Structural, magnetic and electronic properties of 3d transition-metal atoms adsorbed monolayer BC2N: a first-principles study

Feng Chen, Li Fan, XunHou and Zhi-Qian Chen *

Faculty of Materials and Energy, Southwest University, Chongqing 400715, PR *

* Correspondence: Correspondence: address: chen_zq@swu.edu.cn

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Abstract: Based on monolayer BC2N structure, the structural, electronic and magnetic properties of 3d transition metal (TM) atoms (V(Vanadium), Cr, Mn, Fe, Co and Ni) adsorbed monolayer BC2N is studied by using first principle method. The results show that 3d transition metal atoms can be stably adsorbed on monolayer BC2N. It has been found out that the most preferable adsorption site is on top of C atoms (Tc) for V, Cr, and Mn atoms, while the others 3d TM atoms (Fe, Co, Ni) are found to prefer the hollow adsorption site (H) of BC2N monolayer. And the majority of TM atoms were chemically adsorbed on BC2N, whereas Cr and Mn atoms were physically adsorbed on BC2N. Except for Ni, most 3d transition metal atoms can make the monolayer BC2N magnetization, and the spin-charge density indicated that the magnetic moments of adsorption systems are mainly concentrated on the TM atoms. Moreover, Our results provide fundamental knowledge of TM atoms adsorption on BC2N, which will be useful for not only for spintronics applications but also the development of magnetic nanostructures.

Keywords: monolayer BC2N; transition metal atom; adsorption; magnetism

1. Introduction

Because of the peculiar electronic properties, two-dimensional materials have many excellent properties that are different from three-dimensional materials [1-3]. In 2004, Novoselov and Geim successfully obtained graphene by mechanical stripping method [4]. The discovery of graphene opens the way for the study of two-dimensional materials. Subsequently, graphene-like materials, such as two-dimensional hexagonal boron nitride (h-BN), were successfully prepared [5] and its properties were studied theoretically and experimentally [6-8]. The spatial structure of monolayer h-BN and graphene was found. They are very similar, but their electronic structure is very different, and their properties can complement each other in shape [9]. So researchers have a lot of interest in BCN, a new compound that can be formed by combining the two compounds. Since the B-C-N layered material family has been synthesized by chemical vapor (CVD) [10, 11], scientists have begun to study B-C-N materials theoretically and experimentally. The early studies on BCN ternary compounds were mainly focused on BCN compounds. In 1989, Liu and Cohen et al. put forward the monolayer BCN structure model by first-principles calculation for the first time [12]. Subsequently, Nozaki and Itoh et al. studied the structure and properties of monolayer BCN by the semiclassical method [13]. In experiments, Song Li et al. prepared h-BCN nanocrystalline films by chemical vapor deposition. By adjusting the experimental parameters, the ratio of B, C and N elements could be adjusted, thus the BCN compounds were prepared [14].

Due to the application prospect of two-dimensional materials in nanoelectronics and spin electronic devices, the magnetic properties of two-dimensional materials have attracted much attention. In order to realize their practical application, it is very important to modulate their electronic structure and magnetic properties [15-17]. In recent years, the research on the magnetic
properties of the system by modulating two-dimensional materials has been paid more and more attention. Some theoretical studies have shown that defects can make BC$_2$N produce magnetic phenomena [18]. It is found that the structure with vacancy defects has higher formation energy and local spin magnetic moment than the system with inverse defects. Interestingly, a large number of studies on graphene and h-BN have shown that [19-22] transition metal atoms can also magnetize graphene and monolayer hexagonal boron nitride, resulting in strange spin-poles in the adsorption system. The electronic structure is modulated. There are many ways of modulation, such as adsorption, doping, applying stress and applied an electric field, etc., among which adsorption is an effective way [23-29].

Combining two-dimensional BC$_2$N combines the advantages of graphene and h-BN [30], but no magnetic limitation limits its use in nanoelectronics and spintronics. So, in order to expand the scope of application of monolayer BC$_2$N, we select two-dimensional BC$_2$N structure and use TM atoms to modulate the magnetic and electronic properties of two-dimensional BC$_2$N.

For this, the transition metal atom is considered to adsorb on the monolayer BC$_2$N, and the calculation is done in the case of spin polarization to investigate the stability structure, magnetic properties and electronic properties of the adsorption system. It has been found that the transition metal atom can be stably adsorbed on the two-dimensional BC$_2$N. Except for Ni, the TM atoms can magnetize the two-dimensional BC$_2$N. In addition, we also explored the impact of GGA+U on the adsorption system.

2. Calculation method and structural model

The calculations implemented with CASTEP code based on density functional theory (DFT) [31-33] were performed to investigate structural, magnetic and electronic properties of 3d transition metal atoms (V, Cr, Mn, Fe, Co and Ni) adsorbed monolayer BC$_2$N. The 4×4 supercell was used to reduce the interaction between neighboring TM atoms. A vacuum space of 15 Å in the Z orientation is chosen to avoid the interactions between the neighboring images. The interelectron exchange-correlation potential is used to describe the phase between electrons and ions by using PW91 [36] under the generalized gradient approximation (GGA). Interatomic Grimme’s DFT-D method is added to consider van der Waals interaction [35].

The plane wave truncation energy is 500eV, and the Brillouin region integral adopts the special k-point sampling method of $7 \times 7 \times 1$ monkhost-pack to ensure the accuracy of the results [36]. In calculating the electronic and magnetic properties of the system, the special k-point sampling of monkhost-pack is increased to $10 \times 10 \times 1$. All structures are relaxed under the consideration of spin polarization. The convergence of relaxation is based on the stress of all atoms being less than 0.05 eV/Å. In the process of self-consistent calculation, the convergence criterion is that the total energy variation of the system is less than $10^{-6}$eV. On site Coulomb interaction (GGA+U) was introduced to describe the d electrons of TM atom [37].

The lattice constants and binding energies of two-dimensional BC$_2$N optimized by PW91 are 4.920Å, 8.821Å, respectively. These results are in agreement with previous theoretical reports [38]. The two-dimensional BC$_2$N structure is direct bandgap semiconductor with a certain band gap. After optimization, the bond lengths of C-C bond, B-N bond, C-N bond and C-B bond are 0.142Å, 0.141Å, 0.139Å and 0.152Å, respectively, They are in good agreement with that reported [39], which means that C-N bond is the most effective in this structure. Fig. 1(a) is a schematic diagram of transition metal atoms adsorbed on two-dimensional BC$_2$N. For the adsorption of TM atoms, five possible adsorption positions are considered on 4×4 supercell of BC$_2$N monolayer, i.e., H site (above the center of the hexagonal ring of BC$_2$N), Ts site (on top of B atom), Tc site (on top of C atom), TN site (on top of N atom), and Bri site (above the middle of B-C bond in Fig. 1(b).
3. Result and discussion

BC\textsubscript{2}N has been structurally optimized and contains three kinds of atoms (4 carbon, 2 boron and 2 nitrogen). As shown in Fig. 2(a), consider calculating the band structure of BC\textsubscript{2}N under the condition of spin polarization. M and K represent the two height symmetry points of the Brillouin zone of the supercell, that is (0, 0.5, 0) and (-1/3, 2/3, 0). The Fermi level is set to zero energy and is represented by a horizontal black dotted line. It can be seen from Fig. 2(b) that the total density of states of BC\textsubscript{2}N.

3.1. Stability

We have selected six magnetic 3d TM atoms (V, Cr, Mn, Fe, Co and Ni) to adsorb on monolayer BC\textsubscript{2}N and calculate the adsorption system under the spin polarization state. To evaluate the most favorable configuration, adsorption energy is adopted which is defined as

$$E_{\text{adsorption}} = E_{\text{adatom+BC}_2\text{Nsheet}} - E_{\text{BC}_2\text{Nsheet}} - E_{\text{adatom}}$$

(1)

Where $E_{\text{adatom+BC}_2\text{Nsheet}}$ denotes the spin-polarized total energy of TM atoms adsorbed BC\textsubscript{2}N sheet. $E_{\text{BC}_2\text{Nsheet}}$ and $E_{\text{adatom}}$ are the total energy of the isolated pure BC\textsubscript{2}N sheet and the spin-polarized total energy of the corresponding free metal atom, respectively. Fig. 3 shows the adsorption energy of TM atoms at different adsorption positions of monolayer BC\textsubscript{2}N. The adsorption system of V, Cr and Mn has the lowest adsorption energy at the H site, while Fe, Co, and Ni have the lowest...
adsorption energy at the Tc site. By definition, a negative value corresponds to exothermic adsorption. The smaller the adsorption energy is, the more stable the 3d TM atom adsorption is, the stronger the interaction force between the TM atoms and the monolayer BC\(_2\)N is, the stronger the binding strength is, the further the structural stability can be determined. So the most preferable adsorption site is on top of C atoms (Tc) for V, Cr, and Mn atoms, while the others 3d TM atoms (Fe, Co, Ni) are found to prefer the hollow adsorption site (H) of BC\(_2\)N monolayer. The corresponding most stable structure of all adsorption systems are shown in Fig. 4. The relative stabilities of these sites are judged by comparing their adsorption energies \((E_a)\). Table 1 lists the adsorption position, the adsorption energy \((E_a)\), \(d_{TM-h}\) perpendicular distance between TM atoms and monolayer BC\(_2\)N. Except for adsorption system of Cr and Mn, the adsorption energies of other TM atoms (V, Fe, Co, Ni) adsorbed on monolayer BC\(_2\)N are quite sizable, ranging from -1.574 to -0.582 eV. Obviously, their adsorption energy is greater than 0.5 eV, which is chemical adsorption, while the adsorption energy of Cr and Mn is less than 0.5 eV, which belongs to physical adsorption. We know that the 3d orbital of free Cr, Mn atoms are half-filled. The half-filled d orbitals weaken the interaction between TM atoms and BC\(_2\)N monolayer, reducing the adsorption energies of these systems. The scenario is similar for the adsorption of Mn atom on the other 2d material, for example two-dimensional InSe [39].

**Figure 3.** is the adsorption energy of transition metal atoms adsorbed to different sites of single layer BC\(_2\)N.

**Figure 4.** The top view of the most stable structures for transition metal atoms adsorbed monolayer BC\(_2\)N.
Table 1. lists the adsorption position, the adsorption energy (\(E_a\)), the perpendicular distance between TM atoms and monolayer BC\(_2\)N (\(d_{TM}\)).

<table>
<thead>
<tr>
<th>Adatom</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{TM}) (Å)</td>
<td>1.915</td>
<td>2.224</td>
<td>2.218</td>
<td>2.027</td>
<td>1.921</td>
<td>1.871</td>
</tr>
<tr>
<td>(E_a) (eV)</td>
<td>-1.143</td>
<td>-0.299</td>
<td>-0.326</td>
<td>-0.582</td>
<td>-1.131</td>
<td>-1.574</td>
</tr>
</tbody>
</table>

In order to explore the different trends of adsorption energy of adsorption atoms and monolayer BC\(_2\)N, we calculated the charge density difference of the adsorption system. In order to clearly reveal the charge density difference, the cutting plates determined by transition metal atoms and single layer BC\(_2\)N and perpendicular to the BC\(_2\)N plane are selected, as shown in Fig. 5. The charge density accumulates at the transition metal atoms and the nearest C atom. For the H adsorption configuration, the charge density is accumulated near the transition metal atoms and the hexagonal ring formed by B-C-N is off centered near the C atom. The charge accumulation of the Cr atom adsorption system is the smallest, and the combined strength with BC\(_2\)N is the smallest, so the relevant adsorption energy of Cr is the largest. On the contrary, for Tc adsorption configurations, that is, Fe, Co and Ni adsorption systems, the charge accumulation expands with increasing atomic number, which leads to the shorter bond strength that accounts for the decrease of adsorption energies. Generally, the bond strength is directly related to the bond length of transition metal atoms, while the shorter bond length corresponds to the stronger bond, which leads to lower adsorption energy and more stable configuration. However, the relationship between transition metal atoms and the nearest B, C and N atoms is more complicated. In this case, the charge accumulation between the transition metal atoms and the center of the nearest C or hexagonal ring determines the bond strength. And it becomes the main factor that affects the adsorption energy.

Figure 5. (a)-(f) shows the differential charge density of Ni adsorbed BC\(_2\)N. All the adsorbed atoms are located in the stable position of geometric optimization, the loss of electrons is expressed in blue, and the accumulation of electrons is expressed in red.

3.2. Magnetic properties

On the basis of stable adsorption of transition metal atoms on monolayer BC\(_2\)N structure, the magnetic properties of the adsorbed system were studied by Mulliken layout analysis. Results as shown in Table 2, the Ni adsorption system exhibits zero magnetic moments, that is, the system is nonmagnetic, and the magnetic moment exhibited by Ni atoms adsorbing BC\(_2\)N is zero, the result of adsorption graphene [40]. However, the adsorption of other transition metal atoms can make the system exhibit larger magnetic moments. It can be seen that in the adsorption systems of V, Cr,
Mn, Fe and Co, the total magnetic moments are 5.0, 6.0, 5.0, 4.0, 1.0 μB, respectively. The contributions of V, Cr, Mn, Fe, Co metal atoms to the system are respectively 4.33, 5.69, 5.32, 4.24, 0.59 μB. It can be concluded that transition metal atoms have the greatest contribution to the total magnetic moment of the system. The magnetic moments of V, Cr, Mn, Fe, Co, and Ni atoms in the free state are 5, 6, 5, 4, 3, and 2 μB, respectively. Their total magnetic moment is equal to that of their free state. This characteristic can be used to fabricate molecular magnets with metal covered BC: N.

In addition, the introduction of transition metal atoms (V, Cr, Mn, Fe, Co) makes the nonmagnetic BC:N produce a small amount of magnetic moment, and the B, C and N atoms near the best adsorption site contribute slightly to the total magnetic moment of the system. In the adsorption system of transition metal atoms (V, Cr, Mn, Fe, Co), the contribution of C atoms to the total magnetic moment is 0.4, 0.06, -0.24, 0.11, -0.03 μB, and the contribution of B atoms is 0.16, 0.03, -0.04, -0.04, -0.01 μB, and the contribution of N is 0.11, 0.03, -0.07, -0.05, -0.02 μB. Clearly, the magnetic moment contribution is positive or negative due to the difference of the transition metal atoms introduced. For V, Cr adsorption system, the contribution of B, C and N atom to the total magnetic moment of the adsorption system is positive. In the adsorption system of Mn, Fe and Co atom, the contribution of B, C and N atom to the total magnetic moment is almost negative. In all stable adsorption systems, C atoms contribute the most to the total magnetic moment of the adsorption system because the transition metal atoms have the most pronounced effect on the induction of C atoms in BC:N and are the most coupled.

Table 2. shows the most stable position of each metal atom adsorption system, the adsorption energy (Ea), the vertical height (d-h) of the adsorption atom and the BC:N plane, the total magnetic moment (μtot) of the adsorption system, magnetic moment of adsorption atom (μTM), and atomic magnetic moment of B, C and N (μi) is the magnetic moment of the free-standing states of transition metal atoms.

<table>
<thead>
<tr>
<th>Adatom</th>
<th>site</th>
<th>d-h (Å)</th>
<th>Ea (eV)</th>
<th>μtot (μB)</th>
<th>μTM (μB)</th>
<th>Mp (μB)</th>
<th>M↑ (μB)</th>
<th>M↓ (μB)</th>
<th>μi (μB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>H</td>
<td>1.945</td>
<td>-1.143</td>
<td>5.0</td>
<td>4.33</td>
<td>0.16</td>
<td>0.34</td>
<td>0.11</td>
<td>5</td>
</tr>
<tr>
<td>Cr</td>
<td>H</td>
<td>2.224</td>
<td>-0.299</td>
<td>6.0</td>
<td>5.69</td>
<td>0.03</td>
<td>0.06</td>
<td>0.03</td>
<td>6</td>
</tr>
<tr>
<td>Mn</td>
<td>H</td>
<td>2.028</td>
<td>-0.326</td>
<td>5.0</td>
<td>5.32</td>
<td>-0.04</td>
<td>-0.24</td>
<td>-0.07</td>
<td>5</td>
</tr>
<tr>
<td>Fe</td>
<td>Tc</td>
<td>2.027</td>
<td>-0.582</td>
<td>4.0</td>
<td>4.24</td>
<td>-0.04</td>
<td>0.11</td>
<td>-0.05</td>
<td>4</td>
</tr>
<tr>
<td>Co</td>
<td>Tc</td>
<td>1.921</td>
<td>-1.131</td>
<td>1.0</td>
<td>0.59</td>
<td>-0.01</td>
<td>-0.03</td>
<td>-0.02</td>
<td>3</td>
</tr>
<tr>
<td>Ni</td>
<td>Tc</td>
<td>1.871</td>
<td>-1.574</td>
<td>1.0</td>
<td>0.59</td>
<td>-0.01</td>
<td>-0.03</td>
<td>-0.02</td>
<td>2</td>
</tr>
</tbody>
</table>

In order to better understand the magnetic distribution of transition metal atoms adsorbed on BC:N, we use the spin charge density (SCD). Spin charge density is defined as ρ(r) = ρ↑(r) − ρ↓(r), where ρ↑(r) and ρ↓(r) represent the spin-up and spin-down charge density of the BC:N system adsorbed by the transition metal atoms, respectively. As shown in Fig. 6, We have calculated the spin charge density diagram of the adsorption system. It can be seen from the SCD diagram that the spin-polarized charge is localized around the transition metal atoms, which indicates that the magnetic moment of the adsorption system is mainly provided by the transition metal atoms. There is no spin-polarized charge around the Ni atomic adsorption system, which indicates that the magnetic moment of the free Ni atom is annihilated when the Ni atom is adsorbed on the monolayer BC:N, so the magnetic moment of the system will be zero. From the SCD diagram we can not know exactly whether the magnetic moment is related to the 3d orbital of the transition metal atom. So, the magnetic characteristics of the adsorption system will be analyzed by the density of state.
Figure 6. is the spin charge density (SCD) of transition metal atoms adsorbed BC$_2$N, and (a)-(f) represent the SCD of BC$_2$N adsorbed by V, Cr, Mn, Fe, Co, and Ni, respectively. The isosurface value of the charge density is set to 0.003e/Å$^3$.

3.3. Electronic structures

In order to understand the influence of 3d transition metal atoms on the electronic structures of BC$_2$N monolayer, the total DOS (TDOS) of all adsorption systems are shown in Fig. 7. Obviously, the former five transition metal atoms induce the asymmetric distribution between spin-up and spin-down states, meaning the adsorption of those atoms from V to Co can induce effectively the magnetism in BC$_2$N monolayer. The spin-polarized states mainly lie around the Fermi level. To analyze the case of the spin polarization [41], we define the spin polarizability as:

$$ P(E_{(f)}) = \frac{D(E_{(f),\uparrow}) - D(E_{(f),\downarrow})}{D(E_{(f),\uparrow}) + D(E_{(f),\downarrow})} $$  \hspace{1cm} (2)

where $D(E_{(f),\uparrow})$ and $D(E_{(f),\downarrow})$ represent the density of states (DOS) of the majority (spin up) and the minority spin (spin down) at the Fermi level, respectively. In addition, in order to analyze the source of the local magnetic moment in detail, the DOS and the PDOS of the most stable adsorption system are calculated as shown in Fig. 7. The positive and negative DOS represent spin up and down, respectively, and the Fermi level is set to zero level and is represented by a vertical dashed line. According to Fig. 7, it can be seen that some impurity states are produced in the band gap of monolayer BC$_2$N due to the adsorption of 3d transition metal atoms. And the spin-polarization is not remarkable for those states far away from the Fermi level (below -1.8 eV and above 1 eV) in all magnetic systems. However, the source of magnetism in the adsorption system is the polarization of frontier orbitals. However, for the structure of Ni adsorbed on monolayer BC$_2$N, the PDOS of all orbitals is up and down. The spins are symmetrical, and the system exhibits the characteristic of zero magnetic moment. As shown in Fig. 7(a), when V is adsorbed at the most stable position on the monolayer BC$_2$N, we can clearly see that there is one DOS peak for spin-up states at the Fermi level, while there are no states for the spin-down at Fermi level. Therefore, the spin polarizability reaches 100% for V adsorbed system. Meanwhile, the magnetic moment is mainly related to the state of the majority-spin channel of V near the Fermi energy level, and the contribution of the states below -1.8 eV to the magnetic moment of the system is almost zero. Through the analysis of the PDOS, the spin polarization near the Fermi energy level is mainly contributed by the 3d and 4s orbitals of V, and the contribution of the 3d orbitals is greater than that of the 4s orbitals. In addition, in the vicinity of Fermi energy level, the 2p orbital of B, C and N also contribute to the spin polarization, which derives from the coupling between 3d and 4s orbitals of V and 2p orbital of B, C and N atoms. Compared with the contribution of the 2p orbitals of B, C and N atoms to V adsorbed
system, the contribution of C atom is the largest than others. This is because the coupling between V atom and C atom is stronger than that between V atom and others atom at the best adsorption site.

**Figure 7.** (a)-(f) shows the TDOS of the monolayer BC₃N adsorbed by V, Cr, Mn, Fe, Co and Ni, the PDOS of the transition metal atoms and the PDOS of B, C and N in monolayer BC₃N. The TDOS of the system is represented at the top, the PDOS of the 3d transition metal atoms is in the middle, and the PDOS of the B, C and N in the BC₃N is at the bottom.

The density of states of the Cr atom adsorbed at the H position is shown in Fig.7(b). When the Cr atom is adsorbed at the H position, the minority spin states is zero at the Fermi level, while majority spin the states is nonzero, therefore, the spin polarization of Cr adsorbed system is 100%. In addition, the magnetic moment of the system is mainly related to the spin upward state at the Fermi energy level and the spin upward state in the energy range of [-1.35 eV, -0.312 eV]. The PDOS is analyzed. The main contribution of spin polarization is derived from the 3d orbital and 4s orbital of Cr, and the contribution of 3d orbital and 4s orbital to spin polarization is equivalent, But the state at the Fermi energy level is not the biggest contribution to the magnetic moment of the system, and the most important state is in the energy range of [-1.35 eV, -0.312 eV], which is mainly provided by the 3d and 4s orbitals of Cr. At the same time, the spin upward states both in the Fermi energy level and in the energy range [-1.35 eV, -0.312 eV] slightly come from the 2p orbit of B, C and N atoms, Because the 3d and 4s orbitals of V and the 2p orbit of the nearest neighbor B, C and N atoms are hybrid, the spin polarization of the 2p orbital of B, C and N atoms is induced. The stronger the hybrid, the stronger the induction. The spin states of V and the 2p orbitals of C have the strongest hybridization.
Compared with the contribution of the B and N atoms to the spin polarization, the contribution of the C atom is the greatest.

From Fig. 7(c), we can see that Mn is adsorbed to the H position of monolayer BC\textsubscript{2}N, there is no state at the Fermi energy level, and the spin down state exists, so the spin polarizability at the Fermi level is 100%. It is found that the spin polarization near the Fermi energy level is mainly contributed by 4s orbital of Mn, the contribution of 3d orbit of Mn is almost zero. The contribution of the state at the Fermi level to the overall magnetic moment of the system is small. The unoccupied state of the electron at 0.75 eV contributes greatly to the magnetic moment of the system, which is mainly attributed to the 3d contribution of Mn.

The DOS value of minority spin for Fe adsorbed system is zero at the Fermi level, while that of the majority spin is nonzero as shown in Fig. 7(d), meaning 100% spin polarization of the system. The spin polarization at the Fermi level is mainly contributed by the 3d orbital of Fe, and the contribution of the 4s orbital to the spin polarization at the Fermi level is almost zero. The electron occupied states of spin up state from -0.49 eV to 0.06 eV are mainly contributed by the 4s orbital of Fe, and the contribution of 3d orbital of Fe atom is almost zero. B, C and N atoms also contributes to the magnetic moment of the system, and the nearest neighbor to the adsorption site, B, C and N atoms, contributes greatly to the spin polarization. This is due to the existence of hybridization between the 4s orbital of the Fe atom and the 2p orbital of the B, C and N atoms. The 4s orbital of Fe atom and the 2p orbital of C atom have the strongest hybridization, so the contribution of C atom to spin polarization is the greatest.

Fig. 7(e) shows the DOS of the most stable adsorption system for Co atoms. There is a minority peak just below the Fermi level for Co adsorbed system, which is mainly contributed by 4s and 3d states of Co. Therefore, the spin polarization of Co adsorbed system reaches 100% nearly Fermi level. The spin-down states at Fermi level and the states in [-1.89 eV, -0.51 eV] play a major role in the magnetic moment of the system. The PDOS analysis shows that the spin-down state at Fermi level is mainly contributed by 3d orbital of Co, 4s orbital of Co provides a small contribution. 3d and 4s orbitals of Co are hybrid with the monolayer BC\textsubscript{2}N. The spin-polarized state of Co interacts with B, C and N atoms, which induces spin polarization induced by monolayer BC\textsubscript{2}N.

Fig. 8(f) is the DOS of Ni atom adsorbed monolayer BC\textsubscript{2}N. The spin-up states and the spin-down states are completely symmetric. Therefore, there is no spin polarization for Ni adsorbed system. Through the analysis of the PDOS, the spin-up and spin-down states in the energy range of [-1eV, 0.96 eV] are mainly contributed by the 3d and 4s orbitals of Ni. And the contribution of the spin-up state is the same as that of the spin-down state. At the same time, the 3d and 4s orbitals of Ni have very strong hybridization with the 2p orbitals of the nearest adjacent B, C and N atoms, and the strong coupling of Ni atoms with monolayer BC\textsubscript{2}N makes the 2p states of B, C and N also induce symmetric spin states.
Figure 8. The calculated total DOS of TM-BC$_2$N (TM = V, Cr, Mn, Fe, Co, Ni) by GGA and GGA+U with U=0, 2, 4, 6, 8 eV for TM-3d electrons.

It is well known that when the adsorption system consisting of 3d TM elements, the Coulomb force between d-d electrons has a strong influence on the electronic structure, especially the Fermi level of the adsorption system. Adsorption system considered in this study contain a transition metal, the electronic positioning of 3d transition metals is not well described in GGA, and thus it is necessary to study how d electronic localization affects the electronic states. To illustrate this problem, GGA+$U$ [37] has been considered to calculate the Hubbard-type Coulomb interaction. Fig. 8 shows the DOS of the adsorption system with GGA+$U$ (U=2, 4, 6, 8) for 3d orbitals of TM atoms. When U=0, the spin polarization of the adsorption system reaches 100% at the Fermi level (half-metallic property). It could be seen that the adsorption systems (V, Co, Mn) are still half-metallic materials with U changes from 2 to 8 eV for TM-3d electrons. However, when U is considered, half-metallic property for the adsorption systems of Fe and Cr atoms disappear. This phenomenon indicates that the half-metallicity of adsorption systems (V, Mn, Co) remains the same when Coulomb interaction is taken into account.
4. Conclusions

In summary, the stable structure, magnetic and electronic properties of 3d transition metal atoms adsorbed on 4 × 4 monolayer BCN have been investigated by the first-principles method. The calculated results show that the transition metal atom (V, Cr, Mn, Fe, Co, Ni) can stably adsorb on monolayer BCN. The study on its structure shows that the most preferable adsorption site is on top of C atoms (Tc) for V, Cr, and Mn atoms, while the others 3d TM atoms (Fe, Co, Ni) are found to prefer the hollow adsorption site (H) of BCN monolayer. By studying its adsorption energy, Cr and Mn are physically adsorbed on monolayer BCN, whereas TM atoms (V, Mn, Fe, Co, Ni) are chemically adsorbed on monolayer BCN. Studies on magnetic properties show that the most 3d transition metal atoms can make the monolayer BCN magnetization, and the spin charge density indicated that the magnetic moments of adsorption systems are mainly concentrated on the TM atoms. Through the analysis of the DOS, it can be seen that the introduction of 3d TM atoms (V, Cr, Mn, Fe, Co) leads to the spin polarization of the adsorption system, and the spin polarizability reaches 100% (half-metallic property), which has the characteristics of spin filter material. And there is a hybrid phenomenon between the 3d orbital of TM atoms and the 2p orbital of its nearest neighbor B, C and N atom. Since the 3d TM atoms have spin-polarization characteristic, 3d orbitals can also induce auto-spin-polarization of the 2p orbitals of the nearest adjacent B, C and N atoms. In addition, the influence of Hubbard U value on magnetic (V, Cr, Mn, Fe, Co) adsorbed system is also considered. When U = 0, it can be seen from the DOS at the Fermi level that all five configurations are semi-metallic. As the U increases, half-metallic property for the adsorption systems of Fe and Cr atoms disappears, the system can transform from half metal to metal. Furthermore, the results show the TM adsorbed monolayer BCN can be used as spintronic device and nanomagnets.

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References


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