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Density functional study of manganese atom adsorption on hydrogen-terminated armchair boron nitride nanoribbons

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ABSTRACT

In this paper, we have investigated stable structural, electric and magnetic properties of manganese (Mn) atom adsorption on armchair hydrogen edge-terminated boron nitride nanoribbon (A-BNNRs) using first principles method based on density-functional theory with the generalized gradient approximation. Calculation shows that Mn atom situated on the ribbons of A-BNNRs is the most stable configuration, where the bonding is more pronounced. The projected density of states (PDOS) of the favored configuration has also been computed. It has been found that the covalent bonding of boron (B), nitrogen (N) and Mn is mainly contributed by s, d like-orbitals of Mn and partially occupied by the 2p like-orbital of N. The difference in energy between the inner and the edge adsorption sites of A-BNNRs shows that Mn atoms prefer to concentrate at the edge sites. The electronic structures of the various configurations are wide, narrow-gap semiconducting and half-metallic, and the magnetic moment of Mn atoms are well preserved in all considered configurations. This has shown that the boron nitride (BN) sheet covered with Mn atoms demonstrates additional information on its usefulness in future spintronics, molecular magnet and nanoelectronics devices.

1. Introduction

Recent experimental synthesis of boron nitride nanoribbons (BNNRs) [1] has triggered great research interests because of its noble chemical and thermal stabilities [2,3]. However, there are some challenges that need to be addressed before it can be used for various fields of applications. The main challenge is the insulating nature of this material. This problem needs to be overcome before BNNRs can be proposed for nanoscale applications ranging from spintronics to nanophotonics. Finding the right methods and mechanism of modifying the electronic properties has motivated further studies [4–12]. One of the methods of tuning band gap of BNNRs involves application of transverse electric field [13].

Alternatively, half-metallic behavior of BNNRs can be achieved by the charge injection and fluorination of edges [14,15]. Moreover, density functional theory (DFT) calculations have shown that hydrogen terminated BNNRs with different edge orientations such as armchair and zigzag edges boron nitride nanoribbons (A-BNNRs and Z-BNNRs) are non-magnetic with wide energy gap [13,16]. The induced magnetism based on substitutions (or adsorption) of carbon atom on B or N vacancies of the BN sheet has been confirmed and also carefully explained [2,5,8].

In spite of numerous studies on BNNRs edge-termination with different nanostructures [14,17,18], theoretical investigations of adsorption of metallic nanostructures on the surface and the edges of BNNRs have received less attention. It has been reported that Z-BNNRs with a doped carbon atom chain can exhibit significant magnetic moment and tunable band gap [19]. More recently, attention has now been shifted to study the effects of transition metals (TM) atoms adsorption on boron nitride (BN) and its ribbons because of their tendencies to induce noble changes in electric and magnetic properties such as half-metallicity and

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narrow band-gap semiconducting behaviors which are needed for spintronics and related field of application [20,21].

A current study in this perspectives reported spin gapless semiconducting behavior for the majority of stable Fe adsorption on hydrogen-terminated BNNRs systems [22]. This recent approach has provided a platform for the possible future fabrication of spintronics devices particularly for the preservation of magnetic moment of the Fe atom, which is found to be almost the same as the value of an isolated Fe atom. Therefore, it is quite interesting to theoretically extend the study to the rest of magnetic TM atoms so that a clear mechanism can be found on the possible future utilization. We have considered Mn atom in this study because of its high local spin magnetic moment compared to rest of the members in the group. It has also been reported based on first-principles investigation that armchair edge BN nanoribbons are more energetically stable than the zigzag ones [23].

In this work, we have investigated the structural, electric and magnetic properties of A-BNNRs system with adsorbed Mn atom based on first-principles method. The results are discussed based on the available literatures and a clear statement will be established on the electronic structures of all the considered configurations.

2. Calculation method

Our calculations have been performed based on first-principles [24] density functional theory implemented in the QUANTUM ESPRESSO simulation package [25]. The electron–electron interaction has been considered within generalized gradient approximation (GGA) and spin polarized GGA as parameterized by Perdew–Burkew–Enzerhof (PBE) [26] exchange correlation scheme. Electron–ion core interaction has been treated by ultrasoft pseudopotentials for B, N and H (2s, 2p, and 1s valence orbitals as in the pseudopotential file, respectively), and Mn ($3s^2 3p^6 4s^2 3d^5 4p^0$) [27]. All pseudopotentials can be found from the plane-wave self-consistent field (PWSCF) pseudopotentials online references [28]. To expand the wave functions, we have used plain wave basis set with kinetic energy cut-off of 500 eV. For integrals, smearing has been employed to aid convergences and to be specific, Marzari–Vanderbilt method with small Gaussian spreading of 0.03 eV has been used [29]. For Brillouin zone (BZ) integrations, we have sampled $1\times1\times22$ set of k-points with the Mankhorst–Pack scheme [30]. In modeling pristine A-BNNR, we have used two periodic units along the ribbons growth directions and a width of nine dimer lines (2×9 periodicity) comprising of 44 atoms per unit cell. The pristine BNNRs have been constructed with experimental lattice constant of 2.51 Å [31]. To minimize the interaction between the adatom in the BNNRs and its neighboring image, a vacuum space of 14 Å perpendicular to the ribbons has been considered in all configurations.

It is important to note that all calculation parameters have been tested for convergences. The convergence has been considered to be achieved when there are two consecutive iterative steps with energy difference less than 1 meV. In the case of Mn adsorption on BNNRs, eight possible initial adsorption sites as shown in Fig. 1 have been considered which can be classified into two namely, the inner and edge adsorption sites. The inner sites comprise the adsorption sites in which the Mn atom are located above N atom, B atom, B–N bond and the center of the hexagonal BN namely T_N, T_B, Bri and H sites, respectively. The edge sites consist of the following adsorption sites, the Mn atom situated above B atom, B–N ribbons side, above the bay site of B–N and above B–H bond namely ET_B, EBN, EBri and EBH, respectively. The relaxations for each configuration are performed along all the atomic coordinates by keeping the cell dimension fixed. We have used Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm for the forces and energy minimization process during structural relaxation.

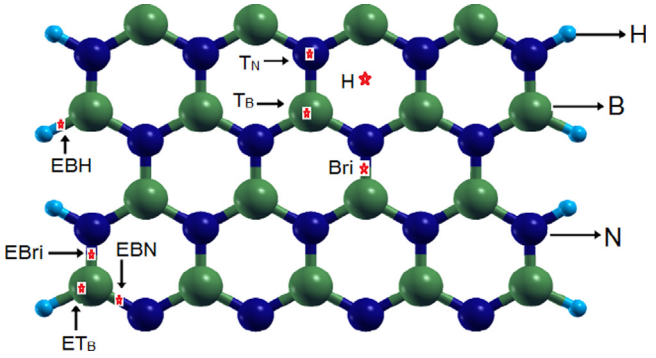

Fig. 1. The top view of the various adsorption positions of Mn atom indicated by the red star.

Table 1
Details of the optimized properties for Mn/A-BNNRs systems. The optimized properties of the favored configuration are highlighted in bold. The binding energies E_b, the average bond length between Mn adatom and B, N and H denoted as d_{Mn-B}, and d_{Mn-N}, and d_{Mn-H}, respectively. The charge transferred into the A-BNNR based on Lowdin's charge analysis, magnetic moment per unit cell, electronic character of the Mn/A-BNNRs system and the approximate band gap are denoted by Q, M, EC and BG, respectively.

Site	E_b (eV)	d_{Mn-B} (Å)	d_{Mn-N} (Å)	d_{Mn-H} (Å)	Q (electrons)	M (μ_B)	EC	BG (eV)
H	0.59	4.15	4.15	–	0.02	5.00	SC	3.48
Bri	0.59	4.05	3.90	–	0.02	5.00	HM	–
T_N	0.59	–	3.94	–	0.02	5.00	SC	3.50
T_B	0.59	3.92	–	–	0.02	5.00	SC	3.50
EBN	**0.84**	**2.22**	**2.37**	–	**0.25**	**5.00**	**SC**	**0.70**
EBH	0.61	3.67	–	3.63	0.01	5.00	SC	1.75
ET_B	0.77	2.21	–	–	0.25	5.00	SC	1.29
EBri	0.76	2.22	2.26	2.79	0.25	5.00	SC	0.77

3. Results and discussions

In this work, we have considered Mn atom adsorption on the A-BNNRs system at various adsorption sites. Table 1 summarizes the detail structural stabilities parameters and magnetic moment per unit cell for the obtained various A-BNNR with adsorbed Mn atom, *i.e.*, the binding energy, bond lengths between Mn and the atoms in the A-BNNRs, the electronic character of the Mn/A-BNNRs system and the approximate band gap. The charge transfer into the A-BNNR is based on Lo wdin's charge analysis [32]. The stability for Mn adatom is measured by the binding energy E_b defined as

$$E_b = E_{total} - (E_{BN} + E_{Mn}), \quad (1)$$

in unit of eV/atom, where E_{total} represents the spin-polarized total energy of the Mn A-BNNRs system, E_{Mn} stands for the total energy of an isolated Mn atom and E_{BN} is the total energy of pristine ABNNRs. Detailed discussions are presented in the following paragraphs.

Among the eight initial structural configurations for A-BNNR with adsorbed manganese atom, the favored binding site for Mn is located on the edge site of the B–N ribbons named EBN as shown in Fig. 1. It is interesting to know that the binding energies listed in Table 1 are virtually the same within the various adsorption sites in the central part of the A-BNNRs, which is in agreement to the