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Adsorption of formaldehyde molecule on the pristine and transition metal doped graphene: First-principles study

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ABSTRACT

The adsorption of H₂CO molecule on pristine and transition metal (Ti and V) doped graphene samples were investigated via a first-principles approach based on density functional theory. The most stable adsorption geometry, energy and charge transfer of H₂CO molecule on pristine and doped graphene are discussed respectively. We have found that Ti and V dopant atoms can significantly enhance the interaction between H₂CO molecule and graphene. The calculated net electron transfers, electronic density difference images and densities of states give the evidence that the H₂CO molecules stay on Ti (or V) - doped graphene by chemisorption. After H₂CO adsorption, there are significant changes in electronic structure near the Fermi level, for both two systems of Ti and V doped graphene. This indicates distinct changes of electron transport properties. We have also found that H₂CO molecule has a larger absorption energy on V-doped graphene (1.939 eV) compared with Ti-doped graphene (1.120 eV). It is shown that the Ti-doped graphene has enough binding energy, adequate changes in electronic structure and reasonable short recovery time 10⁻³ s, making it a promising candidate for detecting formaldehyde gas.

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1. Introduction

Free-standing graphene was first studied in 2004 [1]. Since then, graphene has attracted much attention owing to its 2D stabilized structure and novel electrical properties [2]. It has been reported that graphene can be used to make highly sensitive gas sensors, because graphene is highly sensitive to NH₃, CO, and H₂CO, especially to NO₂ [3,4]. The sensitivity of graphene to gas molecules could be further improved by doping transition metal elements [5]. Wang et al. created vacancies in graphene by high-energy atom/ion bombardment, and then doped with a desired atom at the vacancy [6]. This method can offer a practical way to produce functionalized graphene [7]. In addition, as the energy of high speed particles varies, mono-vacancy and bio-vacancy graphene can be obtained. Previous research shows that transition metal doping in graphene can alter its electronic properties significantly, including a shift of

the Fermi level and shallow acceptor states in the graphene, which greatly extends its applicability [8].

H₂CO is a common environmental pollutant with strong toxicity. A great amount of effort has been devoted to find a sensitive gas sensor to detect H₂CO. Nowadays, there are several types of gas sensors: semiconductor gas sensors, electrochemical gas sensors, optical gas sensors, etc. An excellent sensor material should show high sensitivity to toxic gas, and it should also be easily reactivated for reuse. After introducing dopants into 2D nanosheets of graphene, the interactions between small molecules and graphene can be highly enhanced [9]. Recently, to search for a high sensitivity sensor, Chi et al. investigated the adsorption of H₂CO on the intrinsic and Al-doped graphene sheets. Compared with the intrinsic graphene, they have found that H₂CO molecules are strongly adsorbed onto the Al-doped graphene with a high binding energy value (3.703 eV) [10]. However, the Al-doped graphene cannot meet the above standards for an excellent sensor material because the extremely large absorption energy results in a long recovery time. In order to solve this problem, a better gas sensor with a reasonable recovery time and yet an adequate binding energy is designed via a first-principles approach based on DFT in this work.

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In this paper, we perform first-principles calculations for H₂CO molecules adsorbed on pristine graphene and the X(X = Ti, V) doped graphene. The model systems are carefully chosen to cover several basic issues. By investigating the structural and electronic properties of substrate-H₂CO complexes, we try to identify the good gas sensors, which can adsorb H₂CO with a drastic change of the DOS around the Fermi energy and with a reasonable binding energy for easily reuse. We find that the Ti and V doped graphene can meet the above criterions for the excellent sensor material. We hope that our results may provide new insight to the gas sensors for practical applications.

2. Computational details

The calculations are based on a density functional theory (DFT), and are performed using the Vienna *ab initio* simulation package (VASP) which is based on the density functional theory and the projector augmented wave (PAW) representation [11,12]. The Perdew-Burke-Ernzerhof (PBE) gradient-corrected function [13] is used to calculate the exchange-correlation energy. The substrates are pristine graphene, Ti-doped graphene and V-doped graphene. All graphene structures are obtained on the foundation of a 4 × 4 graphene supercell (32C atoms). We use a plane wave basis set with a cutoff energy of 500 eV. The mesh of K space is set as 19 × 19 × 1 grids and a Gaussian smearing of 0.05 eV. A vacuum region of 18 Å along the Z axis direction is employed. In an optimizing atomic structure, the force convergence criterion is set to 0.02 eV/Å. As a preliminary test, we optimized the atomic geometries of the pristine graphene. A single layer of 4 × 4 pristine graphene supercell was constructed with a 18 Å vacuum region. After fully relaxation, the calculated C–C bond length in graphene is 1.426 Å, which is well consistent with that of the experimental value 1.42 Å [14].

3. Results and discussion

3.1. Adsorption structure and adsorption energy

In order to obtain the most stable structure of H₂CO adsorbed on the pristine and doped graphene. Various types of initial adsorption geometries are considered. Fig. 1(a) shows three possible adsorption sites that are considered: a hollow site (H) at the center of a carbon hexagon, a bridge site (B) in the middle of a C–C bond and a top site (T) on the top of a carbon atom. A carbon atom is replaced by Ti atom in Fig. 1(b), and by V atom in Fig. 1(c), respectively. After fully relaxation, the Ti and V atoms are 1.42 Å and 1.29 Å higher than the graphene plane, respectively. For each site, four possible initial adoption configurations are considered, as shown in Fig. 1(e–h) for the top site. In Fig. 1(e), H₂CO molecule is parallel to the graphene plane, whereas in Fig. 1(f–h) the H₂CO molecule is in a plane perpendicular to the graphene, with the O atom pointing up or down, and one of the H atoms pointing to down, respectively. Therefore, there are 12 types of initial configurations of H₂CO adsorbing onto each type of substrate.

Then the stable systems can be obtained after full relaxation of the 36 types of initial configurations of adsorption systems with different substrates. In Fig. 2, we present the stable configurations of the adsorption structures, for the isolated H₂CO molecule and the three different graphene substrates with adsorbed H₂CO molecule, respectively. There are not magnetic moments for all the three systems. Some important bond length and bond angles of these optimized structures are also labeled in Fig. 2. The bond length (*l*) of B1, B2 and B3 in the most stable pristine graphene, are shown in Table 1. It is worth to mentioned that the stable configuration

Table 1

The bond length (*l*) of B1, B2 and B3 in the most stable pristine graphene, Ti-doped graphene and V-doped graphene before and after the adsorption of H₂CO molecule, respectively.

System	Configuration	Bond	Bond length <i>l</i> (Å)
H ₂ CO/graphene	Before adsorption	B1	1.426
		B2	1.426
		B3	1.426
	After adsorption	B1	1.425
		B2	1.425
		B3	1.425
H ₂ CO/Ti-doped graphene	Before adsorption	B1	1.939
		B2	1.939
		B3	1.939
	After adsorption	B1	1.930
		B2	1.940
		B3	2.030
H ₂ CO/V-doped graphene	Before adsorption	B1	1.863
		B2	1.863
		B3	1.863
	After adsorption	B1	2.051
		B2	1.862
		B3	1.862

Table 2

Adsorption energies for the most stable pristine graphene, Ti-doped graphene and V-doped graphene, respectively.

System	Adsorption energy (eV)
H ₂ CO/graphene	-0.162
H ₂ CO/Ti-doped graphene	-1.120
H ₂ CO/V-doped graphene	-1.939

of H₂CO/Ti-doped graphene is different from the configuration in reference [15] that is a metastable state.

The adsorption energy *E*_{ad} is defined as *E*_{ad} = *E*_{substrate+H₂CO} – (*E*_{freeH₂CO} + *E*_{substrate}), where *E*_{substrate+H₂CO} is the energy of graphene substrate absorbed with H₂CO, *E*_{freeH₂CO} is the energy of the free H₂CO molecule and *E*_{substrate} is the energy of doped or pristine graphene substrate, respectively. The values of adsorption energy (*E*_{ad}) for the three different graphene substrates are listed in Table 2.

Compared with the clean pristine graphene, the adsorption of H₂CO does not result in significant distortion of the graphene structure. The C–C bonds (B1, B2 and B3 in Fig. 1(b)) are only slightly shorten by 0.001 Å. And the structure of adsorbed H₂CO on pristine graphene does not change obviously in comparisons with isolated H₂CO. The plane of H₂CO molecule is parallel to the plane of graphene. The distance (defined as the distance of nearest atoms between substrate and H₂CO molecule) between H₂CO molecule and pristine graphene surface in this configuration is 3.351 Å. The adsorption energy of H₂CO on pristine graphene is -0.162 eV. The small adsorption energy (i.e. the absolute value of adsorption energy is smaller than 0.2 eV [16]) and large values of distance indicate that H₂CO undergoes physical adsorption on the pristine graphene.

The properties of H₂CO/Ti-doped graphene and H₂CO/V-doped graphene are also investigated. We find H₂CO molecules are strongly adsorbed onto the Ti-doped graphene with an adsorption energy of -1.120 eV. The adsorption energy of H₂CO/Ti-doped graphene is about 7 times that of the H₂CO/graphene system. After the adsorption of H₂CO, the lengths of Ti–C bonds are elongated from 1.939 Å to 1.940 Å, 2.030 Å and 1.863 Å for B1, B2 and B3 bonds in Fig. 1(b), respectively. The C–H bond length in an isolated H₂CO molecule is 1.117 Å, which is reduced to 1.101 Å and 1.103 Å in H₂CO in H₂CO/Ti-doped graphene complex. The C–O bond increased from 1.214 Å to 1.258 Å after adsorption. And the bond angle ∠H–C–H increased obviously from 116.174° to 119.144°. Ti atom is about 1.51 Å higher than the graphene plane. The distance

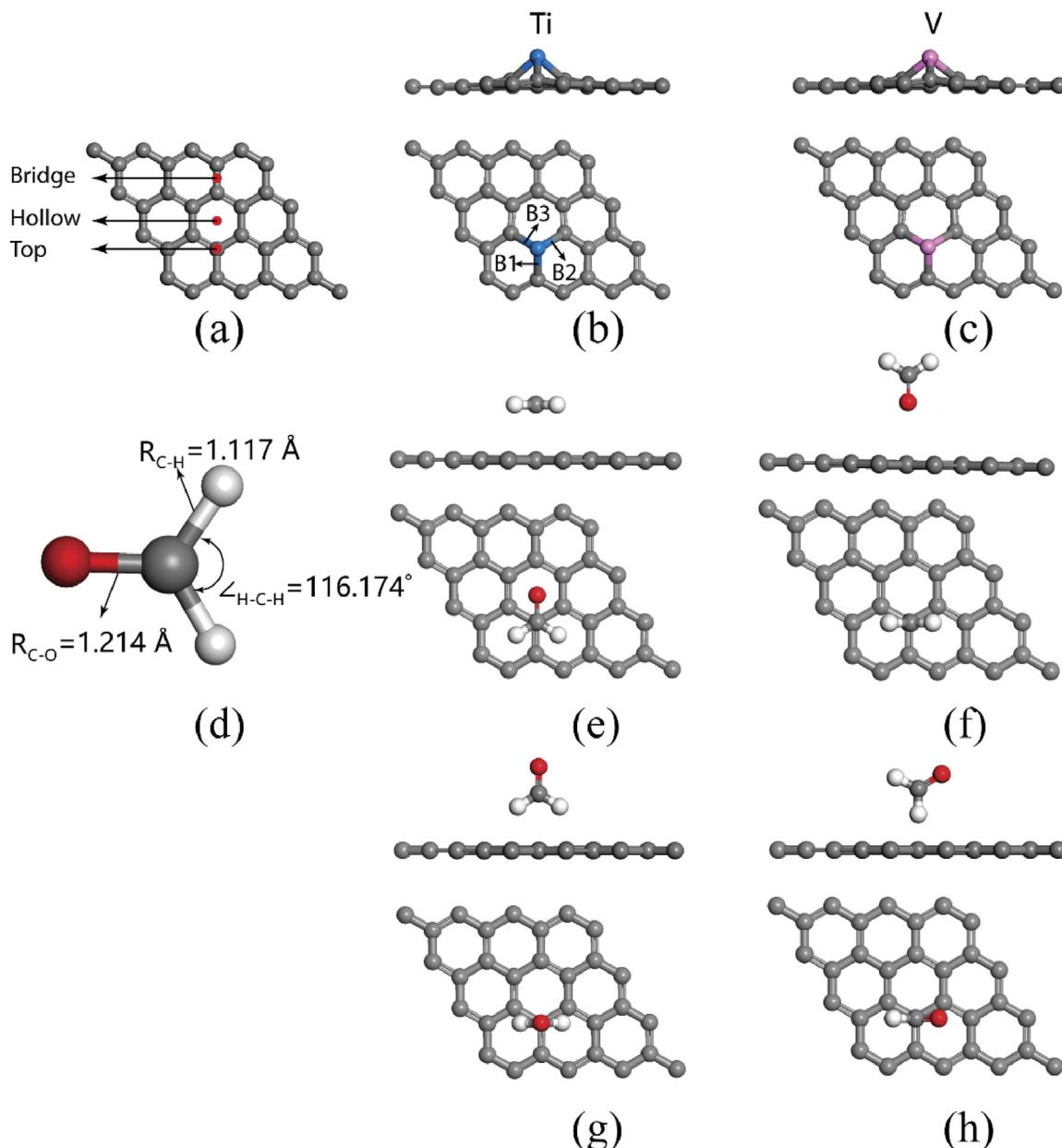


Fig. 1. (color online). (a–c) The initial configurations for the individual substrates. (d) The optimized structure of free H_2CO . (e–h) The four kinds of typical initial configurations for the H_2CO molecule floating above the substrates (see description in the text). C, H, O, Ti and V atoms are shown as gray, white, red, blue and purple, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

between Ti atom and O atom in H_2CO molecule is 2.085 \AA , which means there is a covalent bond formed between Ti and O atom.

Compared with the pristine graphene and Ti-doped graphene, V-doped graphene has the highest adsorption efficiency. The adsorption energy value of $\text{H}_2\text{CO}/\text{V}$ -doped graphene is about 1.5 times that of the $\text{H}_2\text{CO}/\text{Ti}$ -doped graphene. The C–O bond length in H_2CO is increased from 1.214 \AA to 1.349 \AA after adsorption. The C–H bond length in H_2CO reduced slightly from 1.117 \AA to 1.102 \AA . V atom is about 1.42 \AA higher than the graphene plane. It is notable that the distance between V atom and O atom in H_2CO is 2.086 \AA and the distance between V atom and C atom in H_2CO is 1.859 \AA . That means two covalent bond (C–V and O–V) are formed after H_2CO adsorbed on the Ti-doped graphene.

The above evidence reveals that Ti-doped and V-doped graphene are more favorable for the adsorption of H_2CO molecules than pristine graphene. Especially, the H_2CO molecules are more tightly adsorbed on V-doped graphene than the other two sub-

strates. The research of electronic properties can give us detailed explanations about the results above.

3.2. Net electron transfer and contour plots of the differences of electron charge densities

In order to understand the interaction mechanism of H_2CO adsorbed on the pristine graphene and the X ($X=\text{Ti}, \text{V}$) doped graphene, net electron transfer and the contour plots of differences of electron charge densities are presented in this section. The net electron transfer Δq is calculated by Bader charge analysis [17–19]. The values of net electron transfer (Δq) for the three different graphene substrates are listed in Table 3. Δq reflects the amount of electrons transferring from the graphene sheet to H_2CO molecule. About 0.008 e is transferred from the intrinsic graphene to the H_2CO molecule. Such a small Δq value indicates that the inter-

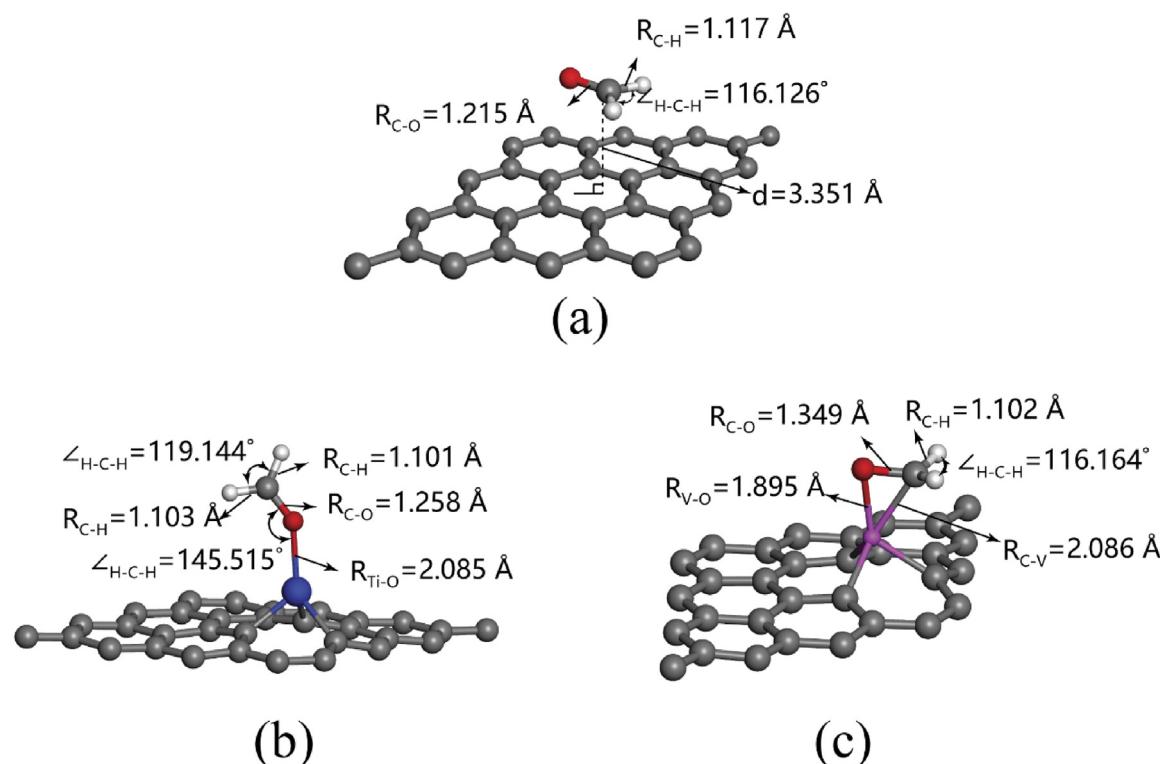


Fig. 2. The most stable configurations of (a) $\text{H}_2\text{CO}/\text{graphene}$, (b) $\text{H}_2\text{CO}/\text{Ti-doped graphene}$ and (c) $\text{H}_2\text{CO}/\text{V-doped graphene}$ complex. C, H, O, Ti and V atoms are shown as gray, white, red, blue and purple, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3

The net electron transfer (Δq) of the most stable pristine graphene, Ti-doped graphene and V-doped graphene.

System	Δq
$\text{H}_2\text{CO}/\text{graphene}$	0.008
$\text{H}_2\text{CO}/\text{Ti-doped graphene}$	0.301
$\text{H}_2\text{CO}/\text{V-doped graphene}$	0.692

action between the H_2CO molecule and the intrinsic graphene is not chemical adsorption.

About 0.301 e charge is transferred from the Ti-doped graphene to the H_2CO molecule, which is about 38 times that of the $\text{H}_2\text{CO}/\text{graphene}$ system. It is clear that H_2CO adsorption on the Ti-doped graphene undergoes a totally different mechanism from the H_2CO adsorption on the pristine graphene. The large Δq value means that a strong bond formed after the adsorption of H_2CO molecule. About 0.692 e charge transferred from the V-doped graphene to the H_2CO , which is about 2 times that of the $\text{H}_2\text{CO}/\text{Ti-doped graphene}$ system. The bond between the H_2CO molecule and the V-doped graphene is definitely stronger. Two strong bonds formed in $\text{H}_2\text{CO}/\text{V-doped graphene}$ system results in a larger Δq value than that of Ti doped graphene.

The charge transfer between the H_2CO molecule and the substrates as well as the interaction properties between them can be characterized by the contour plots of the differences of electron charge densities. In Fig. 3, the charge density difference, $\Delta\rho = \rho(\text{H}_2\text{CO}/\text{sub}) - \rho(\text{sub}) - \rho(\text{H}_2\text{CO})$, is plotted. Here $\rho(\text{H}_2\text{CO}/\text{sub})$, $\rho(\text{sub})$ and $\rho(\text{H}_2\text{CO})$ are the charge density of the optimized adsorption system, substrate and H_2CO molecule, respectively.

The charge density difference of $\text{H}_2\text{CO}/\text{graphene}$ adsorption system is displayed in Fig. 3(a) and Fig. 3(b). The value of charge density difference varies from -0.0034 to 0.0091 e which is very weak compared with other two systems. There is no obvious charge accumulation between H_2CO molecule and graphene. The redistribu-

bution of charge density on graphene substrate is mainly induced by the dipole of H_2CO molecule. In Fig. 3(c) and Fig. 3(d), it is obvious that the charge redistribution in $\text{H}_2\text{CO}/\text{Ti-doped graphene}$ adsorption system is much stronger than $\text{H}_2\text{CO}/\text{graphene}$, due to the wider value range of charge density difference from -0.229 to 0.138 e. There is an obvious accumulation of the charge in the region between the Ti and O atom, which indicates that the covalent bond formed between the adsorbed H_2CO and the Ti doped graphene. In Fig. 3(e) and Fig. 3(f), $\text{H}_2\text{CO}/\text{V-doped graphene}$ adsorption system shows the strongest charge redistribution among all the three adsorption systems, which has the widest value range of charge density difference varies from -0.305 e/ \AA^3 to 0.685 e/ \AA^3 . Charge obviously accumulated in the region between V and O atom as well as V and C atom. This fact illustrates that two covalent bonds formed in the process of H_2CO adsorbed on V doped graphene. That is the origin of the highest adsorption efficiency showed by V-doped graphene.

3.3. Density of states

To investigate the effects of adsorbed H_2CO molecule on doped and pristine graphene, the total electronic densities of states (DOS) for the free H_2CO molecule, the stable substrates and $\text{H}_2\text{CO}/\text{substrates}$ are calculated, as shown in Fig. 4. The DOS of the free H_2CO molecule is shown in Fig. 4 (a). Sharp peaks can be recognized easily. There is a peak located at -0.21 eV near the fermi level. Fig. 4 (b) shows the DOS of the pristine graphene with and without H_2CO adsorption. There is few variance of DOS upon the adsorption of H_2CO near the Fermi level, and the Dirac point of this adsorbed system is clearly visible. The molecular orbitals of the adsorbates are recognizable as sharp peaks in the DOS of $\text{H}_2\text{CO}/\text{Graphene}$. The H_2CO electronic states contribution to the total DOS of the pristine graphene with H_2CO adsorption are localized in the range between -8 and -2 eV in the valence bands and

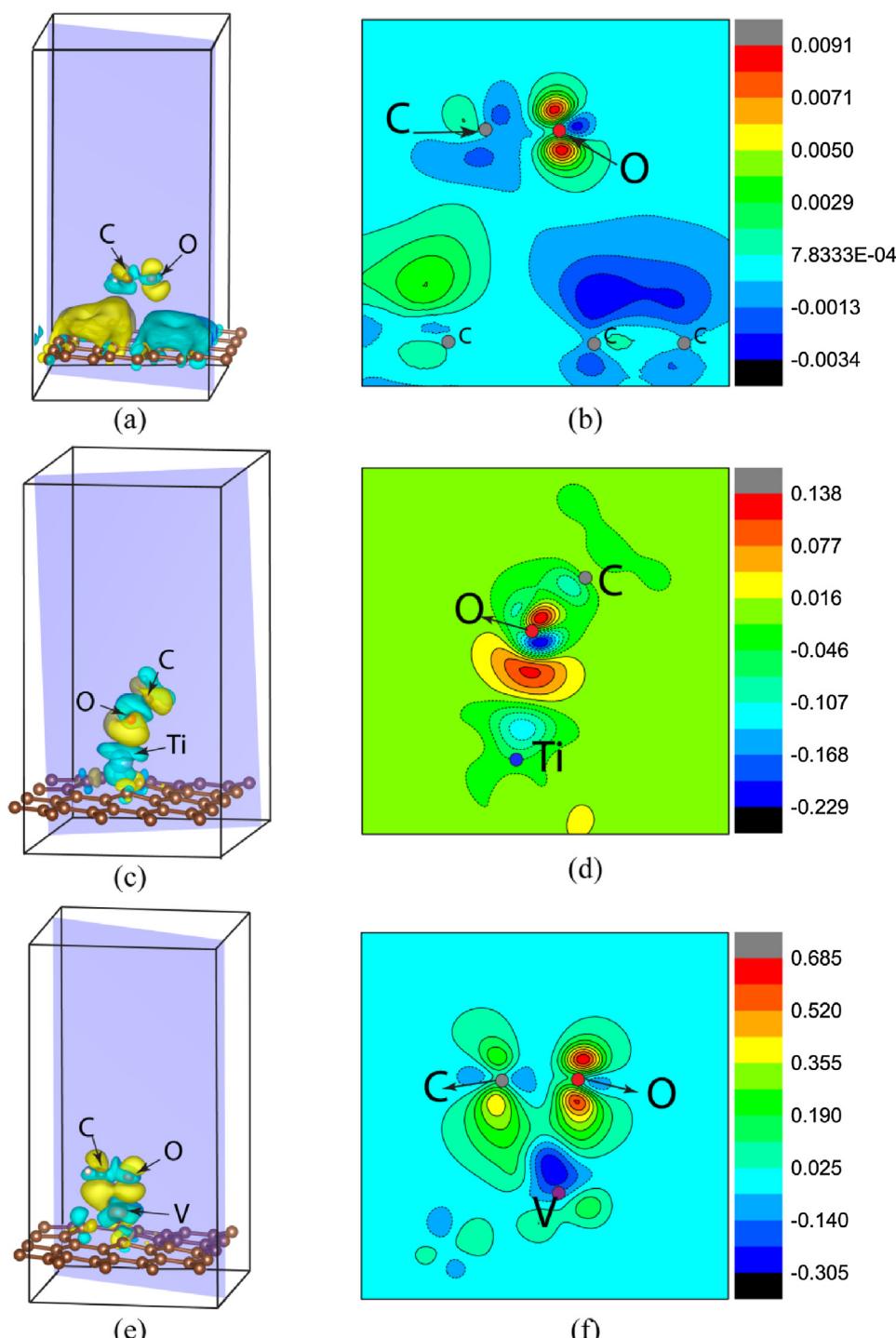


Fig. 3. (color online) Plots of charge density differences for three adoption cases: (a) and (b) for H₂CO/graphene; (c) and (d) for H₂CO/Ti-doped graphene; (e) and (f) for H₂CO/V-doped graphene. (a), (c) and (e) are 3D plots, (b), (d) and (f) are 2D plots on the light purple shown in the 3D plot. C, O, V and Ti atoms are denoted with grey, red, purple and blue balls. Solid and dashed lines in panels (b), (d) and (f) correspond to $\Delta p > 0$ and $\Delta p < 0$, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the range around 1.5 eV in the conduction bands, which are far away from the Fermi level. These results show that the graphene electronic states, especially for the states near the fermi level, are nearly unaltered after the adsorption of the H₂CO molecule. Therefore, pristine graphene cannot be a good sensor material to detect the presence of H₂CO molecules. The adsorption of H₂CO on Ti-doped graphene causes the new high peak of the DOS in the region just around the Fermi level, shown in Fig. 4(c). This phenomenon is

also expected to increase the conductance of this system compared with the Ti-doped graphene without H₂CO adsorption. In contrast, Fig. 4(d) shows that the large peak around the Fermi level for the DOS of V-doped graphene without H₂CO adsorption are dramatically decreased after the H₂CO adsorption. This fact is expected to decrease the conductance of H₂CO/V-doped graphene compared with the V-doped graphene without H₂CO adsorption. These different phenomena for the Ti-doped V-doped graphene is due to

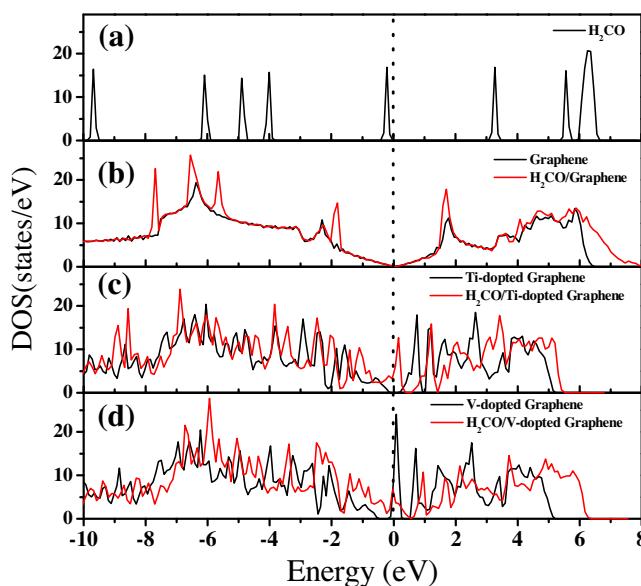


Fig. 4. Total electronic density of states for (a) free H_2CO ; (b), (c) and (d) stable substrates and H_2CO /substrates. The Fermi level is set at zero.

that V atom has one more electron than Ti atom. These above phenomena indicate the electron transport properties of the Ti-doped and V-doped graphene systems may change drastically after the adsorption of H_2CO molecule.

3.4. Recovery time

The above calculation results indicate that the Ti-doped and V-doped graphene are sensitive for H_2CO molecules, but strong bonding implies that the desorption of the H_2CO molecules from the doped graphene could be difficult [19]. According to the conventional transition state theory, the recovery time can be expressed as [19]

$$\tau = v_0^{-1} e^{(-E_{ad}/k_B T)}$$

where T is temperature, k_B is the Boltzman's constant and v_0 is the attempt frequency. v_0 can be obtained from the data in Ref. [19] as $E_{ad} = -3.04 \text{ eV}$, $T = 600 \text{ K}$, $\tau = 10^{10} \text{ h}$ for NO_2 on D-graphene. Increasing the adsorption energy E_{ad} will prolong the recovery time of the gas sensor. The Ti doped graphene can be regenerated to its initial state within the recovery time 10^{-3} s by annealing at 600 K in short UV irradiation, which is remarkable shorter than that 10^4 s for V doped graphene. The recovery time of Ti doped graphene is preferred for practical application.

4. Conclusion

In summary, based on the first-principles calculations, the adsorptions of H_2CO on the pristine, Ti-doped and V-doped graphene have been investigated. The adsorption structures, total energies, charge density difference, DOS and recovery time are calculated. The results suggest that the adsorption of H_2CO molecule on pristine graphene is a weak physisorption. The adsorption

energy value of the H_2CO molecule on V-doped graphene is over 11 times more than that on pristine graphene. Furthermore, the calculation results of electronic structures show the sensor based on Ti-doped graphene and V-doped graphene could be more sensitive and useful. Therefore, Ti-doped graphene and V-doped graphene can be used as adsorption hosts for H_2CO gas. Furthermore, the Ti-doped graphene has the reasonable shorter recovery time and moderate binding energy value, making it to be a promising candidate for practical detection of formaldehyde gas.

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