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Ab initio study of electronic properties of armchair graphene nanoribbons passivated with heavy metal elements

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ABSTRACT

In this study, electronic properties of graphene nanoribbons with armchair edges (AGNRs) have been investigated with Density Functional Theory (DFT). Effects of heavy metal (HM) elements, including Zinc (Zn), Cadmium (Cd) and Mercury (Hg) atoms on electronic behavior of AGNRs have been calculated by passivating for both one and two edges of AGNRs in detail. To explain the electronic behavior of investigated AGNRs, the electronic band structure, the density of states (DOS), total energy have been calculated. Energetically favorable structures have been determined using calculated binding energy values. The obtained bandgap values of investigated structures changes between 0.30 and 0.64 eV. Increasing atomic number of passivation atoms have led to an increment in the bandgap of AGNRs.

1. Introduction

Carbon-based materials have been attracted more attention of researchers over the last decade, due to their unique structural and electronic properties [1–6]. Graphene is one of them which attracted much attention since it is discovered experimentally in 2004. It is a monolayer honeycomb lattice of sp^2 bonded carbon [7,8]. Because of its unique and exceptional electronic transport properties, graphene has the potential application in many fields such as nanoelectronics and renewable energy storage [7,9].

Graphene nanoribbons (GNR) are the one-dimensional (1D) materials obtained from the graphene and have been appealed in great amount regards in the fields of materials science and physics [1,10]. According to the feature of edge, the GNRs are divided into zigzag edge graphene nanoribbons (ZGNRs) and armchair edge graphene nanoribbons (AGNRs) [11–13]. The GNRs have been studied theoretically and experimentally because of their unique electronic structures and transport properties [14]. The electronic structure of GNRs depends on their width and edge structure [15]. Generally, AGNRs show mostly semiconductor properties, ZGNRs have a metallic behavior as known. However, these properties of GNRs can be changed with doping, edge passivation, applied electric field perpendicular to nanoribbons [16–18]. As well as metallic and semiconductor properties of GNRs, spin-dependent structures can be obtained in these ways [19]. By this means, the electronic behavior of GNRs can be mostly controlled.

In recent years, graphene and carbon nanotubes (CNTs) have been experimentally used for detections of heavy metal (HM) elements [20]. Graphene-based sensors for such HM elements are useful even small concentrations of HM atom concentrations [21]. Therefore, detection of HM elements is important for many industrial applications, especially for medical applications. Despite a presence of interactions between graphene and HM elements, however, there is lack of numerical calculations about the effect of HM elements on the electronic properties of low dimensional carbon-based materials like nanoribbons.

In this study, effects of some HM elements used as passivation on electronic properties of AGNRs have been studied with density functional theory (DFT) method. Discusses on the structural stability and the electronic behavior of the each studied structures on calculating binding energy, electronic band structures, density of states (DOS) have been made.

2. Calculation method

In this work, we explore the electronic band structure and the DOS of asymmetrical AGNRs passivated with H and HM elements including Zn, Cd, and Hg. The calculations were carried out Atomistix Toolkit-

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Virtual NanoLab (ATK-VNL) software package based on DFT was used to perform the calculations in order to obtain the electronic properties of investigated asymmetrical AGNRs [22,23]. ATK can be used for the calculation of basic material properties such as electronic, structural and optical properties of atomic scale materials using Density Functional Theory. The used pseudopotentials are varied with the upgraded versions of the software. In our calculations, which are calculated with ATK 2017.2, SG15 Optimized Norm-Conserving Vanderbilt (ONCV) pseudopotentials [24] are used to perform high accuracy in the required calculations. As an exchange-correlation function, the spin-polarized version of the generalized gradient approximation (SGGA) was used in the form of Perdew, Burke and Ernzerhof (PBE) correlation functional [25]. An energy cut-off value of 500 eV was selected to ensure accurate results. Brillouin zone integration was performed using a regular Monkhorst-Pack Scheme with $1 \times 1 \times 100$ k-point grid. All atoms were fully relaxed and maximum force components on all atoms were accepted to be less than $0.05 \, eV\text{Å}^{-1}$. The calculations for zigzag and armchair edges of GNRs were performed, but the results of zigzag edges GNR weren't presented due to their metallic electronic band structures. Also, the electronic calculations were carried out for different widths, however, nanoribbons with different widths show similar results with each other. The width of the investigated asymmetrical AGNR structures in this study was N = 8 as illustrated in Fig. 1 (a). In asymmetrical AGNR, the supercell is periodic along z-direction as shown in Fig. 1 (a). In our calculations, we modeled asymmetrical AGNRs with one and both edges passivated with Zn, Cd, and Hg so that they are compared with each other in terms of the structural stability, the electronic band structure, and the band gap. Structural stability of investigated structures was determined using Eq. (1).

$$E_b = E_T - E_{T:bare} - nE_H - mE_P \qquad (1)$$

where, E_b is binding energy, E_T, and $E_{T:bare}$, are total energies of the structure including HM elements and bare structure, E_H is energy of isolated H, E_P is energy of isolated passivation atom, n and m are numbers of H and passivation atoms, respectively.

3. Results and discussions

The atomic configuration and the electronic band structure of the AGNR passivated with H atoms have been shown in Fig. 1. The electronic band structure and DOS of asymmetrical AGNR show a semiconductor behavior as expected. Fermi level is in the middle of conduction and valence bands and represented with a red line. The bond length of AGNR passivated with H atoms has been found as 1.10 Å, the calculated binding energy and the electronic band gap has been obtained as 0.85 and 0.46 eV, respectively. Previously, the calculated
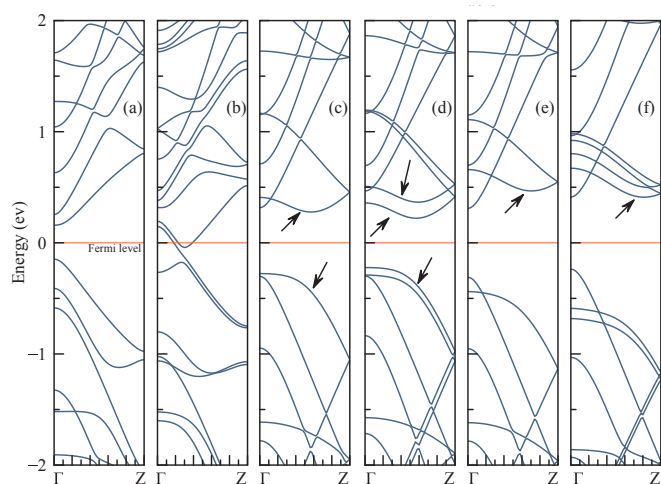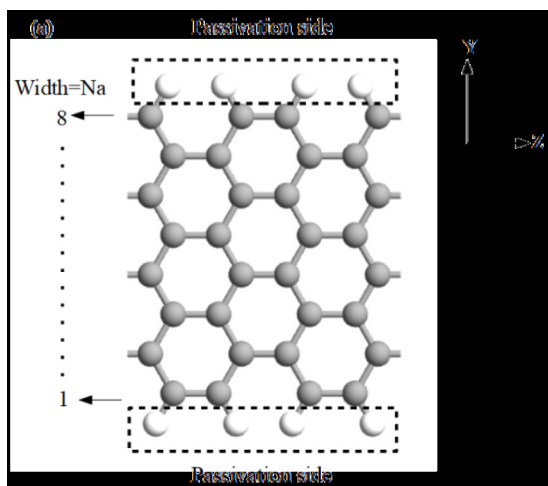

Fig. 2. Band structures of AGNR passivated with HM elements. (a), (c), (e) are represented one edge passivated structures for Zn, Cd, Hg, respectively. (b), (d), (f) are shown passivated structures on both edges with Zn, Cd, Hg, respectively.

energy band gaps for AGNR passivated with H atoms are found to be give similar results with this study [26,27].

Fig. 2 shows the electronic band structures of AGNRs passivated with the investigated HM elements. While Fig. 2a), c) and e) figures show one edge passivated structures, others represent passivated structures on both edges. All investigated AGNRs have a semiconductor behavior except the structure passivated with Zn on both edges. While AGNRs passivated with Zn and Hg atoms have observed a direct bandgap, the structure passivated with Cd atom has an indirect bandgap. In the investigated structures, any spin polarization has not been observed. This shows that the AGNRs passivated with HM elements have still a magnetization symmetry, however, previously some studies present that when non-metal Aluminum (Al) and metallic Iron (Fe) atoms are adsorbed on the edges of ZGNRs, these atoms generate the spin polarized ZGNRs [28,29]. These results have been explained with breaking of the magnetization symmetry in ZGNRs. The source of the spin polarization inducing is deterioration in edge states of GNRs by adsorbed or passivated atoms. It is shown that the impurity bands marked by arrows for some band structures are formed due to hybridization of π-orbitals of C atoms and d and f orbitals of passivation atoms, compared with the electronic band structure pure AGNR. For the structures passivated on both edges, a numerous of band splittings are observed due to overlap of band states related to each similar passivated edge. The bandgap of the structures is higher as the atomic
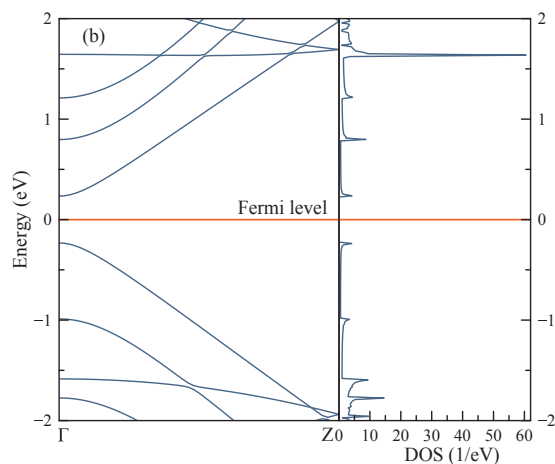

Fig. 1. a) Atomic configuration of used AGNRs b) electronic band structure and DOS passivated AGNR with Hydrogen atoms.
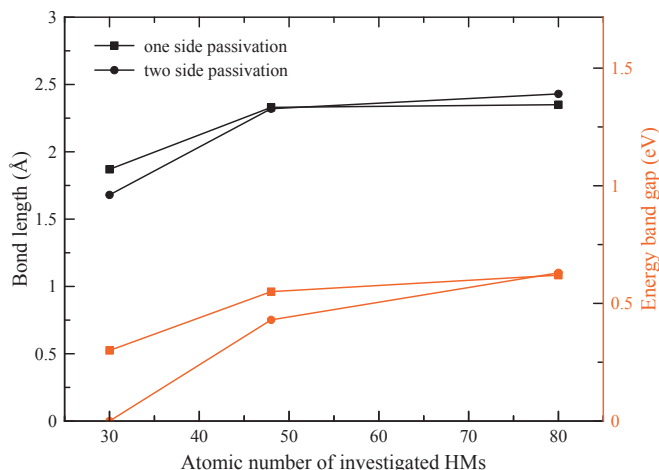
Table 1
Calculated electronic and structural parameters for AGNRs with the investigated HM elements.

Structure	E_b (eV) per atom	E_{gap} (eV)	Type of bandgap	Bond length of C-HM (Å)
One edge Zn	−0.69	0.30	Direct	1.87
Both edges Zn	−0.03	0	Metallic	1.68
One edge Cd	−0.52	0.55	Indirect	2.33
Both edges Cd	−0.19	0.43	Indirect	2.32
One edge Hg	−0.45	0.62	Direct	2.35
Both edges Hg	0.44	0.64	Direct	2.43

Fig. 4. Bond length and energy bandgap of investigated structures depending on the atomic number of the investigated HM elements.

number of the investigated HM elements is increased. Moreover, one edge passivated AGNRs have a higher bandgap than both edges passivated structures due to overlap of band states related to each similar passivated edge. The calculated bandgap values are listed in Table I.

DOS of the investigated structures are shown in Fig. 3. Similar to adsorption studies, there is no spin-dependent result in AGNR structure passivated with Zn, Cd and Hg [30]. In pure AGNR, one dimensional (1D) DOS behavior is shown from Fig. 1b). Investigated AGNR structures with HM elements indicate quasi one-dimensional (Q1D) and quasi zero-dimensional (Q0D) local density of state behaviours [11]. Observing a Q0D behavior in these structures is expected because of a highly localized d and f orbitals of For the structures passivated on both edges, a numerous of band splittings are observed due to overlap of band states related to each similar passivated edge passivation atoms. Q1D behavior can be associated to nanowire-like bonding of HM elements at the edge of the investigated AGNRs.

Fig. 4 shows changing of the bond length between Carbon (C) and investigated HM elements and energy band gaps in passivated AGNR

with respect to the atomic number of the investigated HM elements. In accordance with the results reported in the literature, the bond length is increased with the increasing of atomic number of HM elements as 1.73 Å, 2.22 Å and 2.28 Å for C−Zn, C−Cd and C−Hg bond lengths, respectively [21,31]. Moreover, the band gap values seen at the electronic band structures given in Fig. 2 are increased with increasing atomic number of the investigated HM elements. It is shown that small strain distributions could be changed the band gap of AGNRs [32]. In our case, passivated AGNRs with high atomic number atoms had small local strain distributions at the edge of nanoribbons. This situation is
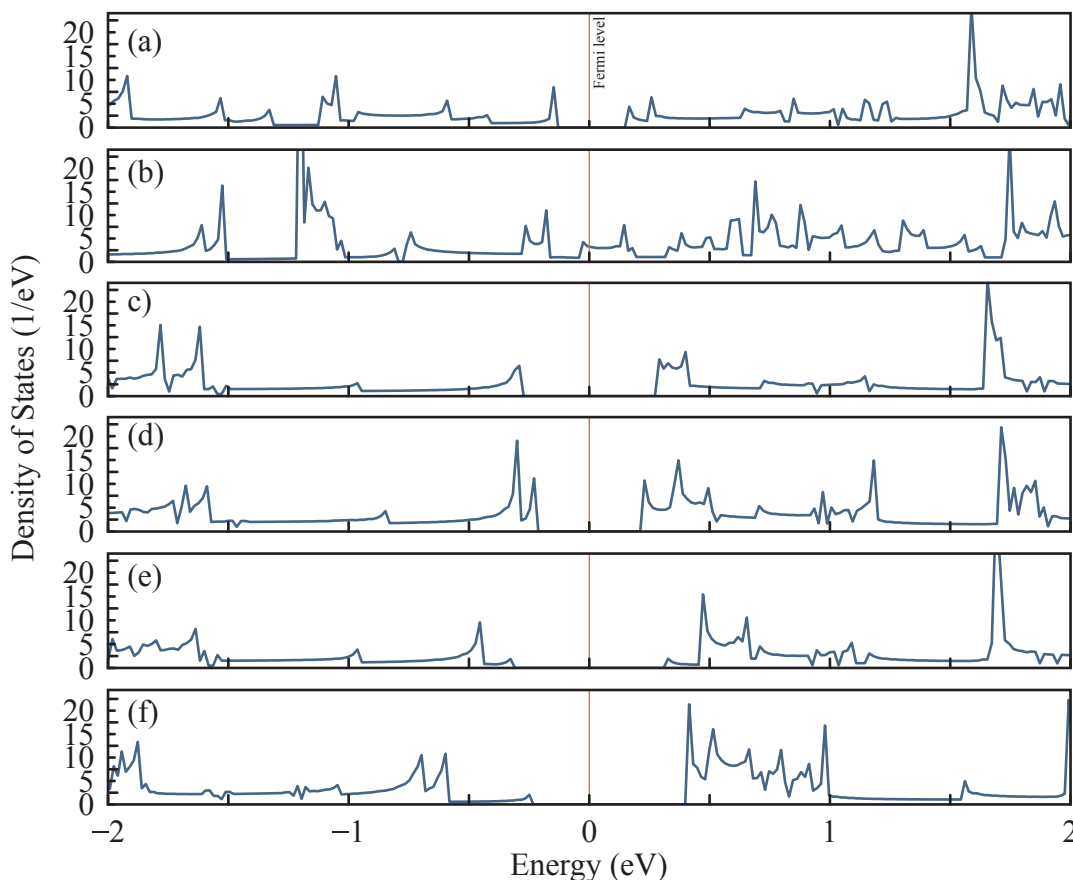
Fig. 3. Density of States of AGNR passivated with Zn, Cd and Hg atoms (a), (c), (e) are represented one edge passivated structures for Zn, Cd, Hg, respectively (b), (d), (f) are shown both edges passivated structures for Zn, Cd, Hg, respectively.

expected to lead a decrease in the band gap.

According to the E_b results listed in Table I, the structural stability of the passivated AGNRs can be interpreted. It can be seen that the structure passivated with Zn one edge is the most stable structure after AGNR passivated with H atom. It is reported that GNRs passivated with transition metals are found to be more stable than both edges passivated structures [33–35].

4. Conclusion

In this study, the investigations of effects of some HM elements as passivation atoms on electronic structures of AGNRs have been studied by means of DFT method. The bandgap of investigated structures is changed from 0.30 to 0.64 eV along with the investigated HM elements. With the increase of the atomic number of HM elements, the band gap values of AGNRs have been increased. Unlike other investigated structures, AGNR passivated with Cd atom shows indirect band gap. Q0D and Q1D type some local DOS behaviors have been shown in the DOS results of AGNRs passivated with the investigated HM elements. The most stable structure is determined as AGNR one edge passivated with Zn among the studied structures with the investigated HM elements interpreting binding energy results for each structure. These results are important in terms of understanding of the effect of HM elements on electronic properties of low dimensional carbon-based materials like graphene nanoribbons.

Acknowledgments

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