABSTRACT

Opening its band gap has become an important task since the discovery of graphene in 2004. Recently, two-dimensional (2D) carbon nitride with a composition near C_2N_3 was successfully synthesized. C_2N_3 has attracted much attention because of its semiconductor behavior. In this study, mechanical behaviors and electronic characteristics of C_2N_3 and C_2N_3H are investigated by first principles calculations. The results reveal that C_2N_3 and C_2N_3H are very soft 2D materials. C_2N_3 exhibits a heavily doped *p*-type semiconductor characteristic, while C_2N_3H shows an intrinsic semiconductor behavior with the HSE06 band gap changing from 4.62 eV to 3.92 eV. Molecular dynamics simulation shows that monolayer C_2N_3 and C_2N_3H at 300 K can sustain the biaxial strain levels of $\varepsilon = 9\%$ and $\varepsilon = 13\%$. The C_2N_3 breaks first from C_3N_3 rings as the strain is further increased, while the C_2N_3H breaks first from the $-NH-$ linking. It is found that interlayer voids in C_2N_3H occupied by O, Na, Mg, S, Si, K, Ca, Cl, Br, or I atoms can increase the interface cohesive energy and enhance structural stability. These interstitial atoms introduce transition levels and fixed charges into the band gap, thus affecting the transport properties of C_2N_3H.

1. Introduction

Previously, the two dimensional (2D) material is considered to be unstable in thermodynamics. More attention has been paid to the 2D material since the success of graphene separation in 2004 [1–14]. Graphene exhibits very high electron mobility and excellent mechanical properties, which has a potential application in the field of electronic devices [15–19]. However, its zero band gap characteristics make the electronic devices unable to achieve switching operation, thus limiting its application [20]. In order to apply 2D materials in the field of electronic devices, on the one hand, people are devoted to open the graphene's band gap by doping technology. On the other hand, we have to search other 2D semiconductors. So far, many kinds of 2D semiconductors have been successfully synthesized, including transition-metal dichalcogenides (MoS_2, WS_2, $MoSe_2$, WSe_2) [21], black phosphorus (P) [22], germanium phosphide (GeP) [23] and carbon nitride (CN) [24–43].

2D carbon nitride can form a structure similar to graphene. It is expected to retain the excellent mechanical and electrical properties of graphene. In recent years, carbon nitride with few atomic layer thickness has attracted intense attentions due to its applications in catalysis, photocatalysis, energy conversion and storage, and field effect transistors [32,43–47]. Carbon nitride is divided into various structures, specifically including C_2N [24–29], C_3N [30–32], CN [33–36], C_3N_4 [37–39], and C_2N_3 [40–43]. In 2015, Mahmood et al. successfully fabricated C_2N by a bottom-up wet-chemical reaction [24]. The crystal exhibits a semiconducting characteristic with the band gap of approximately 1.96 eV. Subsequently, they synthesized C_3N by direct solid-state reaction of organic single crystals [30]. The 2D C_3N is a semiconductor with the experimental band gap of 2.67 eV [30], and calculated band gap of 1.10 eV [31]. CN nanotube was synthesized by the reaction of $C_3N_3Cl_3$ with Na in a stainless steel autoclave [34]. 2D CN is now only theoretical predicted, and still lack of experimental confirmation [36]. They found that the monolayer CN nanosheet is a semiconductor with the band gap changing from 2.75 eV to 2.89 eV. In 1994, Kouvetakis et al. first synthesized C_3N_4 crystal [48,49]. Graphite phase C_3N_4 is the most stable among various carbon nitride compounds, generally obtained by high temperature pyrolysis of nitrogen rich organic compounds [38]. The ideal structures of C_3N_4 include s-triazine and tri-*s*-triazine rings [39]. The density functional theory calculations on s-triazine-based C_3N_4 corroborated a direct band gap between 1.6 and 2.0 eV [37]. Recently, the 2D carbon nitride with H component was

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successfully synthesized [50]. The experimental measurement showed the films have a band gap around 1.6 eV. Some investigations also found that structural distortions in C_3N_4 could affect the band bands and interlayer cohesive properties [51,52].

Poly-triazine-imide (PTI) carbon nitride has attracted specific interests due to its high crystallinity [53]. The planar layers are composed of C_2N_3H, including s-triazine rings (C_3N_3) linked via $-NH-$ groups. This linking is easy to make voids that are occupied by ions. Zhang et al. successfully synthesized bulk well-crystallized form with the stoichiometry of $C_6N_9H_4Cl$ through a solid-state reaction at 1.0–1.5 GPa and 500–550° [40]. X-ray and electron diffraction measurements on the crystal suggest a hexagonal space group with cell parameters of a = 8.438 Å and c = 6.430 Å. It is found that the compound has a 2D C_2N_3H framework with the voids occupied by chloride ions. In 2011, Wirnhier et al. synthesized PTI with intercalation of Li and Cl ions by temperature-induced condensation of $C_2H_4N_4$ in a mixture solvent of LiCl and KCl [41]. In 2017, Miller et al. synthesized 2D carbon nitride nanosheets with an approximate stoichiometry of C_2N_3 through spontaneous dissolution of bulk PTI-based carbon nitride [42]. Because of the technical limitations, it is extremely difficult to measure the physical and chemical properties of these nanomaterials. Some experimental studies have not been completely verified by other groups. So the first principles calculations are useful to interpret the experimental results. At present, there is still a lack of detailed theoretical research on 2D C_2N_3. It is found that the voids in 2D C_2N_3 usually need to be decorated internally with H^+ or Li^+ ions. The pure C_2N_3 still can not be obtained from the experiment. The structural and thermodynamic stability of C_2N_3 still need to be studied in depth. Furthermore, the voids between layers are usually occupied by Cl^- or Br^- ions. The role of interlayer ions should also be investigated.

In this study, we do a detailed study of mechanical behaviors and electronic characteristics for 2D C_2N_3 and C_2N_3H. First, we analyze the structural stability and the strain behavior of C_2N_3. Then, we attempt to analyze how H ions affect its structure and carrier transport characteristic. In addition, some interlayer atoms (O, Na, Mg, Si, S, Cl, K, Ca, Br, and I) are investigated. We explain the effect of these atoms on the structural stability and carrier transport characteristic.

2. Computational details

The unit cell structure of C_2N_3 is shown in Fig. 1 (a). It consists of 12 C atoms and 18 N atoms with the P6/mcm space group, in which each C atom is surrounded by 3 nearest neighbor N atoms, and each N atom is surrounded by 2 nearest neighbor C atoms. The C_2N_3 mainly exhibits armchair and zigzag directions, which is presented in Fig. 1 (b). The C_2N_3H crystal will be formed (see Fig. 2) if the unsaturated N atoms in the C_2N_3 crystal are passivated by the H atoms [41]. The C_2N_3H unit cell consists of 12 C atoms, 18 N atoms, and 6 H atoms. Previous studies showed that O, Na, Mg, Si, S, Cl, K, Ca, Br and I atoms were usually easy to exist in the process of carbon nitride preparation [30,34,41,43]. So, it is of great practical significance to investigate these atoms acting as the filled atoms in the voids. The crystal structure with the molecular formula of $C_6N_9H_3X$ will be formed as the voids between layers in C_2N_3H are occupied by X (O, Na, Mg, Si, S, Cl, K, Ca, Br or I) atoms. Fig. 3 shows the unit cell structure of $C_6N_9H_3X$.

The calculations are performed within the Cambridge Sequential Total Energy Package (CASTEP code) [54], which is based on density functional theory (DFT) plane-wave pseudopotential method. The generalized gradient approximation (GGA) is chosen as exchange-correlation functional to optimize the structure [55]. The optimization will terminate if the force convergence criterion of 0.01 eV/Å is satisfied. The hybrid Heyd-Scuseria-Ernzerhof functional (HSE06) is used to calculate the band gap [56–59]. Previous studies have confirmed that the HSE06 functional can correctly describe the band gap of most semiconductors or oxides [60]. The valence electron configurations for C, N, O, Na, Mg, Si, S, Cl, K, Ca, Br, and I are considered as $2s^22p^2$, $2s^22p^3$, $2s^22p^4$, $2s^22p^63s^1$, $2s^22p^63s^2$, $3s^23p^2$, $3s^23p^4$, $3s^23p^5$, $3s^23p^64s^1$, $3s^23p^64s^2$, $4s^24p^5$, and $5s^25p^5$, respectively. The core electrons are replaced by norm-conserving pseudopotentials. We have carefully test the energy cutoff, k-points sampling generated by the Monkhorst–Pack scheme, and thickness of vacuum region for carbon nitride slabs [32]. The plane wave energy cutoff for all calculations is set to be 680 eV. $2 \times 2 \times 2$ and $2 \times 2 \times 1$ k-point samplings are used for unit cell and monolayer of C_2N_3 and C_2N_3H, respectively. A vacuum region of 10 Å is used to prevent the interlayer interaction. The unit cell structure is used to obtain the lattice constants of the C_2N_3 and C_2N_3H. The strain energy, stress, and bond characteristic versus strain strength are discussed in monolayer C_2N_3 and C_2N_3H slabs. $1 \times 1 \times 2C_2N_3H$ supercell is built to investigate the formation and ionization characteristics of interlayer ions, which is performed with $2 \times 2 \times 1$ k-point sampling. In addition, 3×3 supercell slabs for C_2N_3 and C_2N_3H are used to investigate structure breaking and electron distribution under strain, which is performed with $1 \times 1 \times 1$ k-point sampling.

Molecular dynamics (MD) simulation is a very effective way to study material properties by simulating the motion of atomic or molecular systems [61]. It often gives a clear understanding about the microscopic properties of some macroscopic physical quantities, and explains the phenomena that can not be observed by theoretical analyses and experiments. The MD simulation has made a great achievement, and widely used in the fields of physics, chemistry, and materials. It can be divided into classical MD simulation and first principles MD simulation. Classical MD simulation describes the interaction between particles in the system using an empirical potential functional [2,4–6]. Although the method has achieved great success, it is difficult to describe the system of complex components due to the limitation of potential functional [62–64]. In particular, it is not very good to describe the properties of the bond forming and breaking in the material. First principles MD simulation can give an accurate prediction for material properties [32,65]. In this study, first principles MD simulation in total-energy DFT schemes with NVT ensemble is used to predict the critical strain and fracture mechanism of C_2N_3 and C_2N_3H nanosheets. The calculation is carried out in 3×3 supercell slabs of C_2N_3 and C_2N_3H, which consist of 135 atoms and 162 atoms, respectively. The systems are simulated for 0.5 ps with the time step of 0.5 fs, which is performed with the energy cutoff of 680 eV and $1 \times 1 \times 1$ k-point sampling. The variable electron occupancy with smearing width of 0.1 eV is used to facilitate convergence.

3. Results and discussion

3.1. Structural behaviors and electronic characteristics on C_2N_3

In this study, we first investigate structural characteristics on C_2N_3 unit cell. The calculated lattice constants are a = 7.846 Å and c = 6.549 Å. So interlayer spacing is about 3.28 Å. At present, we can not get the experimental lattice constants of C_2N_3 for comparison. The lattice constant is increased to a = 7.864 Å for monolayer C_2N_3. The bond lengths are 1.366 Å for N(1)−C(1), 1.360 Å for N(2)−C(1), and 1.340 Å for N(3)−C(1). The N(1), N(2), N(3), C(1) and C(2) atoms in C_2N_3 have been marked in Fig. 1(b). The N(1)−C(1) and N(2)−C(1) bond lengths are slightly smaller than 1.414 Å for N−C bond lengths in monolayer C_3N [32], and slightly larger than 1.339 Å and 1.354 Å for N−C bond lengths in monolayer C_2N [66]. The bond angle for C(1)−N (3)−-C (2) is 111.2°. The electron density in monolayer C_2N_3 plane is used to investigate the interaction between atoms, which is exhibited in Fig. 1 (c). Because N atom in electronegativity is larger than C atom, the electrons between C−N bonds are near N atom, which suggests that C−N is a polar covalent bond. The calculated Hirshfeld charges are 0.16 e for C(1) atom, −0.06 e for N (1) and N(2) atoms, and −0.19 e for N (3) atom. Because of the existence of unsaturated bonds, higher electrons are observed near the N(3) atom. Fig. 1 (d) exhibits atomic structure for double layers C_2N_3. The lattice constant is a = 7.861 Å,