Geometric and electric properties of graphitic carbon nitride sheet with embedded single manganese atom under bi-axial tensile strain

Yusuf Zuntu Abdullahi [a, c, *], Tiem Leong Yoon [a], Mohd Mahadi Halim [a], Md. Roslan Hashim [b], Mohd. Zubir Mat Jafri [a], Lim Thong Leng [d]

[a] School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia
[b] Institute of Nano-Optoelectronics Research and Technology Laboratory, Universiti Sains Malaysia, 11900 Penang, Malaysia
[c] Department of Physics, Faculty of Science, Kaduna State University, P.M.B. 2339 Kaduna State, Nigeria
[d] Faculty of Engineering and Technology, Multimedia University, Jalan Ayer Keroh Lama, 75450 Melaka, Malaysia

ARTICLE INFO

ABSTRACT

In this paper, geometric, electric and magnetic properties of graphitic heptazine with embedded Mn atom under bi-axial tensile strain are investigated using density-functional theory with the spin polarized generalized gradient approximation and Hubbard U correction. The binding energy computed for the systems are found to uniformly decrease with the increase in small bi-axial tensile strain (0–5%). The decrease of the binding energy can be related to the increase in the N–C–N bond angle within the cavity which tries to recover its sp^2 hybridized bond. The projected density of states (PDOS) of strained/unstrained systems is also computed. It is found that the covalent bonding of the 6 nitrogen atoms located at the edge of the cavity and the embedded manganese atom in CN1 is mainly contributed by s, d_{zx} and d_{z2} of the Mn atom, as well as the sp-like orbitals of these nitrogen atoms in the majority spin state respectively. Our calculations also predict enhanced band gap (0.67 eV at zero strain, 1.12 eV at 4% strain) induced by small amount of bi-axial tensile strain. The increase in band gap can be attributed to the structural distortions of the sheet caused by the symmetric deformations which lead to the backward shift in the σ-like orbitals states of the CN1 atoms. Such properties may be desirable for diluted magnetic semiconductors, future spintronics, molecular magnet and nanoelectronics devices.

1. Introduction

Owing to its exotic properties and widespread potential applications extending from fuel cells, hydrogen productions and photocatalysis [1,2], two-dimensional (2D) carbon nitride (CN) nanosheet has been an exciting topic for both theoretical and experimental investigations. Among the various allotropes of CN [3,4], graphitic phase of C_3N_4 (g-C_3N_4) is the most stable one under ambient conditions [5]. g-C_3N_4 is a wide gap semiconductor and had been synthesized in a flake-like structure similar to that of graphite [6]. Previous studies have reported that g-C_3N_4 has many isomers which can be grouped according to its heterocyclic building block such as single triazine-based (g-s-C_3N_4) or tri-single triazine-based g-t-s-C_3N_4 (known as heptazine) [7,8].

As a case of comparison, triazine-based g-C_4N_3 is another allotrope of 2D CN which has been successfully synthesized [9]. It is theoretically reported to possess a ferromagnetic ground state with half metallicity around the Fermi energy [10], whereas g-t-s-C_3N_4 is a non-magnetic small-gap semiconductor [11]. Hole doping in the surface of g-C_3N_4 could result in unique ferromagnetism. Hence, encapsulation of some metallic nanostructures in stable g-t-s-C_3N_4 substrate may further enhance its intrinsic electric and magnetic properties. In addition, a g-t-s-C_3N_4 sheet naturally comes with a regularly defined defect (which is the cavity in the g-t-s-C_3N_4 sheet), which makes it a desirable substrate for trapping metallic nanostructures. Interactions between neighboring images of metallic nanostructures located in the cavity are negligible as these sites are spatially well separated apart.

Although extensive efforts have been made to search for semiconducting, magnetic, two-dimensional sheets with enduring spin ordering, yet until now, relatively little results have been fully established. Thus, magnetic coupling in the semiconducting 2D

sheets remain an open question, whether incorporation of light elements into its free-standing form could withstand stable spin ordering. In this regards, the traditional way of manipulating the ferromagnetic structure of a 2D material via adsorption/embedment of TM nanostructures theoretically/experimentally remain one of the most viable approaches [12,13]. In fact, porous g-t-s-C_3N_4 with TM atoms has been successfully synthesized [14–18].

Ghosh et al., have theoretically investigated the structural, electronic and magnetic properties of the first row TM planar atoms embedment on heptazine. Their results indicated that the properties of heptazine can be effectively tuned by TM embedment. Furthermore, they also gave an account based on Monte Carlo simulations that ferromagnetic ordering of some TMs (e.g, V-, Cr-, and Fe-g-C_3N_4) may endure spin ordering at a relatively high temperature [19]. However, the band gap in most cases closes as a result of dispersed TM atoms embedment in the cavity of g-t-s-C_3N_4 sheet. Therefore, recovering its intrinsic band gap while maintaining the induced magnetism by the embedded TM atoms presents a new challenge. One of the effective methods of tuning material properties, which is widely adopted in the band gap manipulation of various 2D monolayer nanosheets (e.g., boron nitride, graphene, silicene and molybdenum disulfide (MoS_2) involves the application of external strain.

First-principles calculations have shown that MoS_2 sheet under bi-axial strain would decrease in band gap, and even be transformed from semiconductor into metal at a relatively small tensile strain of 8% [20]. From experimental point of view, external strain is needed for thin film growth and doping of nanostructures on a particular substrate, and this might likely induce some variations in the material's properties [21]. Therefore, it will be quite interesting to study the modulation of the band gap of g-t-s-C_3N_4 embedded with Mn atoms, induced by symmetric deformation (i.e., bi-axial tensile strain).

In this study, theoretical attempt based on DFT calculations is made to study the geometric, electric and magnetic properties of g-t-s-C_3N_4 with embedded Mn atom under uniform bi-axial tensile strain. Due to the open shell configuration of 3 d^5 orbital of Mn atom, it is expected that spin magnetic moment of the system could be retained. Our results are properly compared with the available literatures and explicit arguments are presented to discuss the geometric and electric properties of the strained and unstrained systems.

2. Calculation method

In our atomic model of bare graphitic g-t-s-C_3N_4, we consider a 2×2 supercell consisting of 56 atoms (see the left figure in Fig. 2a). It is comprised of 4 heptazine units. Each heptazine is formed by 3 C_3N_4 rings (hence the name tri-trizine) (see the right figure in Fig. 2a). For the sake of convenience we shall refer the structure of the supercell in Fig. 2a as CN1, while Mn-embedded CN1 as Mn−CN1. A cavity is vividly seen in the structure of CN1 (encircled by the solid line). It is also referred to as the porous site. In our calculation, a Mn atom is to be placed in the porous site. We use a vacuum space of 15 Å normal to the CN1 plane to produce a negligible interaction between the sheets and their neighboring images. The lattice constant obtained upon relaxation of the bare CN1 is 7.1 Å which is in agreement with the previous theoretical work [22]. To investigate the effects of single Mn atom embedment in the CN1 sheet, the porous sites which maintain a regular pattern and simultaneously maximize the bonding with the Mn atom are initially chosen for relaxation. All atoms are fully relaxed until all remaining force on each atom was smaller than 0.05 eV/Å.

All calculations are performed based on DFT [23] implemented in the QUANTUM ESPRESSO simulation package [24]. Spin

polarized generalized gradient approximation as parameterized by Perdew-Burkew-Enzerhof (PBE) exchange correlation scheme and Hubbard U correction (GGA + U) is used to describe the electron-electron interaction and correlation energy of strongly localized 3d orbital of Mn atom [25]. Ultrasoft pseudopotentials (generated using scalar-relativistic scheme with a semi-core) are adopted for C, N, and Mn atoms to describe electron-ion core interaction [26]. All pseudopotentials can be found from the plane-wave self-consistent field (PWSCF) pseudopotentials online library [24]. To expand the wave functions, plain wave basis set with kinetic energy cut-off of 550 eV is used. For integrals, smearing is employed to aid convergences. To be specific, Marzari-Vanderbilt method with Gaussian spreading is used [27]. The Brillouin zone (BZ) integrations are sampled using a set of $8 \times 8 \times 1$ k-point mesh with the Mankhorst-Pack scheme for self-consistently calculation. The density of state is obtained with a denser set of $15 \times 15 \times 1$ k-point [28].

For the on-site U parameter, a linear response approach proposed by Cococcioni et al. [29], is employed for the single 3d Mn atom. The value of the parameter U in the present work is separately calculated by us, and its value is different than that used by Gosh et al. [19]. The difference arises due to a different bonding environment. The U parameter can be determined by density response function which is expressed as

$$\chi_{kl} = \frac{\partial^2 E}{\partial \alpha_k \alpha_l} = \frac{\partial n_k}{\partial \alpha_l}. \tag{1}$$

n_k is the localized state occupation in the d orbital of site k. Using α as a perturbation potential, the total on-site effective U parameter is obtained self-consistently as defined in Eq. (2).

$$U_{eff} = \left(\chi_0^{-1} - \chi^{-1} \right), \tag{2}$$

where χ_0 and χ represent the non-interacting and interacting density response functions of the system with respect to localized perturbations. As depicted in Fig. 1(a), the noninteracting and interacting inverse matrix is the gradients of the bare and self-consistent regression response functions. The calculated value of the Hubbard U shown in the figure is obtained from the Eq. (2).

3. Results and discussions

It is well known that majority of the 2D nanosheet form either buckled or pucked structures. The CN1 sheet is not an exception because of the interplay in the N atom with sp^3 and sp^2 hybridized structure. To verify the reliability of our computational method, we examine briefly the optimized CN1 sheet as shown in Fig. 2a. Our calculated lattice constant is 7.1 Å, which is in good accordance with the previous values [22]. The bond length labelled l_1, l_2 and l_3 in Fig. 2a tallies well with the previous reports [8]. For the evaluation of the mechanical stability of Mn−CN1 system, the in-plane bulk modulus has been estimated. The bulk modulus is defined as the second derivative of the total strain energy with respect to area of the two-dimensional nanosheets expressed by Eq. (3).

$$G = A \times \left(\frac{\partial^2 E}{\partial A^2} \right) \bigg|_{A_m}, \tag{3}$$

where A represents the area of the unit cell, E is the total strain energy and A_m expresses the unit cell area of the equilibrium structure. As depicted in Fig. 1(b), structural relaxations for the Mn−CN1 system are performed in harmonic elastic region ranging between −15% and 15%. Table 1 shows the total energy and lattice parameters of Mn−CN1 system sheet under applied biaxial strain.