Structures of Pt clusters on graphene doped with nitrogen, boron, and silicon: a theoretical study*

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The structures of Pt clusters on nitrogen-, boron-, silicon- doped graphenes are theoretically studied using density-functional theory. These dopants (nitrogen, boron and silicon) each do not induce a local curvature in the graphene and the doped graphenes all retain their planar form. The formation energy of the silicon-graphene system is lower than those of the nitrogen-, boron-doped graphenes, indicating that the silicon atom is easier to incorporate into the graphene. All the substitutional impurities enhance the interaction between the Pt atom and the graphene. The adsorption energy of a Pt adsorbed on the silicon-doped graphene is much higher than those on the nitrogen- and boron-doped graphenes. The doped silicon atom can provide more charges to enhance the Pt-graphene interaction and the formation of Pt clusters each with a large size. The stable structures of Pt clusters on the doped-graphenes are dimeric, triangle and tetrahedron with the increase of the Pt coverage. Of all the studied structures, the tetrahedron is the most stable cluster which has the least influence on the planar surface of doped-graphene.

Keywords: first-principles, doping, clusters structure, graphene

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1. Introduction

Graphene is a new exciting material with many novel properties which are associated with its truly two-dimensional structure.[1,2] Single-layer graphene is a one-atom thick sheet of hexagonally arrayed sp^2-bonded carbon atoms and is the mother of all graphitic forms of zero-dimensional fullerenes and one-dimensional carbon nanotubes.[1] The hexagonal structure is similar to that of the boron-nitride nanoribbon.[3] Compared with carbon nanotube (CNT), graphene has ultrahigh surface area, high thermal stability and chemical properties, so it is considered as an unrolled CNT.[4−8] Graphene and the nanoparticles have some excellent properties for optics, electronics, catalysis, gas sensor applications.[9] The platinum nanoparticles are very popular in commercial applications such as catalysis, electrode leads, supercapacitors. For better applications, it is important to control the sensitivities to the size and the shape of the particle to promote catalytic activity, as well as to reduce cost and prolong the lifetime of the catalyst.[10−16] The synthesizing of different types of carbons with substitutional dopants such as N, B, transitions metals such as Fe, Co, Ni, Rh and Ir and alkali metals such as Li and K have been reported in the literature.[17−24] The presence of the dopants in lattice leads to change in the property of the original carbon material due to the caused structural and electronic effects.[25−27] These suggest that doping with impurities may allow tuning of the properties and chemical sensitivity of carbon nanostructures.[28−31] Recently, Acharya and Turner[32] researched carbon substituted by boron dopants in graphite and fullerene models. Studies of supported clusters are also technologically driven by the demand of new and more specific catalysts. Seo *et al.*[33] studied the diffusion of Au and Pt nanoclusters on carbon nanotubes. There are just a few studies of Pt atom adsorption on N-, B- and Si-doped graphene. The supporting substrate can have a profound effect on the configuration and the electronic property of the ad-cluster, thereby changing the catalytic activity of the system.

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In this paper, we perform a systematic theoretical study of the ability of graphene doped with different substitutional impurities (N, B and Si) to bind the Pt clusters with different structures. In the periodic table, N and B belong to the second period with the 2s, 2p configurations, while Si and C belong to the same group with very similar valence electron configurations. The aim of this paper is to analyse the cases of different substitutional impurities in graphene and observe the adsorption structures for different Pt clusters on the doped graphene. We establish the Pt atomic configuration by stabilizing nanoparticles on carbon support and conclude that the substitutional dopants contribute to the formation of some stable Pt clusters on the graphene.

2. Model and method

The calculations are performed within the framework of the generalized-gradient approximation (GGA),[34] including spin polarization in all calculations. The Vienna *Ab-initio* Simulation Package (VASP) is used to perform all calculations,[35,36] through employing ultrasoft pseudopotential (US-PP). The Kohn–Sham orbitals are expanded in plane waves with an energy cutoff of 400 eV. The surface Brillouin zone (BZ) integration is performed using 9×9×1 k-point grid. The graphene system is represented by a slab of one graphene sheet and a vacuum region of 15 Å (1 Å=0.1 nm). The system is modeled as a supercell of graphene with dopant to adsorb Pt atoms. We consider the binding of the adatom on three sites of high symmetry: the hollow (H) site in the centre of a hexagon, the bridge (B) site at the midpoint of a carbon–carbon bond and the top (T) site directly above a carbon atom, on the graphene monolayer (see Fig. 1).

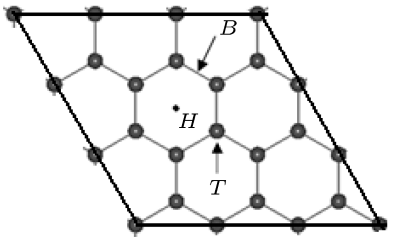


Fig. 1. Schematic diagram illustrating the three high symmetry adsorption sites on the 3×3 graphene surface: the hollow-site (H), the top site (T) and the bridge site (B).

The formation energy ΔE of the dopant is given by the following formula:

$$\Delta E = (E_{\rm gra} + E_{\rm c} - E_{\rm A}) - E_{\rm perf}, \qquad (1)$$

where $E_{\rm perf}$ is the total energy of pristine graphene, $E_{\rm gra}$ is the total energy of doped graphene, $E_{\rm c}$ is the energy of C atom in graphene and $E_{\rm A}$ is the isolated energy of dopant.

The adsorption energy $E_{\rm ad}$ of Pt clusters on graphene is calculated from the following formula:

$$E_{\rm ad} = [(E_{\rm gra}+nE_{\rm M}) - E_{n{\rm M+gra}}]/n, \qquad (2)$$

where $E_{n{\rm M+gra}}$ and $E_{\rm gra}$ are the total energies of a doped graphene with and without Pt adatoms, respectively, $E_{\rm M}$ denotes the energy of an isolated Pt atom and n is the number of Pt atoms. By this definition, a higher value of $E_{\rm ad}$ indicates a stronger preference for the structure.

3. Results and discussion

Our calculated lattice constant of the graphene is 2.468 Å, which is slightly larger than the experimental value of 2.46 Å.[37] In the following calculations, the theoretical lattice constant is assumed. All the atoms are allowed to relax in all directions. For the convenience of description, we assume that the x and the y direction are parallel and the z direction perpendicular to the graphene plane.

3.1. Graphene with substitutional impurities

The dopants (N, B and Si) are introduced into the graphene sheet by replacing the one C atom in the graphene. It is found that all the structures of graphenes with nitrogen dopant (NG), boron dopant (BG) and silicon dopant (SG) retain the planar form, so they did not introduce a local surface curvature into the graphene. The bond lengths between the dopant and its three nearest neighbour C atoms are all denoted as $d_{\rm dc}$. For the NG system, the formation energy (ΔE) is 5.516 eV/atom and the N–C bond length is 1.410 Å. A slightly higher ΔE (5.802 eV/atom) is found for the BG system and the corresponding $d_{\rm dc}$ is equal to 1.471 Å. In contrast, a much smaller ΔE (0.662 eV/atom) and a longer $d_{\rm dc}$ (1.610 Å) are found for the SG system. Compared with the NG and BG

systems in formation energy, the SG system has the lowest formation energy, indicating that the Si atom is easier to be incorporated into the graphene system. In the pristine graphene, the C–C bond length (d_{cc}) is equal to 1.420 Å, which is slightly larger than that of the N–C bond and much smaller than those of the B–C and S–C bonds, indicating the nitrogen substitution stabilizes the graphene structure, which is in accordance with the results in the previous theoretical work.[38,39]

The calculated total densities of states (TDOSs) for the pristine graphene, N-doped, B-doped and Si-doped graphene are shown in Fig. 2. The gap is set at the K point of the Brillouin zone in the pristine graphene (the Fermi level is set at energy zero). The positions of impurity states are above the Fermi level in the NG and SG systems, while the impurity states are below the Fermi level in the BG system. The N atom bonds with three dangling bonds, but it is not stable due to its 3-valent character. The Si atom provides three electrons interacting with dangling bonds, leaving one electron in π orbital along the z coordinate. The B has one electron less than carbon, it has three bonds with the C atoms of the graphene lattice; therefore, the B-doped graphene becomes an electron-deficient. In a word, the graphene can be modified by doping either p-type boron or n-type nitrogen, which is consistent with the result reported in the literature.[40] Besides, these substitutional atoms break the symmetry in the π electrons system of C atoms in graphene.

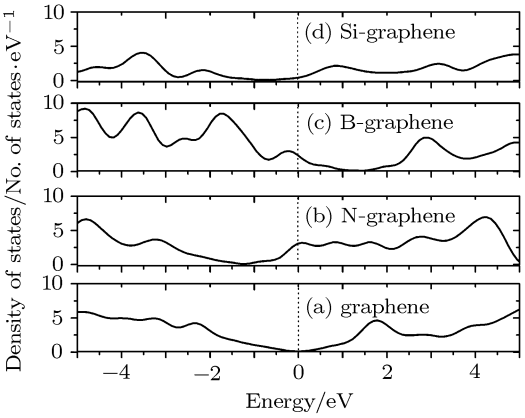


Fig. 2. TDOSs for (a) pristine graphene, (b) N doped graphene, (c) B doped graphene, (d) Si doped graphene. Solid lines represent the total TDOSs for different graphenes and vertical dashed line denotes the position of the Fermi level, which is set as energy zero.

3.2. Adsorption of single Pt atom on the doped graphene

For the adsorption of Pt on the pristine graphene, three sites (H, T and B) of high symmetry shown in Fig. 1 are considered for the binding of a Pt atom. The starting position of a Pt atom is placed near the substitutional impurity. The stable atomic configurations of a Pt atom on the pristine and doped graphene are obtained by geometry optimization and these stable configurations are shown in Figs. 3(a)–3(d), respectively. Figure 3 (a) shows a Pt atom adsorbed in a C–C bond B site on the pristine graphene. The adsorption energy is 2.420 eV/atom, which is larger than those at the T and H sites, indicating that the most stable adsorption site of a Pt atom is at the B site from an energy point of view. Figure 3(b) shows that a Pt atom is adsorbed on the NG system, the substitutional N atom enhances the interaction between the Pt atom and the neighbouring C–C bond and the adsorption energy is 2.847 eV/atom, which is larger than that on the pristine graphene. The adsorptive Pt atom is not stabilized on the T site of nitrogen atom but on the B site of a neighbouring C–C bond due to the N atom is to bond with three dangling bonds, thus the conjugation of π electrons of the NG is stronger, leading the Pt atom to be relatively difficult to be adsorbed at the T site of N atom.

On the BG system, a single Pt atom is stabilized on the B–C bond as shown in Fig 3(c). The adsorption position is the bridge-like, which is similar to the previous reported results.[32] The substitutional B atom contributes no electron to the π electrons system of C atoms, making the adsorptive Pt easier to stabilize at B site, so the bridgelike site on B doped-graphene is a more stable configuration. Figure 3(d) shows the Pt atom adsorbed on T site of a C atom neighbouring to the Si doped-graphene. The electronegativity of Si atom is less than that of C atom. The charges transfer from Si atom to C and thus the electron density around C atom is increased. The Pt atom prefers to be adsorbed at T site. In contrast to the substitutional B and N atoms which have the sp^2 hybridized configurations like C atoms in a graphitic network, the Si dopant is known to strongly prefer the sp^3 like bonding, which eventually saturates dangling bonds in the graphene. The bond between Si and C atoms is similar to that of the sp^3 bonding in the sense of property and the conjugation of π electrons of the SG is

relatively strong. In addition, the radius of Si atom is larger than that of C atom, thus the Si atom protrudes along the z coordinate.

As shown below in Table 1, a comparison between the adsorption energies ($E_{\rm ad}$) of Pt adsorbed on the pristine graphene and the doped-graphene shows that the $E_{\rm ad}$ of the SG system is larger than those of the other systems (the pristine graphene, NG and BG). The Pt adsorption on the T site of C atom is in the most stable position on the SG system. The adsorption height (h) of Pt on the SG system is relatively large as compared with those on the other systems, because the Si has a larger radius than the B and N atoms. Doped with different substitutional impurities in graphene system, the corresponding adsorption sites have also changed due to the fact that substitutional atoms give rise to the variation of the π electron system in graphene.

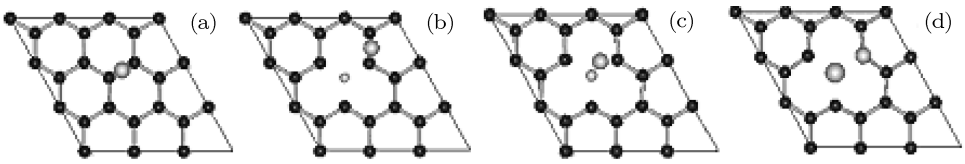


Fig. 3. Atomic configurations for Pt adsorption on doped-graphene, where the small black balls refer to C atoms in graphene and the smaller gray balls at the lattice C site represent the substitutional N-, B-, Si-atoms, respectively and the other bigger gray balls denote the Pt adatoms: (a) pristine graphene, (b) N-doped graphene, (c) B-doped graphene, and (d) Si-doped graphene.

To analyse the interaction between the Pt atoms and the doped-graphene system, we calculate the total valence charge density and the difference in charge density between the three stable configurations (see Figs. 4 and 5). As shown in Figs. 4(a)–4(c), the contour lines in plots are drawn with an interval of about 0.27 e/Å^3 in between. The valence charge densities of substitutional impurities decrease from N-dopant, B-dopant to Si-dopant, which indicates that these dopants provide the different numbers of valence charges and affect the interaction of Pt atom adsorption on graphene. Figure 4(c) shows that the doped Si atom promotes charge-transfer most and enhances the interaction between Pt atom and graphene, so the Pt/SG system has the largest adsorption energy in these configurations.

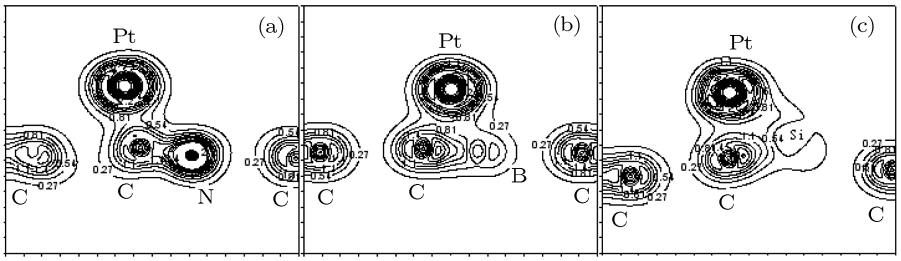


Fig. 4. Total valence charge density plots for the systems of a Pt atom absorbed on (a) N-doped graphene, (b) B-doped graphene and (c) Si-doped graphene, respectively. Contour lines in plots are drawn with an interval of about 0.27 e/Å^3 in between.

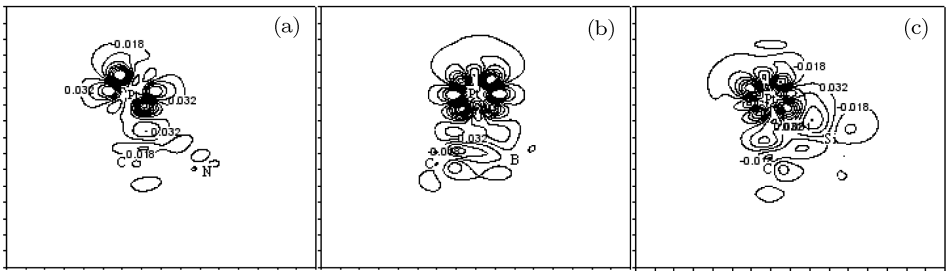


Fig. 5. Electron density difference plots for the systems of a Pt atom absorbed on (a) N-doped graphene, (b) B-doped graphene and (c) Si-doped graphene. The solid lines denote regions with charge accumulation in plots, contour lines in plots are drawn with an interval of about 0.0494 e/Å^3 in between.

The maps of charge density difference shown in Figs. 5(a)–5(c) are obtained by subtracting the sum of the charge density of the isolated adatom and the doped-graphene from total charge density of the doped-graphene with Pt adatom, the contour lines in plots were drawn with an interval of about 0.0494 $e/\text{Å}^3$ in between, with the solid lines denoting the regions of charge accumulation. It is noted that the charge-transfer occurs between Pt and doped-graphene and that the Pt/SG has a greater electron density accumulation between the Pt–C–Si atoms than Pt/NG and Pt/BG, which elucidates the stronger interaction between Pt atom and Si-doped graphene.

3.3. Adsorption of Pt clusters on doped graphene

The calculations using the model approximate the interaction between Pt clusters and doped-graphene. The stable atomic structure of Pt clusters on graphene is obtained by geometry optimization. Figure 6 (1)(a) shows that two Pt atoms are adsorbed on the B sites and form a dimer on the pristine graphene. The adsorption energy (E_{ad}) is 3.152 eV/atom and the d_{pp} of dimer is 2.459 Å, where the d_{pp} is the distance between the Pt atoms within the dimer. For the NG system, Fig.6 (1)(b) shows that two Pt atoms are stabilized near two C–C bridge sites with an E_{ad} of 3.630 eV/atom and the d_{pp} of 2.492 Å. Figures 6 (1)(c) and 6(1)(d) show that two Pt atoms are adsorbed near two T sites of C atoms with higher adsorption energies (3.754 eV/atom and 4.317 V/atom) and bigger d_{pp} values (2.503 Å and 2.740 Å) on the BG and SG systems, respectively. In a word, the two-Pt-atom clusters tend to form a Pt_2 dimer. For three Pt atoms on the pristine graphene, they form a linear chain with each of Pt atoms adsorbed at B site, while three Pt atoms form the triangular Pt_3 structures on the graphene with dopant systems. These structures are shown in Fig. 6(2). Table 1 shows that the adsorption energy of triangle Pt_3 on the doped-graphene is larger than that on the pristine graphene, so the triangular structure is more stable than the linear chain Pt_3. For four Pt atoms on the pristine graphene and the doped-graphene systems, their structures are shown in Fig. 6(3). The Pt atoms all form the tetrahedral Pt_4, indicating that the tetrahedron is a regular structure. Moveover, Table 1 also shows that the substitutional atoms enhance the adsorption energies of clusters and enlarge the Pt–Pt distance (d_{pp}).

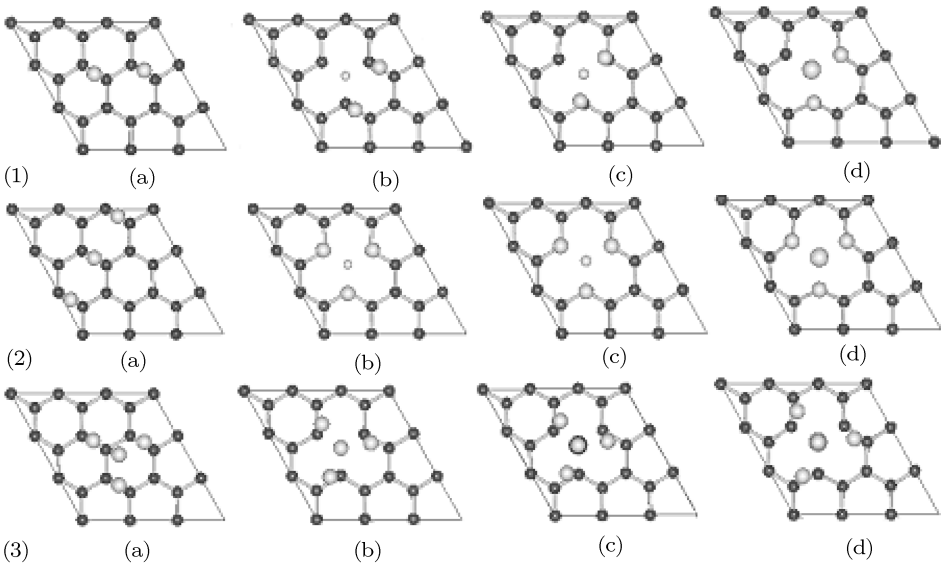


Fig. 6. Atomic configurations for Pt_n clusters on the doped-graphene, where the small black balls refer to the C atoms in the graphene, the smaller gray balls at the lattice C site represent the substitutional N-, B-, Si-atoms, respectively and the other bigger gray balls denote the Pt adatoms. Panel (1) Pt dimer; panel (2) for Pt trimers with (a) a linear chain structure on the pristine graphene, (b), (c), (d) triangle structures on the doped-graphene; panel (3) for tetrahedron structures with (a) pristine graphene, (b) N-doped graphene, (c) B-doped graphene, and (d) Si-doped graphene.

As shown in Table 1, the adsorption energy ($E_{\rm ad}$) values of clusters on the doped-graphene are larger than those on the pristine graphene. A comparison between dimer Pt_2 and triangle Pt_3 shows that the tetrahedron Pt_4 has the largest adsorption energy, so it has the most stable structure. In addition, the adsorption energies of clusters on the SG system are larger than those on the NG and BG systems, so the Pt clusters adsorbed on the SG system are easier to form a stable structure. On the whole, the substitutional impurities enhance the interaction between Pt atoms and doped-graphene system and contribute to the formation of the stable clusters.

Table 1. Adsorption energy ($E_{\rm ad}$) values and the structure parameters of Pt atoms on different graphene systems, n is the number of Pt atoms in the Pt_n cluster, h is the adsorption height of Pt atom, $d_{\rm C}$ is the distance between C atom and planar graphene in z coordinate and $d_{\rm pp}$ is the Pt–Pt distance within the cluster.

Graphene	n	1	2	3	4
Pristine	$E_{\rm form}$/eV	2.420	3.152	3.532	4.260
	h/Å	2.060	2.095–2.108	2.078–2.114	2.066–2.125
N-doped	$E_{\rm form}$/eV	2.847	3.630	4.028	4.350
	h/Å	2.134	2.129	2.102	2.024
	$d_{\rm C}$/Å	0.244	0.155	0.055	0.008
	$d_{\rm pp}$/Å		2.492	2.579	2.683
B-doped	$E_{\rm form}$/eV	3.120	3.754	4.087	4.478
	h/Å	2.007	2.138	2.141	2.005
	$d_{\rm C}$/Å	0.111	0.106	0.072	–0.021
	$d_{\rm pp}$/Å		2.503	2.597	2.672
Si-doped	$E_{\rm form}$/eV	4.547	4.317	4.370	4.630
	h/Å	2.426	2.419	2.441–2.442	2.148–2.149
	$d_{\rm C}$/Å	0.305	0.248	0.173	0.073
	$d_{\rm pp}$/Å		2.740	2.766	3.196

The structural characteristics of clusters Pt_n (for $n = 1 - 4$) on the pristine graphene, as well as those on the N-doped, B-doped and Si-doped systems are shown in Table 1, where the adsorption height (h) is defined as the distance between Pt atom and graphene in the z coordinate. From the pristine graphene to Si-doped graphene, the height (h) values of Pt atoms become equal gradually in the planar form, indicating these atomic structures are more and more stable. The Pt–Pt distance ($d_{\rm pp}$) values in the Pt clusters increase with the number of Pt atoms increasing, so the $d_{\rm pp}$ of the tetrahedral configuration on the SG is the largest in the doped systems. The increasing adsorption energy increases with the number of Pt atoms, so the adsorption energy of tetrahedron is larger than those of the dimer and triangle. In a word, the tetrahedron has a larger adsorption energy and a more stable structure on SG system than on the NG and BG systems. For the structure of tetrahedron Pt_4, the distances between the vertex of Pt atom and the base Pt atoms change slightly from 2.545 Å to 2.562 Å, indicating that the tetrahedron is a stable structure of cluster, which is in consistence with the geometrical rule of the stable clusters.[41] It can be concluded that the different doped-graphenes do not influence the structure of Pt clusters.

The adsorptions of different Pt clusters on the doped-graphene systems may have an influence on the substitutional impurities (N, B and Si). To this end, we have calculated the change of the height (Δz) with the dopant in z coordinate. Comparison between the changes from Pt_1 to Pt_4 shows that the Δz values change about 0.372 Å, 0.042 Å and 0.142 Å for N-, B- and Si-dopant, respectively. It is clearly shown that the doping B atom has the smallest influence while the doping N atom has the largest influence, which causes the local curvature in the graphene. As is also clear from the above calculations, the doping Si atom not only enlarges the adsorption energy but also has less influence than the doping N atom, so it is a better substitutional impurity. The variation of the height ($d_{\rm C}$) of the nearest C atom with the increase of the number of Pt atoms in the adsorbed Pt_n clusters, where $d_{\rm C}$ is distance between the nearest C atom neighbouring with the adsorbed Pt_n cluster and graphene in z coordinate. Comparing the variation of $d_{\rm C}$ from

Pt_1 to Pt_4, it can be seen that these clusters are distorted to different extent with respect to the planar graphene, e.g., the tetrahedron has the least influence on the doped-graphene than dimer and triangle. Additionally, the interatomic interaction of Pt_n cluster is stronger than that between Pt_n cluster and graphene. This is in accordance with that reported in Refs. [42] and [43].

4. Conclusions

We have investigated the interactions between Pt clusters and the graphene doped with different impurities (nitrogen, boron and silicon) by first-principle calculations based on density-functional theory. The doped-graphene systems have a stronger interaction with the Pt clusters than with Pt atoms adsorbed on the pristine graphene. In particular, a Pt atom and SG system has a greater electronic density transformation, the adsorption energy on the SG is larger than those on the pristine graphene, NG and BG systems. The adsorption energy increases with the increasing number of Pt atoms, indicating that the Pt atoms on the graphene preferably form clusters of larger sizes. The calculated stable atomic configurations of Pt_n clusters are dimer, triangle, tetrahedron for $n = 2$, 3, 4, respectively. The structures of clusters are not affected by the different impurities in graphene. Compared with the dimer and the triangle clusters, the tetrahedron is the most stable cluster in structure and has the least influence on substrate. The Si dopant is easier not only to be incorporated into the graphene but also to enhance the stability of Pt cluster on doped-graphene, so it is a better substisutional impurity.

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