

Research Article

First-Principle Study on the Interaction between Fe and Trivacancy in Graphene

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Ab initio calculations using density functional theory (DFT) have been performed in order to explore structure and energy gap opening of graphene with bridged-trivacancy and single adsorbed with Fe atom. Compared to the previous reconstructed trivacancy adsorbed with Fe atom with the energy gap of 0.10 eV, one interesting structure for the Fe-doped bridged-trivacancy complex has been identified, with one Fe atom above the graphene plane, and possesses energy gap with the value of 0.32 eV in the bridged circumstance. The band gap can be explained by the decrease of the free electrons. These results provide insights to engineer graphene's properties through defect addition and manipulation for industrial semiconductor applications such as the photocatalytic technology and graphene based electronics.

1. Introduction

Graphene is among the most potential utilized materials currently studied [1–3]. It exhibits extraordinary properties in electrology [4, 5], magnetism [6, 7], and dynamics [8], proved by various theoretical and experimental studies. However, graphene is a semimetal, which greatly limits the application in the graphene-based electronic field [9–11]. Consequently, in the recent decades, many approaches, such as by employing a staggered AB sublattice potential [12], strain effect [13], intrinsic spin-orbit coupling [14] in single-layer graphene, functionalization with chemical groups [15–17], or applying a perpendicular electric field in bilayer graphene [18], have been explored to open the gap of graphene for designing semiconductor device.

Chan et al. have studied the structures and magnetism about pure graphene adsorbed with many elements such as Li, Na, K, Ca, and Al [19]. However, precise and stable structures of the transition metal (TM) adsorbed on graphene are hardly obtained because TM adsorbents can move freely on the surface of pristine graphene, which limits the use of surface adatom as robust and reliable dopants for nanoelectronic and magnetic applications [20]. Recently, it is forecasted that attaching metal atoms to defected graphene is much firmer

than to pristine graphene by theoretical studies [21–25]. Kim et al. have used X-ray magnetic circular dichroism (XMCD) to study the electronic and magnetic properties of transition metal (TM), for example, Fe, Co, and Ni clusters on monolayer graphene [26]. Also a very high magnetic anisotropy energy (MAE) has been found in single-vacancy graphene adsorbed with Ir dimer [27]. Dynamics of single Fe adatom on graphene vacancies have been studied using focused electron beam irradiation [28]. Vacancy-assisted doping method is one available technique for introducing dopants into graphene.

As a matter of fact, iron in graphene nanostructures are very common in experiment, such as Fe pairs doped in graphene [20], single Fe atoms in graphene vacancies [29, 30], and Fe₃O₄/graphene nanocomposites [31–34]. In previous work, band gap of graphene could be opening via Fe atom adsorption [11]. Recently, an interesting structure of graphene trivacancy, which was achieved by using an electron beam to bombard the graphene sheet, has been commonly observed by Robertson et al. [35]. The new structure has a bridging atom (thereafter called bridged-trivacancy), significantly different from the reconstructed trivacancy (r-trivacancy) observed by Wang et al. [36]. Consequently, a combination

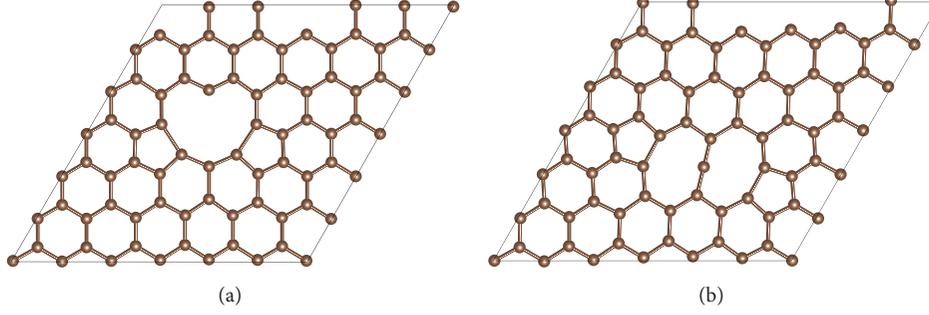


FIGURE 1: (a) Optimized 6×6 graphene supercell with r-trivacancy. (b) Optimized 6×6 graphene supercell with b-trivacancy.

of Fe adsorption and b-trivacancy might contribute to extend the application of graphene by opening the band gap.

This work presents a detailed study of the structure and electronic properties of graphene with r-trivacancy and b-trivacancies trapping Fe atom, using the density functional theory (DFT). Our studies may verify the feasibility of improving graphene electrical properties by controlling TM atom doping and vacancies.

2. Calculation Details

First-principles calculations based on the spin-polarized density functional theory (DFT) were performed using the projector augmented wave (PAW) [37], as implemented in the Vienna Ab initio Simulation Package (VASP) program [38]. The generalized gradient approximation in the Perdew-Burke-Ernzerhof (PBE) [39] parameterization was employed for the exchange-correlation functional. The plane-wave cut-off energy was set to 500 eV. The geometry optimization and total energy calculations were performed until the residual force was within 0.01 eV/\AA and the total energy converged to 10^{-5} eV . The k -point mesh for sampling the Brillouin zone was generated including the gamma point. A $4 \times 4 \times 1$ k -point mesh was used for geometry optimization, and a $6 \times 6 \times 1$ k -point mesh was used for total energy calculations.

We modeled the defect systems using supercells large enough (5×5 and 6×6 supercells in the lateral direction with a 20 \AA thick vacuum in the vertical direction) to minimize boundary effects on the energetics of the systems. Graphene's lattice constant was calculated to be 2.470 \AA , which is similar to the calculated value (2.468 \AA) by Dai et al. and the experimental value of 2.46 \AA [21].

3. Structures for System

Three kinds of trivacancies in graphene have been discovered in previous research, the r-trivacancy observed by Wang in 2012 [35] and the b-trivacancy observed by Robertson in 2014 [36], and the optimized equilibrium configurations for the r-trivacancy and b-trivacancy in our simulations using DFT are shown in Figure 1. The b-trivacancy is not just stabilized by simple bond reconstructions between undercoordinated carbon atoms, as exhibited by r-trivacancy. Reconstructions consist of undercoordinated bridging carbon atoms spanning

the vacancy to saturate edge atoms in b-trivacancy, which matches well with the previous work [36].

All the systems with Fe adsorbate on perfect graphene and defective graphene (containing a r-trivacancy or b-trivacancy) are studied. Three possible adsorption sites of Fe on the perfect graphene are labeled as follows: hollow (H), top (T), and bridge (B). And the complexes of perfect graphene adsorbed with Fe which locates in the three possible sites are indicated as Fe@G(H) , Fe@G(T) , and Fe@G(B) , respectively. For adsorption on defect-free graphene, Fe@G(H) (on the hollow site) is the most stable complex, which is in good agreement with the previous theoretical results [5, 19]. In the case of the adsorption of Fe on the defective graphene, Fe is positioned at different hollow, top, and bridge sites in the trivacancy region as the initial positions and then fully relaxed. The configurations of the adsorption of Fe on defective graphene are shown in Figure 2, in both top view and side view. For convenience, the complex of Fe adsorbed on the graphene with a r-trivacancy is labeled as Fe@RTV , and the one with b-trivacancy as Fe@BTV . From the side views, it is obvious that Fe atom is above the plane of graphene with b-trivacancy and the adatom-graphene distance d (\AA) is 1.38 \AA .

The formation energy E_f of a trivacancy in graphene, indicated by E_f , is defined as

$$E_f = E_s - \frac{N-n}{N} E_g, \quad (1)$$

where $n = 3$ is the number of vacant C atoms in the system, and N is the total number of C atoms in supercells of the perfect graphene. E_s and E_g are the energies of the graphene with r-trivacancy or b-trivacancy and the 5×5 or 6×6 graphene supercells, respectively. The adsorption energy of Fe on the perfect or defective graphene is defined as

$$E_{\text{ads}} = E_s - E_g - E_{\text{Fe}}, \quad (2)$$

where E_s , E_g , and E_{Fe} are the energies for the optimized systems of Fe-graphene with or without trivacancy, the 5×5 or 6×6 graphene supercells with or without trivacancy, and the isolated Fe atom, respectively.

Table 1 summarizes the energetic and structural properties of the 5×5 and 6×6 supercells of graphene with trivacancy adsorbed with Fe. For comparison, the formation energy of the trivacancy in graphene and the adsorption

TABLE 1: Energetic and structural properties of Fe on the defect-free graphene and defective graphene with r-trivacancy and b-trivacancy. The properties listed include the size of graphene supercells s , types of the Fe-graphene complex t , the Fe-graphene distance d (Å), formation energy E_f (eV) of trivacancy in graphene, adsorption energies E_{ads} (eV), bulk band gap Δ (eV), and the magnetization of the adatom μ_{ag} (μ_{B}). For comparison, the magnetization of the graphene with a trivacancy is included.

s	t	d (Å)	E_f (eV)	E_{ads} (eV)	Δ (eV)	μ_{ag} (μ_{B})
5×5	Fe@RTV	0.00	—	-6.35	0.13	2.00
	Fe@BTV	1.24	—	-6.90	0.32	0.00
	Fe@G(H)	1.65	—	-1.04	0.08	2.00
	Fe@G(B)	2.23	—	-0.28	0.00	4.10
	Fe@G(T)	2.06	—	-0.27	0.00	4.10
	r-trivacancy	—	11.68	—	0.00	1.05
	b-trivacancy	—	14.86	—	0.00	1.66
6×6	Fe@RTV	0.00	—	-6.61	0.03	2.00
	Fe@BTV	1.38	—	-6.96	0.25	0.00
	Fe@G(H)	1.50	—	-1.13	0.07	2.00
	Fe@G(B)	2.20	—	-0.29	0.00	4.10
	Fe@G(T)	2.12	—	-0.28	0.00	4.10
	r-trivacancy	—	11.13	—	0.00	1.05
	b-trivacancy	—	14.27	—	0.00	1.66

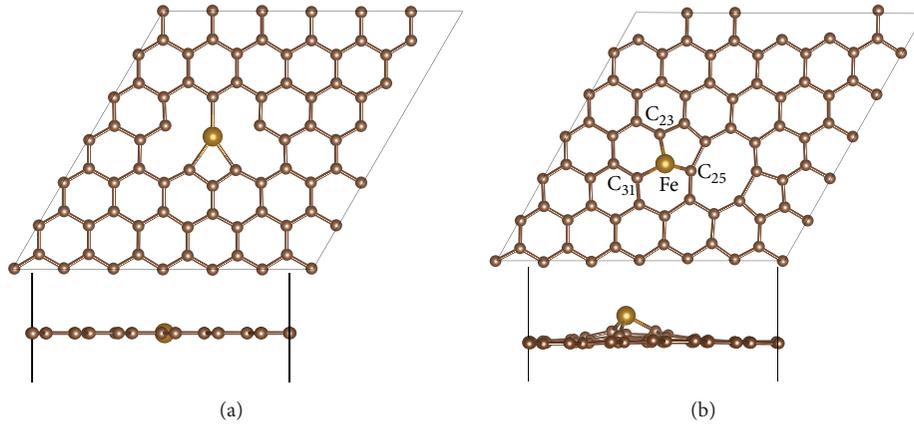


FIGURE 2: The optimized configurations of Fe adsorbed on the 6×6 graphene supercell with a trivacancy in both top view and side view. (a) Fe on the graphene with r-trivacancy (Fe@RTV) and (b) Fe on the graphene with b-trivacancy (Fe@BTV).

energy of Fe on the defect-free graphene are also included in Table 1. The adsorption energy for Fe@G(H) complex is the lowest, indicating that the stable position is the hollow site. The adsorption energy of Fe adsorbed on defective graphene with a trivacancy (Fe@TV) is much lower than that of adsorption on perfect graphene, indicating Fe@TV is more stable, which conforms to the previous studies [22]. It means that the introduction of a trivacancy on graphene will improve the adsorption of Fe atom. The formation energy of r-trivacancy is 11.68 eV, consistent with the result in [21], lower than that of b-trivacancy (14.86 eV), indicating that the b-trivacancy is a metastable structure. It is in good agreement with previous studies [35]. From Table 1, we also notice that graphene supercell with b-trivacancy adsorbed with Fe (Fe@BTV) has a lower adsorption energy in comparison with r-trivacancy adsorbed with Fe (Fe@RTV) in the same concentration, which relates with a better incorporation of the adsorbate into the graphene framework. It is worth noting that the band

gaps of Fe@BTV are 0.32 eV and 0.25 eV for 5×5 and 6×6 graphene supercells, respectively. By contrast, the band gaps of Fe@RTV are 0.13 eV and 0.03 eV for 5×5 and 6×6 supercells, respectively. The system of Fe adsorbed on the perfect graphene has the maximum band gaps of 0.08 eV, which is similar to the result (100.8 meV) in [11]. Fe@BTV system may have a bearing on important applications such as graphene-based electronic device.

4. DOS for Fe@BTV

The graphene with b-trivacancy and r-trivacancy is metallic, as the existence of trivacancy in graphene will increase the number of free electrons in the system. The partial densities of states (PDOS) for spin-up and spin-down electrons of Fe atom and adjacent C atoms and the total density of states (TDOS) in 5×5 and 6×6 graphene are calculated as shown in Figure 3. The indices of C atoms are labeled in Figure 2(b)

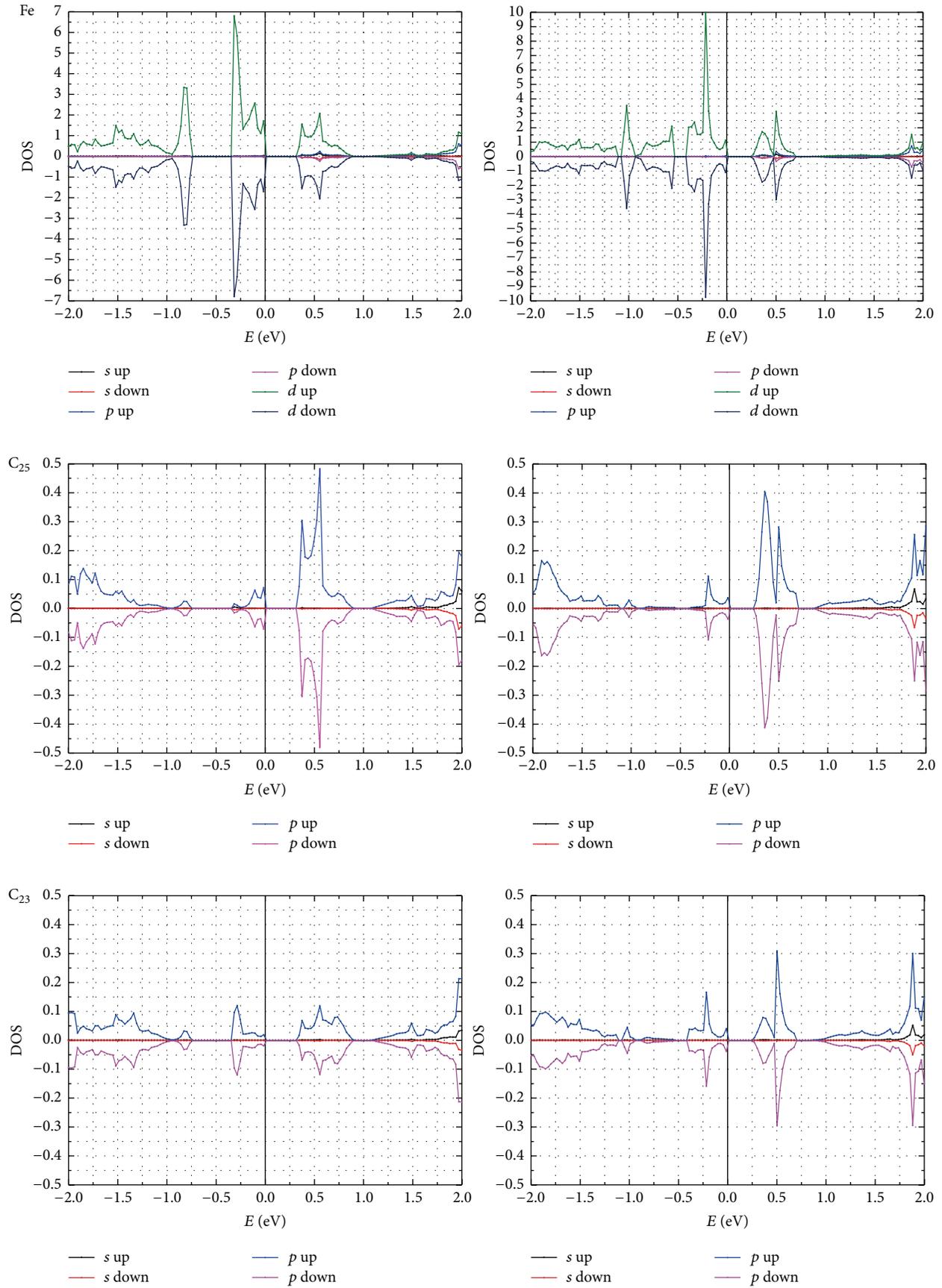


FIGURE 3: Continued.

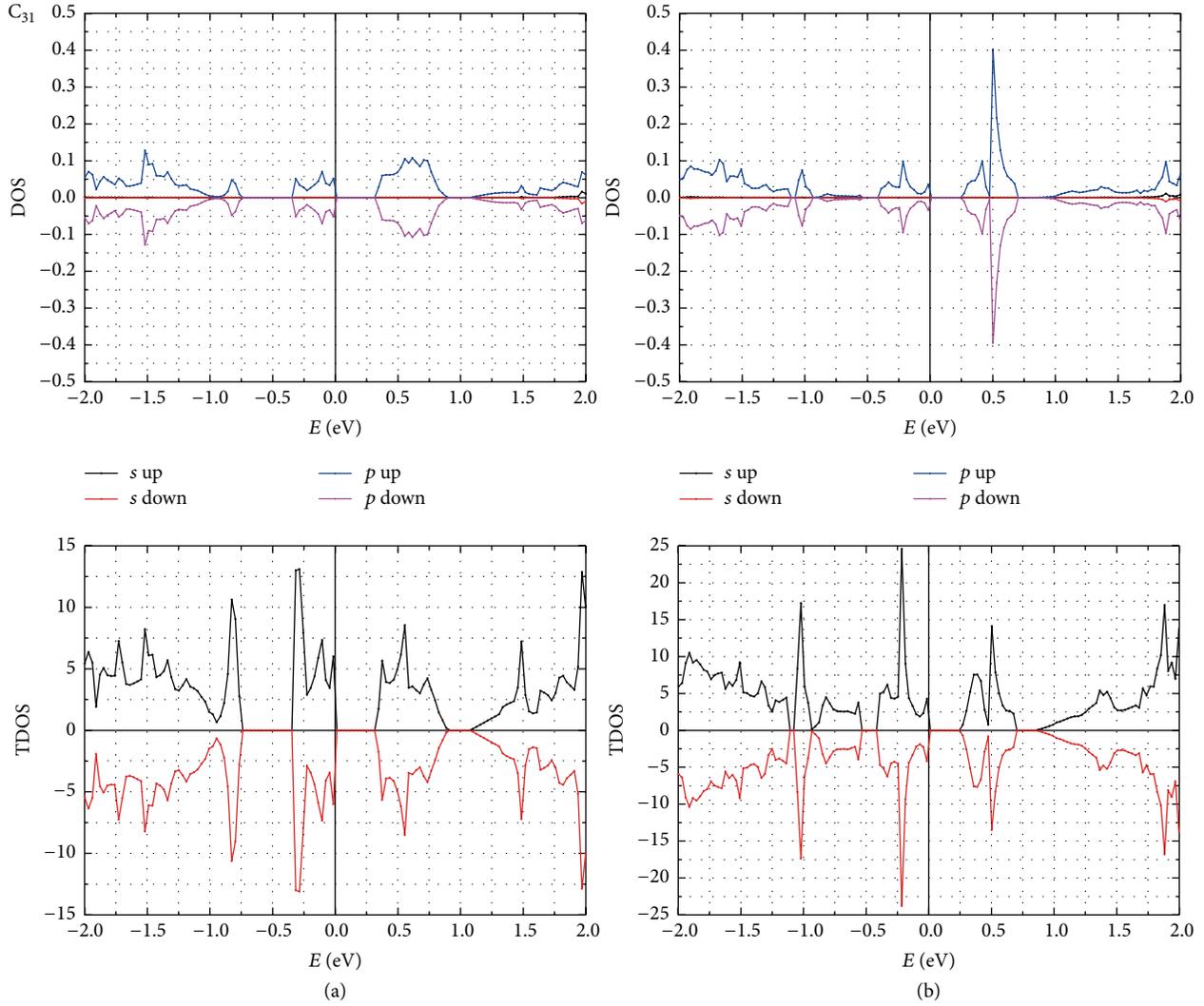


FIGURE 3: The partial densities of states (PDOS) for spin-up and spin-down electrons for Fe atom and C atoms vicinity of adsorbed Fe and the total density of states (TDOS) in 5×5 and 6×6 graphene: (a) 5×5 graphene, (b) 6×6 graphene.

and C_{25} labels the bridge C atom. Obviously, for b-trivacancy, the spin-up and spin-down DOS of C_{25} , C_{23} , C_{31} , Fe, and Fe@BTV is mirror symmetry, indicating no magnetic moment. The PDOS of adjacent C atoms match well with Fe $3d$ orbitals. In 5×5 graphene all the PDOS locate at $-2 \sim -0.75$ eV, $-6 \sim 0$ eV, and $0.32 \sim 0.7$ eV. Similar conclusions can be got in 6×6 graphene. In particular, the PDOS of C_{25} $2p$ orbitals match so consistently with Fe $3d$ orbitals. It suggests that Fe atom has formed covalent bonds with adjacent C atoms. Stronger Fe-C interaction was observed between Fe- C_{25} than that between Fe- C_{23} and Fe- C_{31} . The magnetization of Fe in b-trivacancy is $0 \mu_B$ while the Fe atom in r-trivacancy has magnetization of $2 \mu_B$ (Table 1). This is consistent with the fact that there are enough ten electrons in the $3d$ orbitals of Fe in b-trivacancy after two $4s$ electrons of Fe transferred into $3d$ orbitals and sharing two $2p$ electrons from neighbouring C atoms.

Adsorbate opens the band gap of graphene with b-trivacancy. Fe adatom has formed covalent bonds with

adjacent C atoms in the b-trivacancy region, and the number of free electrons is reduced, resulting in the opening of the energy gap.

The band structures for Fe@BTV are shown in Figure 4. It could be found that an energy gap is opened by trapping Fe to the b-trivacancy and the energy gap is larger in Figure 4(a) than that in Figure 4(b). The value of energy gap is 0.32 and 0.25 for (a) and (b), respectively.

5. Conclusions

In conclusion, density functional theory calculations have been performed to investigate the interaction of Fe adatom with bridged-trivacancy in graphene. The graphene with b-trivacancy trapping Fe atom has one stable structure, namely, Fe@BTV. The adsorption of Fe atom can open a finite energy gap in both r-trivacancy and b-trivacancy. The band gap of Fe@BTV is 0.32 eV, larger than the value of Fe@RTV (0.1 eV), which is close to the value for developing graphene-based

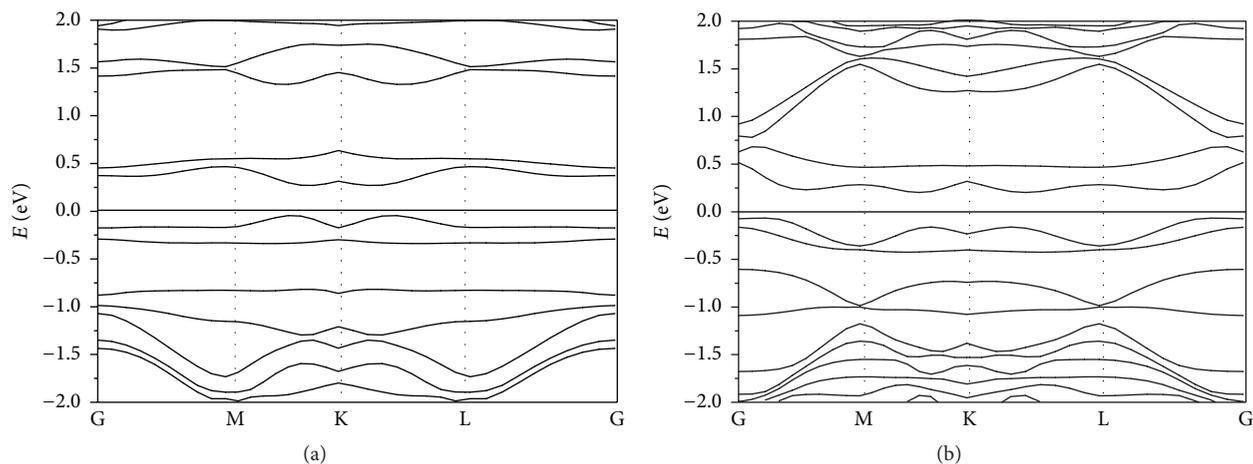


FIGURE 4: Band structures of Fe@BTV complex. (a) Optimized 5×5 graphene supercell with b-trivacancy trapping Fe. (b) Optimized 6×6 graphene supercell with b-trivacancy trapping Fe.

electronics. Fe adatom has formed covalent bonds with adjacent C atoms in the b-trivacancy region, and the number of free electrons is reduced, resulting in the opening of the energy gap. The findings might provide a promising scheme for gap opening of graphene for industrial semiconductor applications and the photocatalytic technology.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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