First-principles study of hydrogen adsorption on titanium-decorated single-layer and bilayer graphenes*

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The adsorption of hydrogen molecules on titanium-decorated (Ti-decorated) single-layer and bilayer graphenes is studied using density functional theory (DFT) with the relativistic effect. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) are used for obtaining the region of the adsorption energy of H_2 molecules on Ti-decorated graphene. We find that a graphene layer with titanium (Ti) atoms adsorbed on both sides can store hydrogen up to 9.51 wt% with average adsorption energy in a range from −0.170 eV to −0.518 eV. Based on the adsorption energy criterion, we find that chemisorption is predominant for H_2 molecules when the concentration of H_2 molecules absorbed is low while physisorption is predominant when the concentration is high. The computation results for the bilayer graphene decorated with Ti atoms show that the lower carbon layer makes no contribution to hydrogen adsorption.

Keywords: hydrogen storage, graphene, titanium, density functional theory

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1. Introduction

Hydrogen has been recognized as an ideal energy carrier and has the potential to reduce our dependence on fossil fuels, which are not only limited but also harmful to the environment.[1,2] So, many hydrogen storage methods have been proposed, such as carbon-fiber reinforced high-strength containers,[3] liquid hydrogen,[4] chemical hydrides,[5] and lightweight carbon-based nanostructures (including carbon nanotubes, fullerene, nanofibers, and graphene).[6,7] In particular, carbon-based nanostructures have been suggested as the most promising materials for hydrogen storage due to their high surface-to-volume ratio. However, pristine graphene is chemically too inert to act as a possible hydrogen storage medium.[8,9] So, more recently, a few novel approaches have been proposed to enhance the storage ability of graphene-based systems. One of them is to decorate metals onto different nanostructures through Dewar coordination, which will then bind multiple H_2 molecules via Kubas interaction.[10–15] For example, by doping the graphene with Li, the binding strength ($E = -0.184$ eV/H_2) increases twofold over that of the undoped material.[10] Transition metal (TM) atoms, such as Ti, Pt, and Pd can also bind multiple H_2 molecules.[13–15]

Previous studies have shown that physical properties of different graphene systems calculated by density functional theory (DFT) are consistent with experimental results.[8–18] So, in the present work, we use the DFT with scalar relativistic correction to study hydrogen adsorption on Ti-decorated single-layer and bilayer graphenes. The favourite adsorption configurations of Ti atoms on a single side and both sides of graphene layer are determined. And then the obtained materials are studied for adsorption of H_2 molecules and their hydrogen storage properties are also discussed.

2. Computational method

In this study, all calculations are performed using the spin-polarized first-principle method as implemented in the DMol^3 code.[19,20] The exchange correlation interaction between electrons is described using LDA (local density approximation) with the Perdew–Wang correlation[21] (PWC) throughout the paper. As is well known, the LDA method generally gives notably higher adsorption energies than the generalized gradient approximation (GGA) method.[10,22,23] Furthermore, some other studies have shown that both LDA and GGA methods are inaccurate in predicting adsorption energies, but can give correct prediction qualitatively.[24,25] The adsorption energy calculated by LDA can be viewed as upper limit while the one calculated by GGA can be regarded as lower limit.[25] Therefore, GGA-PW91 method is also selected in this work in order to give the region of adsorption energies.

For DFT calculations for a transition metal, some researchers suggested that relativistic effects should be

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considered.[26,27] So, the all-electron with scalar relativistic correction is chosen as the core treatment method and a double numeric basis with polarization set is adopted as the basis set. To ensure that the calculated results are comparable, identical conditions are employed for isolated H_2 molecules, Ti atoms, graphene and also for the adsorbed graphene systems. The k point is set to $8\times8\times1$ for all slab models, the real-space global orbital cutoff radius is chosen to be as high as 6.0 Å (1 Å = 0.1 nm), the smearing is 0.002 Ha (1 Ha = 27.21 eV), the convergence tolerance of energy is 1.0×10^{-6} Ha, and the maximum force is 2.0×10^{-3} Ha/Å. Each atom in the storage models is allowed to relax without any constraint.

A uniform $(2\times2\times1)$ graphene supercell is established with an in-plane lattice parameter of 4.920 Å, and a vacuum thickness of 20 Å is employed along the z direction to avoid the interlayer interaction. As shown in Fig. 1, the supercell contains eight carbon atoms, and three-dimensional periodic boundary conditions are applied. In initial models, the H–H bond length is set to be 0.741 Å according to experimental value[28] and the C–C bond length is assumed to be 1.409 Å according to experimental datum.[29]

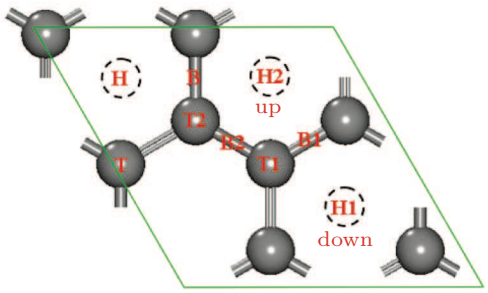


Fig. 1. (color online) Three different sites (H, B, T) for a Ti atom adsorbed on one side of the graphene layer and six different adsorption sites ($H1_{up}$, $H2_{up}$, B1, B2, T1, T2) for the second Ti atom on the other side if the first Ti atom has been already adsorbed on the $H1_{down}$ site. H1 and H2 sites belong to the H site which denote the hollow site of hexagon, B1 and B2 sites belong to the B site which denote the bridge site of the C–C bond, T1 and T2 sites belong to T site which denote the top site of the C atom.

The adsorption energy of Ti atoms onto graphene (E_{a-Ti}) is defined as

$$E_{a-Ti} = [E(\text{graphene} + n\text{Ti}) - E(\text{graphene}) - nE(\text{Ti})]/n, \quad (1)$$

where n is the number of Ti atoms, $E(\text{graphene} + n\text{Ti})$ is the energy of the graphene system adsorbed with n Ti atoms, $E(\text{graphene})$ is the energy of the pristine graphene, and $E(\text{Ti})$ is the energy of an isolated Ti atom in the same slab. The adsorption energy of H_2 molecules on Ti-adsorbed graphene (E_{a-H_2}) is defined as

$$E_{a-H_2} = [E(\text{graphene} + n\text{Ti} + m\text{H}_2) - E(\text{graphene} + n\text{Ti}) - mE(\text{H}_2)]/m, \quad (2)$$

where n and m are the numbers of Ti atoms and H_2 molecules, respectively, $E(\text{graphene} + n\text{Ti})$ is the total energy of the system adsorbed with n Ti atoms, $E(\text{graphene} + n\text{Ti} + m\text{H}_2)$ is the total energy of a Ti-decorated graphene system absorbed with m H_2 molecules, and $E(\text{H}_2)$ is the total energy of a H_2 molecules in the same slab.

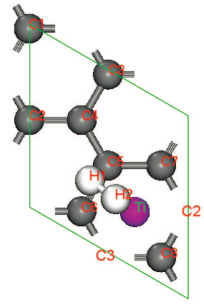
3. Results and discussion

3.1. Adsorption of Ti atoms on a graphene layer

As is well known, the uptake capacity of hydrogen will decrease if fewer metal atoms are adsorbed on the surface of a graphene nanostructure.[30,31] The binding between metal atoms and the surface will be strengthened if more charges are transferred between the metal atoms and the graphene nanostructure. So, the binding can also be enhanced by adding more metal atoms with concomitant additional charges available for electronic transfer.[32,33] However, metal atoms tend to aggregate into clusters when their concentration is large, which may significantly reduce the hydrogen uptake.[34,35] A unit cell with eight C atoms and one Ti atom is used in the present study, which is shown in Fig. 1. The ratio Ti:C=1:8 is quite moderate and moreover strictly obeys the doping rule for high coverage metal which makes it possible for us to achieve a relatively high storage capacity. The test indicates that the critical distance between Ti atoms on graphene is about 3.1 Å, at which the formation of clusters is avoided. And the calculation indicates that in this unit cell the Ti–Ti distance is 4.895 Å which is large enough to avoid the clustering of Ti atoms on graphene.

For one Ti atom, although different adsorption sites are considered, our calculations show that the most stable position for a Ti atom is above the center of a hexagonal carbon (as shown in Table 1). After relaxation, the equilibrium distance between a Ti atom and the graphene layer (d_1) is 1.725 Å and the adsorption energy is -2.207 eV calculated by LDA and the values calculated by GGA are 1.781 Å and -0.998 eV, respectively. In Table 1, charges of each atom near the Ti atom are given, which are obtained by Hirshfeld analysis. Before the adsorption of H_2 molecules, the adsorbed Ti atom has positive charge 0.256 e calculated by LDA (0.242 e calculated by GGA) while each C atom nearby has negative charge -0.043 e calculated by LDA (-0.041 e calculated by GGA). Note that the other two C atoms in the simulation cell have very few charges, which means that there exist interactions mainly between Ti atom and the six C atoms nearby. Due to the positive charge on the Ti atom and the negative charge on carbon atoms, an electric field is induced between the Ti atom and the graphene layer, which in turn leads to a back-transfer of charge from the graphene layer to the Ti atom.

Table 1. (color online) Hirshfeld charge analysis for a Ti-adsorbed graphene storage system, where the unit of atom charge is one electron charge e.

Structure	Atom	Hirshfeld charge (LDA)		Hirshfeld charge (GGA)	
		before	after	before	after
	H1	0.000	–0.063	0.000	–0.143
	H2	0.000	–0.073	0.000	–0.144
	Ti	0.256	0.309	0.242	0.399
	C1	0.002	0.015	0.001	0.016
	C2	–0.043	–0.034	–0.041	–0.025
	C3	–0.043	–0.035	–0.041	–0.025
	C4	0.002	0.016	0.001	0.017
	C5	–0.043	–0.033	–0.041	–0.020
	C6	–0.043	–0.033	–0.041	–0.025
	C7	–0.043	–0.035	–0.041	–0.025
	C8	–0.043	–0.034	–0.041	–0.025

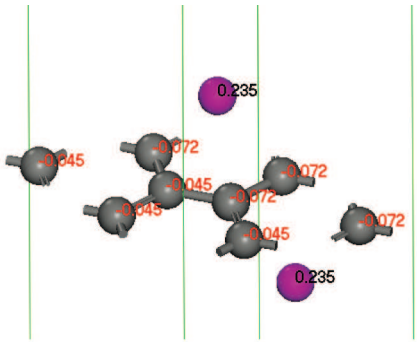


Fig. 2. (color online) Stable configuration of the graphene system with two Ti atoms adsorbed and the charges of each atom, where the unit of charge is one electron charge e. The results are calculated by LDA.

We consider, next, the adsorption of Ti atoms on both sides of the graphene layer in order to increase the available surface area for hydrogen storage since the charged metal atoms are the nucleation centers for hydrogen adsorption. After geometry optimization of different configurations, the lowest-energy configuration is realized that the two Ti atoms are positioned on two shoulder-by-shoulder carbon hexagons but on opposite sides of the graphene layer (as shown in Fig. 2) and the average adsorption energy is -2.367 eV (-1.342 eV) calculated in the LDA (GGA). The graphene layer is now more negatively charged as compared with the previous single Ti atom case while Ti atoms are more positively charged (the charges of each atom are given in Fig. 2), which lead to stronger adsorption energy of the two Ti atoms on the graphene.

3.2. Adsorption of H_2 molecules on Ti-adsorbed single-layer and bilayer graphenes

For one hydrogen molecule, our value of $E_{a-H_2} = -0.889$ eV/H_2 calculated by GGA with relativistic effects as shown in Table 2 is close to other literature datum of $E_{a-H_2} = -0.920$ eV/H_2.[11] This value can also be compared with the one for the nanotube case given in Ref. [36]. These authors found that the adsorption energy of a single hydrogen molecule in a dissociated state was -0.830 eV/H_2,[36] which is similar to what we find. According to the comparisons mentioned above, we can see that the method we used is effective to describe these hydrogen storage systems and can at least give correct results qualitatively. Furthermore, as shown in Table 2, the resulting adsorption energies per molecule, calculated by GGA, are -0.710, -0.611, -0.443, and -0.221 eV/H_2 in the cases of two, three, four, and five molecules, respectively (the values are obtained to be -0.994, -0.990, -0.882, and -0.538 eV/H_2 in the LDA, respectively). If we further increase the number of H_2 molecules, after relaxation, the results show that no more H_2 molecules can be adsorbed. Therefore, it is predicted that the maximum number of H_2 molecules adsorbed on a single side of a $2\times2\times1$ graphene unit cell is five which is the first time to be predicted for Ti-decorated graphene system. According to the magnitudes of adsorption energies, we can see that the chemisorption is predominant for H_2 molecules when $m = 1$, 2 or 3 while the physisorption is predominant when $m = 4$ or 5. Table 2 also gives the distance between Ti atom and graphene layer (d_1), the distance range between H_2 atoms and Ti atom (d_2) and the average H–H bond length (d_{H-H}) for all H_2 molecules adsorbed. We can see that as m increases, d_1 and d_2 increase but d_{H-H} decreases, which means that the interaction between a Ti atom and graphene or H_2 molecules becomes weak. It is in accordance with the above conclusion. The same conclusion can also be obtained through the Hirshfeld charge analysis for hydrogen storage systems as shown in Fig. 3. The total charges of H, Ti, and C atoms can be found at the right of each plot in Fig. 3 from the top down. It shows that when m increases from 1 to 4, all hydrogen atoms and carbon atoms have negative charges which decrease while the Ti atom has positive charges which decrease too. This indicates that the charges transferred between Ti atom and hydrogen atoms or carbon atoms decreases, which leads to the weakening of the interaction between them. We can also draw the conclusion that the interaction takes place mainly between hydrogen atoms and the Ti atom rather than the carbon sheet, and the latter is only used as the carrier of Ti atoms in the process of hydrogen storage, which is in accordance with the view given in Ref. [11].

Table 2. Summary of the results for Ti-decorated graphene with m H_2 molecules adsorbed. The m is the number of H_2 molecules, E_{a-H_2} the average adsorption energy defined in the text, d_1 the distance between Ti atom and graphene layer, d_2 the distance range between a hydrogen atom and a Ti atom at the same side, and d_{H-H} is the average H–H bond length of all H_2 molecules.

	m	E_{a-H_2}/eV		d_1/Å		d_2/Å		d_{H-H}/Å	
		LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
Single side	0			1.725	1.781			0.740	0.740
	1	–0.995	–0.889	1.770	1.896	1.760–1.810	1.701–1.738	1.034	1.954
	2	–0.994	–0.710	1.785	1.846	1.794–1.818	1.830–1.841	0.936	0.892
	3	–0.990	–0.611	1.792	1.851	1.842–1.881	1.892–1.928	0.880	0.841
	4	–0.882	–0.443	1.850	1.929	1.765–1.896	1.866–1.959	0.877	0.827
	5	–0.538	–0.221	2.046	2.143	1.841–2.033	1.866–2.044	0.866	0.826
Both sides	0			1.729	1.841			0.740	0.740
	2	–1.023	–0.691	1.807	1.887	1.692–1.719	1.702–1.726	1.867	2.083
	4	–1.020	–0.570	1.765	1.820	1.793–1.816	1.836–1.850	0.941	0.892
	6	–0.968	–0.520	1.797	1.875	1.799–1.878	1.840–1.921	0.891	0.843
	8	–0.844	–0.375	1.855	1.932	1.795–1.883	1.850–1.928	0.860	0.823
	10	–0.518	–0.170	2.110	2.220	1.787–1.922	1.866–2.044	0.839	0.821

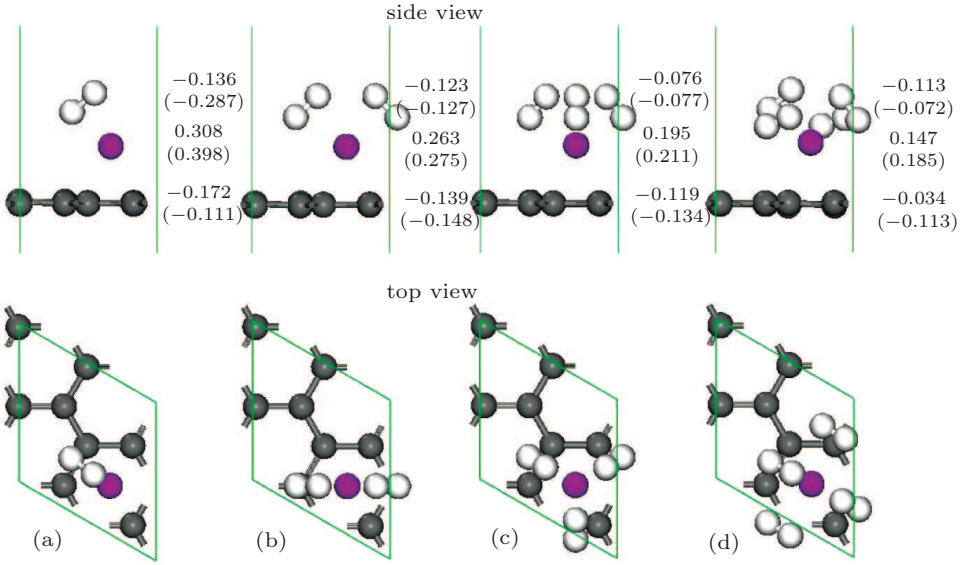


Fig. 3. (color online) Relaxed hydrogen storage systems based on a Ti-decorated single side of graphene. The panels (a)–(d) show the relaxed models when the number of H_2 molecules increases from 1 to 4. The figures at the right of each panel from the top down are the total charges of H, Ti, and C atoms, respectively, where the unit of charge is one electron charge e. The figures in brackets are calculated in the GGA while the others are calculated in the LDA.

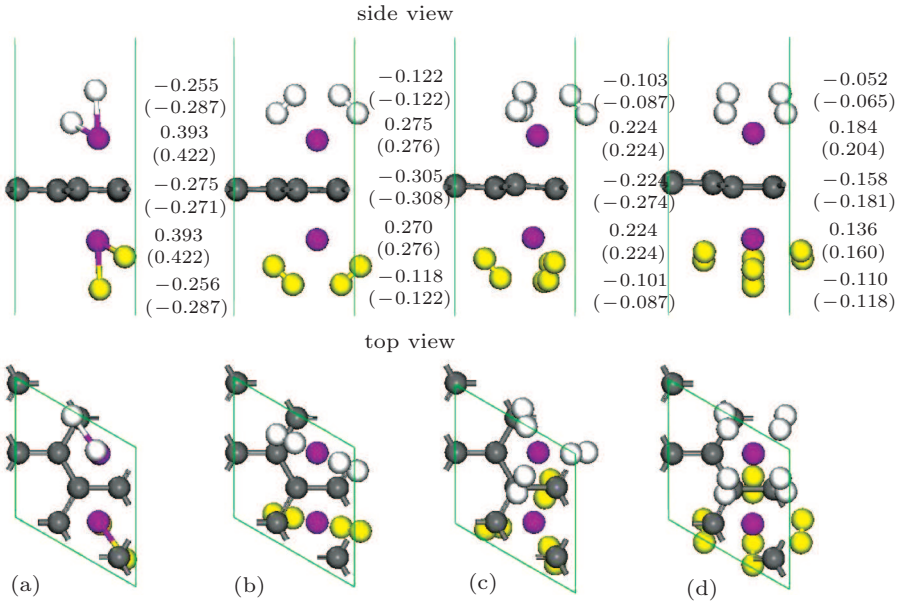


Fig. 4. (color online) Relaxed hydrogen storage systems based on Ti-decorated both sides of graphene. The panels (a), (b), (c), and (d) show the relaxed models when the numbers of H_2 molecules are 2, 4, 6, and 8, respectively. The figures at the right of each panel from the top down are the total charges of H atoms above the graphene layer, the Ti atom above the graphene layer, C atoms, the Ti atom under the graphene layer, and H atoms under the graphene layer, respectively, where the unit of charge is one electron charge e. The figures in brackets are calculated in the GGA while the others are calculated in the LDA.

The above conclusion can also be verified through analyzing the density of states (DOS). Figure 5 displays the DOSs of H_2 molecules, Ti atom and graphene layer when one, two, three, and four H_2 molecules are adsorbed, respectively. It is readily seen from Fig. 5 that all the bands of H_2 molecules, Ti atoms, and C atoms overlap each other in the high energy range from 0 to 7.5 eV and have the tendency of reduction with m increasing. Then, the main peaks of H atoms and Ti atom are located at about -2.5 eV when $m = 1$. And as m increases, the main peak reduces and shifts toward the low energy state about -8 eV as shown in Fig. 5. The above phenomenon shows that the interaction between a hydrogen atom and a Ti atom becomes weak with m increasing. As shown in Fig. 4, the scenarios and results of one, two, three, and four H_2 molecules adsorbed on each side of Ti-adsorbed graphenes are similar to those in the case of a single side.

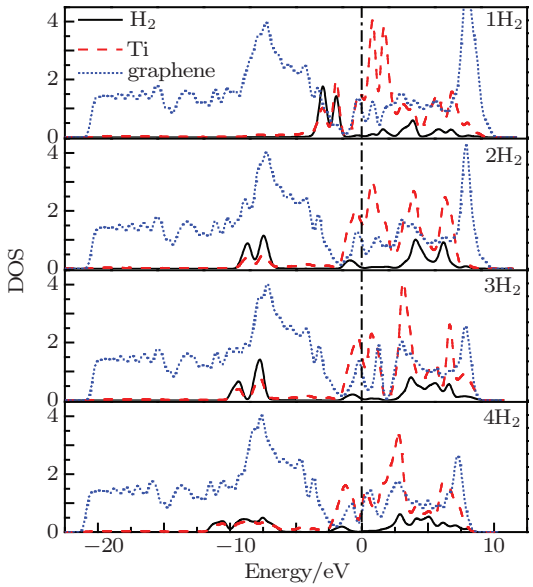


Fig. 5. (color online) The density of states (DOSs) of H_2 molecules, Ti atoms and C atoms in graphene systems of one, two, three, and four H_2 molecules adsorbed. The Fermi level is set to be zero.

For five H_2 molecules, in order to display the adsorption site of the fifth H_2 molecule better, we plot a $4\times4\times1$ supercell as shown in Fig. 6. It indicates that H_2 molecules are arranged into two layers and the fifth H_2 molecule is located in the bridge site between two Ti atoms as shown in Figs. 6 and 7. It is clear that the adsorption site of the fifth H_2 molecule is very different from those of other four H_2 molecules, which leads to the different degree of the interaction between Ti atom and the fifth H_2 molecule compared with that between Ti atom and other four H_2 molecules. Figure 7 displays the electron density and Hirshfeld charges of the system with five H_2 molecules adsorbed. We can see that the charges of the fifth H_2 molecule are much more negative than the others', which means the interaction between Ti atom and the fifth H_2 molecule is much stronger than that between a Ti atom and the other H_2 molecules. We can also see that the fifth H_2 molecule is shared by the two Ti atoms while the other four H_2 molecules are only adsorbed by one Ti atom. The same phenomenon also appears in the case of a Ti-adsorbed graphene system with ten H_2 molecules adsorbed on both sides.

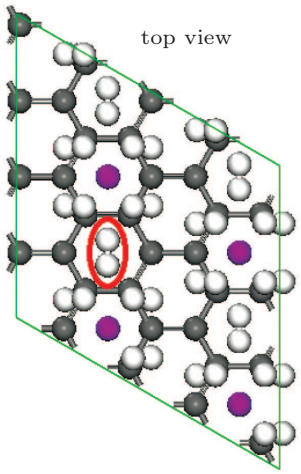


Fig. 6. (color online) The stable configuration of a graphene system with five H_2 molecules adsorbed on single side. In this figure, we plot a $4\times4\times1$ supercell to display the adsorption site of the fifth H_2 molecule (in the elliptic frame) better.

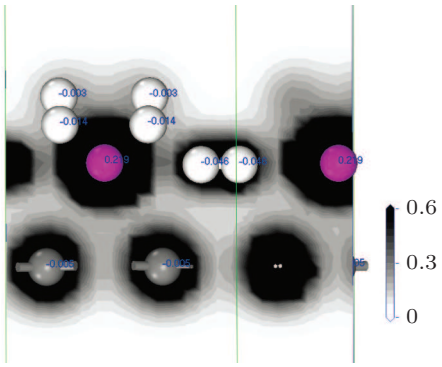


Fig. 7. (color online) Electron density distribution for the Ti-decorated graphene system with five H_2 molecules adsorbed. The figures are the charges of atoms, where the unit of charge is one electron charge e. The results are calculated in the GGA.

Therefore, the Ti-adsorbed graphene system can adsorb a maximum of five H_2 molecules on a single side and ten H_2 molecules on both sides. The hydrogen storage capacity is up to 9.51 wt% with average adsorption energy in a range of -0.170 eV/H_2 (calculated in the GGA) to -0.518 eV/H_2 (calculated in the LDA). Note that the obtained hydrogen storage capacity is in excess of 6 wt%, surpassing the target of the US Department of Energy (DOE), and the obtained average adsorption energy is almost within the required range from -0.2 eV/H_2 to -0.6 eV/H_2.[37] The results are perfect as long as these values are provided, which means Ti-decorated graphene system may be a kind of wonderful hydrogen storage material just as shown in some other references.[11,14] But, as discussed above, though the physisorption is predominant

when $m = 5$ for a single side of Ti-decorated graphene system, it has a strong interaction between the fifth H_2 molecule and the Ti atom. And then the chemisorption is predominant when m is small. The same conclusion can be obtained in the case of H_2 molecules adsorbed on both sides of Ti-decorated graphene, which is a big barrier for hydrogen desorption. And H_2 molecules may not be recovered into a gas state easily and completely by only warming up the system, which will reduce the hydrogen storage capacity for the next hydrogen storage. So, this is a limitation for Ti-decorated graphene to recycle unless some suitable methods for desorption are used.

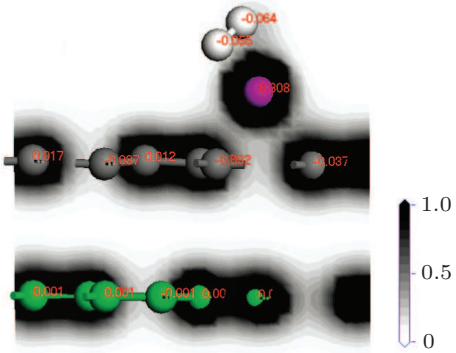


Fig. 8. (color online) Electron density distribution for the Ti-decorated bilayer graphene system with one hydrogen molecule adsorbed. The figures are the charges of atoms, where the unit of charge is one electron charge e. The results are calculated in the LDA.

It has been reported that the hydrogen absorption can be enhanced on Li-doped bilayer graphene compared with single-layer graphene and under a negative electric field hydrogen binding can be weakened more easily than in the case of single-layer graphene.[32] Otherwise, bilayer graphenes can possibly exist in the preparation process of graphene. So, the adsorption of H_2 molecules on Ti-adsorbed bilayer graphene is also studied. When a second layer of graphene is added, a bilayer is obtained. The usual stacking of bilayer graphene is Bernal stacking,[38] in which two carbon layers are stacked in the natural graphite order. As shown in Fig. 8, the distance between the two layers is 3.236 Å which is slightly lower than the distance in graphite (3.4 Å).[39] Obviously, this is due to the absence of layers on both sides of the bilayer. In order to figure out whether the lower carbon layer of the bilayer graphene has contribution for hydrogen adsorption, the illustration of electron density distribution for a Ti-adsorped bilayer graphene system with one hydrogen molecule adsorbed is given in Fig. 8. In this system, no electron exists in the region between two layers of the system and electrons only appear in the region among H_2 molecules, the Ti atom and the upper carbon layer, which supports the notion that the lower carbon layer makes no contribution to hydrogen adsorption. The same conclusion can also be obtained by analyzing the Hirshfeld charge of a Ti atom as shown in Fig. 8. It can be seen that the Hirshfeld charges of carbon atoms which belong to a lower layer are about zero and that of a Ti atom is 0.308 e calculated in the LDA which is exactly the same as that shown in Fig. 3(a).

4. Conclusions

In the present paper, adsorptions of Ti atoms on graphene and of H_2 molecules on a Ti-decorated single-layer and bilayer graphenes are studied using both LDA and GGA methods with relativistic correction. We find that Ti atoms are strongly adsorbed on graphene. Furthermore, Ti dispersed on graphene can bind up to 10 H_2 molecules, resulting in a high hydrogen storage capacity as high as 9.51 wt%. The average adsorption energy is in the range of -0.170 eV to -0.518 eV. After analyzing the adsorption energy, the density of states and the electron density distribution, we find that chemisorption is predominant for H_2 molecules when m is small, which means H_2 molecules cannot be desorbed easily and completely at room temperature and ambient pressure unless some suitable methods of desorption are used. The computation results for the Ti-decorated bilayer graphene show that the lower carbon layer has no contribution to hydrogen adsorption. For achieving the target of the high hydrogen storage capacity as high as 9.51 wt%, as few as possible bilayer and multilayer graphenes should be contained in the material production.

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