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The adsorption enhancement of graphene for fluorine and chlorine from water

Chaohong Guan^a, Xiaojun Lv^{a,*}, Zexun Han^a, Chang Chen^a, Zhenming Xu^{b,c}, Qingsheng Liu^d^a School of Metallurgy and Environment, Central South University, Changsha 410083, China^b John. A. Paulson School of Engineering and Applied Sciences, Harvard University, 29 Oxford St, Cambridge, MA 02138, USA^c University of Michigan–Shanghai Jiao Tong University Joint Institute, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China^d Faculty of Resource and Environmental Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

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ABSTRACT

A high concentration of F (Cl) element in drinking water threatens people's health. Hence, in this work, we systematically investigated the F and Cl atoms adsorption on pristine graphene (PG) or defective graphene (vacancy and Al, B, Si-doped) by using density functional theory calculations to explore materials with stronger adsorption performance for F and Cl elements removal from water. Based on the analysis of adsorption energy, PDOS and charge population, results indicate that F/Cl atom preferentially adsorbed on the Top site of graphene. We also find that the vacant graphene and doped graphene are good candidates for the adsorbents for F and Cl atom because the single F or Cl atom can be strongly trapped in the positions of defects. The negative adsorption energy and the diffusion barrier suggest that the F/Cl-AlG system has the most thermodynamic stability among our considered systems. In the H₂O environment, the adsorption energy for the co-adsorption of F(Cl) atom and H₂O molecule on Al-doped graphene is -4.2 eV (-3.77 eV), suggesting that the strong adsorption performance still presents between F(Cl) atom and Al-doped graphene in a background of H₂O molecule.

1. Introduction

Nowadays, environmental issues have been considered as the hottest topic in order to build a more friendly planet for people living. Meanwhile, the unavoidable development of industry has also brought some serious pollution problems, especially water pollution. The wastewater produced by industrial process usually contains many harmful elements both fluorine (F) and chlorine (Cl) are the important pollutants among them [1]. It is a health hazard when the two elements present in drinking water at high enough concentration. In fact, the World Health Organization (WHO) has reported that the maximum concentration of F in drinking water is 1.0 mg/L and correspondingly [2], it will cause some diseases including skeletal fluorosis and dental fluorosis at high enough concentration. According to the survey, the incidence of dental fluorosis will be as high as 45% or more when drinking water with a fluorine content of 1.5 mg/L [3]. However, suffering from skeletal fluorosis is even more terrible. Early symptoms contain limbs, spine bones and joint pain, etc., even cause paralysis if not effectively controlled and treated. In addition, the specific hazards of high concentration Cl main include loss of appetite, the changes of dry skin, chapped, even carcinogenic. Therefore, it is crucial to control

the level of fluorine and chlorine for protecting public health. Many techniques have been employed to remove F or Cl such as adsorption [4–6], electrodialysis [7], ion exchange [8,9] and precipitation [10], etc. Overall, the method of adsorption is the most promising attribute to the features of higher efficiency, more environment-friendly and lower cost [4–6]. In the recent years, great efforts have been contributed to study the efficient alternative materials with a higher adsorption capacity of fluorine or chlorine in an aqueous system, which materials contain activated alumina [11–13], layered double hydroxides [14], zeolites [15,16] and CeCO₃OH nanosphere adsorbent [1]. In general, activated alumina is the most common adsorbent for removing fluorine but the relatively low adsorption capacity and aluminum dissolution limit its wide application [17]. In addition, the density functional theory (DFT) has been a great tool to predict the atomic adsorption behaviors. Lv et al. [18] have studied the adsorption of fluorine on nitrogen-doped MgAl₂O₄ surface by DFT calculation, which indicates that this doped material is a promising candidate for fluorine removal. The previous work [6] also studied the adsorption of Cl at perfect and defective Ag surface and the results show the hollow site is an energetic preference site for the adsorption of Cl atom. Different adsorbents including Ge(0 0 1) surface [19], Fe(1 0 0) [20], InAs [21] etc have also

* Corresponding author at: School of Metallurgy and Environment, Central South University, No. 932, South Road Lushan, Changsha, Hunan 410083, China.

E-mail addresses: lvxiaojun@csu.edu.cn (X. Lv), zhenmingxu@seas.harvard.edu (Z. Xu).

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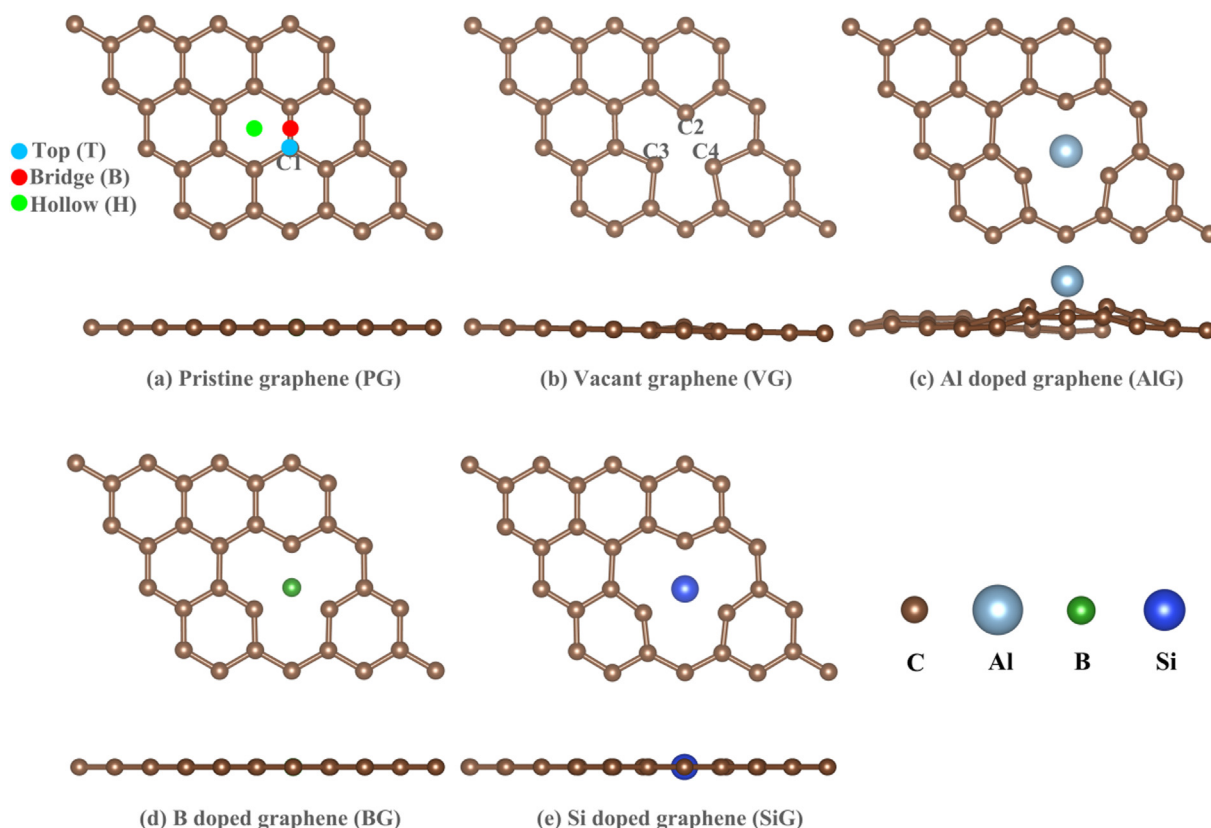


Fig. 1. Optimized structures of PG, VG and Al, B, Si-doped graphene.

been investigated for adsorption of F or Cl atoms.

Graphene, a 2D single-layered material of carbon, has caught people's eyes since its first discovery in experiment in 2004 [22]. Dozens of theoretical and experimental studies based on the application of graphene have been carried out attribute to its unusual transport and electronic properties, the applications include sensors, catalysis, adsorbents, energy storage and nanoelectronic devices [23–27]. In addition, graphene has been employed as an atom (molecule) sensing or capture material because of low cost and high surface area [28], while atoms or molecules will bind with graphene to reach high adsorption concentration and storage capacity. For instance, previous reports have described some toxic gaseous (such as HF, CO₂, CO, NH₃) [29–31] or some atoms (Li, Hg) [32,33] adsorption on graphene. To further enhance the adsorption ability of graphene, considerable research efforts have been devoted to change the local reactivity via doping elements such as Al, Mn, Au, Ti, B and Si [34–37]. Liu [33] et al. did the calculation of the mercury adsorption on Al-doped (AlG) graphene and found the chemisorption process presents between mercury atom and AlG surface. Ali Shokuhi Rad [38] et al. reported that the AlG can adsorb NO₂, CO₂, N₂O and CO molecules stably. The defects have been considered for fluorine atoms interaction with graphene by Song et al. [39], which indicates that it is impossible for fluorine to penetrate the pristine and vacancy surface due to the high energy barrier.

Therefore, graphene has great potential for removing or capturing F and Cl elements from aqueous systems. To the best of our knowledge, there are relatively few studies devoted to the adsorption behaviors of F or Cl on graphene doped by Al, B and Si. The thermodynamic stability of these adsorption systems is not clearly understood, which is essential for the graphene to maintain excellent adsorption performance. In this work, the adsorption strength and thermodynamic stability of F/Cl atom on pristine or defective graphene are studied by density functional theory (DFT) through calculating the adsorption energy, partial density of states and diffusion barriers. The co-adsorption of F/Cl atom and H₂O

molecule on Al-doped graphene are also investigated, suggesting the Al-doped graphene is a perfect candidate for capturing F and Cl in H₂O environment.

2. Computational methods

All first principle calculations were performed in the CASTEP [40] program based on a plane-wave expansion of the wave functions. The Perdew-Burke-Ernzerh function (PBE) with a Generalized Gradient Approximation (GGA) was adopted to compute the electron exchange-correlation energy [41,42], the ultrasoft pseudopotentials were selected to describe the ion-electron interaction. The dispersion interactions were considered through the DFT-D developed by Grimme [43]. In addition, the energy cutoff of 600 eV and the Brillouin zone of $7 \times 7 \times 1$ Monkhorst-Pack [44] grids were selected based on the convergence test of energy cutoff and k-point mesh. The 15 Å vacuum layer was used to ignore the interactions between adjacent layers in the z-direction. In order to calculate the adsorption of F or Cl atom on the pristine and defective (including vacancy and dope) graphene, a $4 \times 4 \times 1$ supercell with periodic boundary conditions was adopted to simulate, which contains 32 carbon atoms and additionally, one of the carbon atoms was replaced by atoms to form doped graphene models. In addition, we have studied the behaviors of F/Cl adsorption on Top site of 5×5 graphene sheet. The bond lengths of F-C, Cl-C are 1.53 Å and 2.76 Å. For F adsorption on graphene, the C atom will out of the graphene sheet with a distance of 0.341 Å. These phenomena are consistent with the results of F/Cl adsorption on Top site of 4×4 graphene sheet, suggesting that the 4×4 sheet is suitable for our study.

The adsorption energy (E_{ads}) was applied to evaluate the binding between adsorbates and adsorbents in this work, which can be defined as follows [31]:

$$E_{ads} = E_{total} - (E_{F/Cl} + E_{PG/doped})$$

where E_{total} corresponds to the adsorbed systems, $E_{F/Cl}$ and $E_{PG/doped}$ represent the energy of single F or Cl atom and the energy of doped-graphene sheets. $E_{F/Cl}$ could be calculated by putting an isolated F(Cl) atom in a $10 \text{ \AA} \times 10 \text{ \AA} \times 10 \text{ \AA}$ cubic box. Furthermore, negative adsorption energy represents a stable adsorption system. On the contrary, a positive value indicates that the F or Cl atom will preferably be in atomic state so that the adsorption for atoms on graphene is not unfavored.

3. Results and discussion

3.1. Structure of pristine and defective graphene

The optimized structures of PG, VG, and Al, B, Si-doped graphene are shown in Fig. 1. The bond lengths between carbon atoms and carbon atoms or dopant atom will be adjusted to reach a balanced state during geometry optimization. In this work, the computed C–C bond length of PG is 1.42 \AA , which is well consistent with previous reports [44]. For the vacant graphene (VG), the C3C–C4 bond length of 2.091 \AA closes to the theoretical values of 2.096 \AA . Obviously, the balanced configurations of defective graphene are different from pristine graphene, Table 1 displays the distance between dopant and neighbouring carbon atoms, which will be compared with the reported values. The same length can be found between dopants and carbon atoms of C1, C2 and C3. In Al-doped graphene (AlG), the distance between Al atom and C1 (C2, C3) is 1.846 \AA , and the distances between B or Si atom and C1 are 1.483 and 1.648 , respectively. The bond lengths match very well with the previous works by DFT calculations [45–49]. These consistencies guarantee the accuracy of our calculations.

3.2. Fluorine and chlorine adsorption on pristine and vacant graphene

To model the adsorption of F, Cl on the PG, three inequivalent adsorption sites were considered in our work. As shown in Fig. 1(a), the F and Cl atoms can adsorb on top of a carbon site (denoted as T), on a bridge site above a CC–C bond (denoted as B), and above the center of the hexagon of graphene (denoted as H). For the adsorption systems, the distance of carbon atom or dopant atoms deviated graphene surface was defined as d . According to the parameters of Section 2, the systems of F and Cl atoms adsorption on T, B and H sites of graphene were optimized. The adsorption energy of F on T, B and H sites is -2.42 eV , -0.75 eV and -0.002 eV , as shown in Table 1, indicating that it is a thermodynamically favorable process for F atom adsorption on graphene surface. Obviously, the most favorable site, i.e. the site with the most negative adsorption energy, is the T site, indicating a chemisorption process occurs in the T site. As for the H site, the smallest adsorption for F atom on graphene would be considered as physisorption. This result is in accordance with the previous studies [50]. The small adsorption energy of Cl atom on graphene illustrates that Cl atoms are favorable to adsorb on graphene surface by a slight vdW interaction, i.e. the physisorption. Compare to the adsorption of Cl atom

Table 2

Atomic charges of F, Cl- defective graphene by Hirshfeld method.

	PG	VG	AlG	BG	SiG
F	−0.16	−0.189	−0.29	−0.2053	−0.18
Cl	−0.003	−0.1448	−0.21	−0.1389	−0.12

on B and H sites, the adsorption on T site is the most stable due to the fewer adsorption energy of -0.82 eV , this result is in line with the reported value of 0.8 eV [51]. Similarity, D of F-graphene systems is the shortest at the T site, the D is larger in B and H sites. Due to the strong interaction between F atom and carbon atom in the T site, the slightly structural distortion of graphene occurs and the deviated distance d of carbon atom is 0.329 \AA . The large D of Cl-graphene system shows that the smaller interaction between Cl atom and graphene surface than that between F and graphene. With the introduction of a vacant defect, the adsorption strength for F and Cl atoms increase according to the more negative adsorption energy of -2.85 eV and -1.81 eV . Therefore, the presence of vacancy can promote graphene to capture fluorine and chlorine atoms.

To deeply understand the adsorption mechanisms of F and Cl atoms on PG and VG, the charge population analysis, electron density and projected density of states (PDOS) of the most stable adsorption configurations were discussed. In this work, the charge population analysis is calculated by Hirshfeld method. The atomic charge of adsorbates (F and Cl) for the most stable adsorption systems are listed in Table 3. About 0.16 e (0.003 e) is transferred from PG to F (Cl) atom. The small value of charge population for Cl-PG indicates the interaction between Cl atom and PG is slight physical adsorption. The chemical adsorption may occur between F atom and PG due to the bigger charge transition. Further, the introduction of vacancy promotes the charge transition for F-VG and Cl-VG systems. About 0.189 e (0.1448 e) is transferred from VG to F (Cl) atom. The stronger interaction induces the chemical adsorption for F-VG system, and a strong bond also formed after Cl atom adsorption on vacant site. Comparison of charge transition for F-PG/VG and Cl-PG/VG reveals the interaction between F and graphene is stronger than that between Cl and graphene. This phenomenon matches well with the adsorption energy calculations.

Fig. 2 shows the PDOS and electron density for F and Cl atoms adsorption on PG and VG. The result shows the large hybridization between p orbital of F atom and p orbital of PG in a range of -10 to 0 eV . The p orbital of F overlaps with p and s orbitals of C in PG, i.e. the obvious overlapping with neighboring peaks around the energy area of -24.5 eV . Hence, covalent bond exists between F and PG due to the strong orbital hybridization. In the contrary, as we can see, there is no overlapped area between Cl-p orbital and C-p orbital, demonstrating that a non-bond interaction in the Cl-PG adsorption system. On the other side, the overlapped area of DOS will increase with the introduction of vacancy defect. For F-VG, the hybridization between F-p orbital and C-p orbital from -10 eV to 2 eV , the overlapped area is

Table 1

Adsorption energy (E_{ads}) for F or Cl atoms adsorbed on PG, VG and doped graphene surfaces. (a and a_1 represent the bond length between dopant atom and surrounding carbon atoms (C1, C2, C3) or C–C bond length for PG from the current work and previous theoretical calculations, respectively. D is the distance between F or Cl atom and closest carbon, vacant or dopant atoms, d is the distance of dopants out of the graphene plane.)

Adsorption sites	a (Å)	a_1 (Å)	F adsorption			Cl adsorption		
			$D/\text{\AA}$	$d/\text{\AA}$	E_{ads}/eV	$D/\text{\AA}$	$d/\text{\AA}$	E_{ads}/eV
PG(T)			1.521	0.329	−2.02	2.767	0	−0.88
PG(B)	1.42	1.421[44]	2.118	0	−0.75	3.107	0	−0.13
PG(H)			2.398	0	−0.022	2.989	0	−0.22
VG	2.091	2.096[45]	1.486	0	−2.85	2.006	0	−1.81
AlG	1.846	1.85[46,47]	1.679	1.25	−7.37	2.123	1.238	−4.85
BG	1.483	1.48[48]	1.469	0.738	−3.62	1.948	0.447	−3.41
SiG	1.648	1.65[49]	1.614	0.926	−2.56	2.065	0.922	−2.23

Table 3
Diffusion barriers (eV) of several pathways for F or Cl atom diffusion on graphene surfaces.

	Diffusion pathways			
	1	2	3	4
F-PG	0.41	0.6	0.40	
F-VG	3.15	2.82	1.73	
F-AlG	3.87	3.24	–	
Cl-PG	0.023	0.01	0.003	
Cl-VG	–	0.61	–	
Cl-AlG	–	3.27	3.11	–

larger than F-PG system. Also, there is a larger overlapping appeared in Cl-VG system than Cl-PG, showing a strong hybridization between Cl-p orbital and C-p orbital. Overall, the stronger hybridization illustrates that the covalent interaction presents in the adsorption systems of F-VG and Cl-VG. These conclusions are consistent with the electron density of F and Cl adsorbed on PG and VG. An overlap of electron density suggests a strong interaction between F/Cl and PG/VG. Therefore, the larger overlap area of F and Cl adsorbed on VG indicates the vacancy facilitates graphene adsorption of F and Cl atoms. But in the case of Cl adsorption on pristine graphene sheet, the overlap does not occur and hence, the adsorption is physical adsorption based on the VDW interaction.

3.3. Fluorine adsorption on doped graphene

To improve the adsorption performance of graphene for F and Cl atom, Al, B-doped, as well as Si-doped graphene were considered. Single F atom was added to the top of doped atoms and was then allowed to optimize its position. Fig. 3 exhibits the stable configurations of F atom adsorbed on Al-, B- and Si-doped graphene. By evaluating the structural influence of these doped defects on adsorption, it is found that the doped defects have a marked impact on the adsorption of F atom, with all of the doped systems showing much stronger adsorption. As shown in Table 1, the adsorption energy of F adsorbed on Al-, B- and Si-doped graphene is -7.37 eV, -3.62 eV and -2.56 eV, respectively. These values are all larger than the adsorption energy of F-PG (-2.02 eV) and hence, the chemisorption occurs between F and Al-, B- and Si-doped graphenes. Among the three adsorption systems, the AlG is the most favourable for F adsorption attribute to the most negative adsorption energy. Compared with the adsorption of F on MgAl_2O_4 (adsorption energy is -5.02 eV) [18], the AlG has a stronger adsorption performance. Similar behaviour is observed in the all doped systems that the d increases when adsorption occurs. Moreover, the d is bigger due to the stronger adsorption, suggesting the great dependence of d on the structure of graphene. Hence, the doped-graphenes in this work are perfect candidates for capturing F from aqueous system from an energetic perspective.

Calculated charge population are collected in Table 2, which shows about 0.29e, 0.2053e and 0.18e charge is transferred from the AlG, BG and SiG to F atom and the number of transfer charge is larger than F adsorbed on PG, suggesting the stronger bond formed after the adsorption of F atom on doped-graphene. Meanwhile, the order of transferred charge is $\text{AlG} > \text{BG} > \text{SiG}$ ($0.29\text{e} > 0.2053\text{e} > 0.18\text{e}$), which is in line with the result of adsorption energy. In addition, the calculated PDOS for the doped systems are graphically represented in Fig. 4. It can be clearly seen that the doped graphene has a marked influence on the F adsorption. After the adsorption of F atom, an overlap of PDOS between F-2p orbital and Al-3p or 3s orbital occurs in the range of -5.7 eV to 2.4 eV for Al-doped graphene, and there is a slight overlap between F-2s and Al-3p orbitals around -22.5 eV. Respectively, a hybridization occurs between F-2p and B-2s orbitals in the area of -8 eV to 0 eV for B-doped graphene and Si-3p orbital overlaps

with the F-2p orbital from -9 eV to -1.4 eV for Si-doped graphene. These results indicate a strong covalent interaction of these adsorption systems. Besides, the peaks of s,p-orbital of Al, B and Si atoms agree well with the corresponding peaks of C s,p-orbitals, indicating the strong hybridization of its orbitals and hence, the AlG, BG and SiG sheets are still stable though the strong bonding between F and doped atoms. Noted that the DOS at Fermi level is greater than zero and so the three adsorption systems show partial metallic, which is consistent with the recent DFT calculations. From the PDOS curves of Fig. 4, it is found that the main contributions of peaks near the Fermi level for F-AlG are dominated by the p orbitals of C and Al atoms. This is agree well with the previous studies, which predicted that an Al atom doped in graphene induces the conductivity increases. Similarity, the partial metallic of F-BG and F-SiG is dominated by the p orbitals of C atoms. Comparisons of all TDOS and PDOS of F-doped graphene reveal that the TDOS below Fermi level are main determined by the contributions of s,p orbitals of C atoms, doped atoms and F atom. But for the TDOS above the Fermi level, which is only dominated by the contributions of s,p orbitals of C atoms and doped atoms. The more unoccupied electron states above Fermi level for Al, B and Si indicate a charge transfer from doped-graphene to electronegative adsorbate F that is consistent with the results of charge population analysis.

3.4. Chlorine adsorption on doped graphene

Let us discuss the impacts of doped graphene on the adsorption of Cl atom. The optimized adsorption configurations of Cl adsorbed on Al-, B- and Si-doped graphene are presented in Fig. 5. It can be clearly seen that the presence of doped atoms on graphene has a marked enhancement on the Cl adsorption compared to the PG system. It also can be concluded from Table 2 that AlG sheet is the most favourable for the adsorption of Cl in terms of the most negative adsorption energy. Certainly, the strong adsorption occurs not only in the Cl-AlG system, but also in the Cl-BG and Cl-SiG systems due to the negative adsorption energy. Therefore, the doped atoms will protrude out of the graphene plane. The adjacent C atoms also protrude in varying degrees. These phenomena are consistent with F adsorbed on doped graphene, suggesting the strong bonding presents between Cl and doped graphene. Besides, from Table 2, it is found that about 0.21e, 0.1389e and 0.12e transferred from AlG, BG and SiG to Cl atoms, respectively. The results also imply that the Al-, B- and Si-doped graphene can promote the adsorption of Cl and the adsorption performance is stronger than pristine graphene.

We now concentrate on the PDOS of adsorption systems for Cl adsorbed on doped graphene to further understand the impact of doped atoms. All PDOS are collected in Fig. 6, it can be seen that the Cl-s,p orbital hybridizes with Al-s,p orbitals at -14.2 eV, and from -6 to -1 eV relative to Fermi level and the peaks of Cl-s,p orbitals agree well with the corresponding peaks of B-s,p and Si-s,p orbitals, which indicates the strong interaction between Cl and doped atoms (Al, B and Si). These results match well with the adsorption energy and the charge population analysis. In addition, the peaks of s, p orbitals of Cl are under Fermi level in the Cl-AlG, BG and SiG adsorption systems, suggesting the main contributions for TDOS above Fermi level are dominated by the C-s,p orbitals and the s,p orbitals of doped atoms. Hence, the more unoccupied electron starts of Al, B and Si atoms also indicate a charge transfer from doped atoms to Cl atom that is consistent with the results of charge population analysis, because the electronegativity of Cl is larger than Al, B and Si elements. In general, combining the analysis of adsorption energy, charge population and DOS, it can be concluded that the AlG, BG and SiG sheets would be a promising sensor material to capture and detect Cl in aqueous system.

3.5. Fluorine and chlorine atoms migration on defective graphene

In summary, there is the strongest interaction between F/Cl and Al-

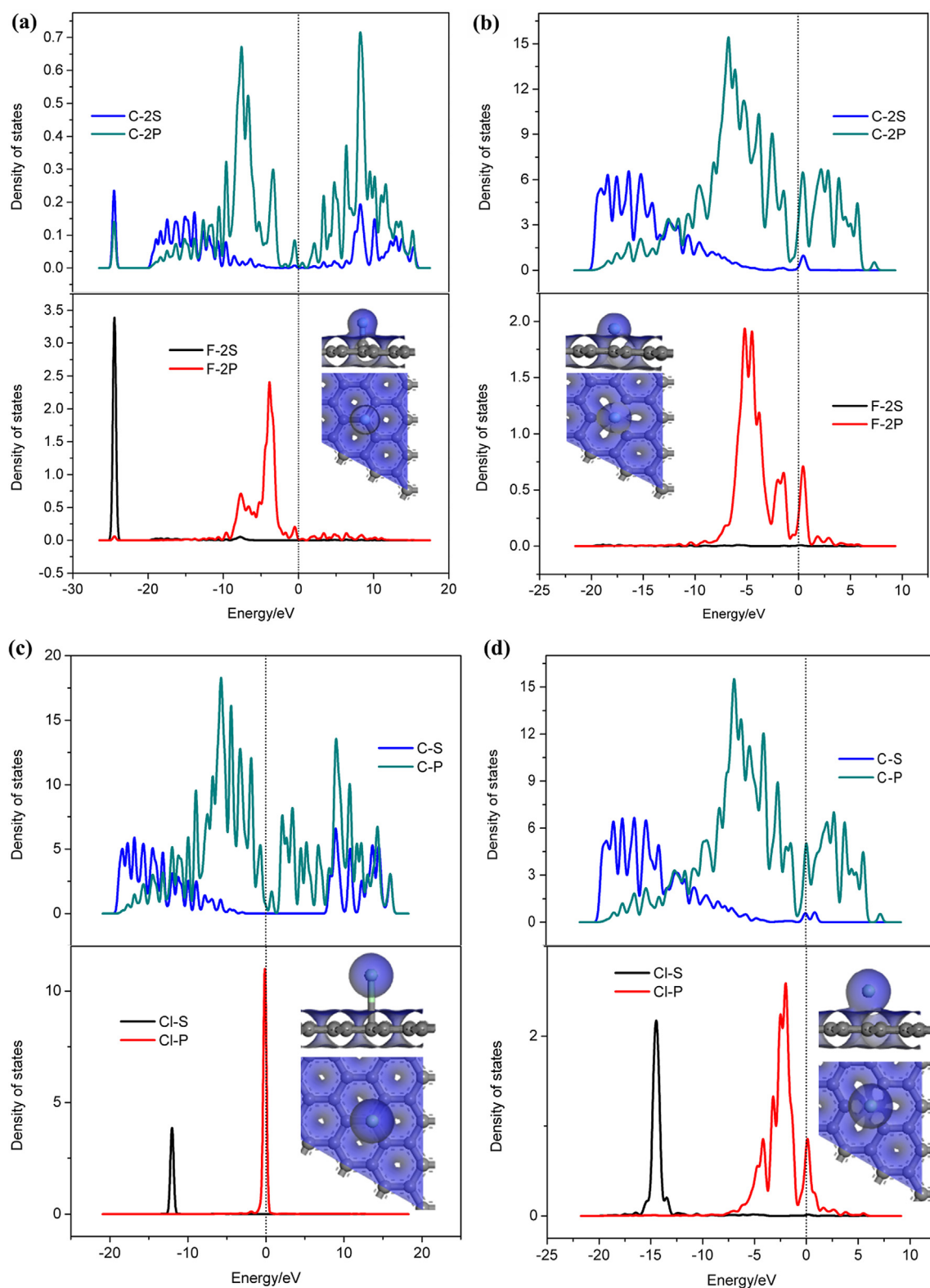


Fig. 2. The PDOS of atom for F adsorption on (a) PG and (b) VG, (c) and (d) are the PDOS curves for Cl adsorption on PG and VG, respectively. The embedded map in the PDOS is the isosurface of electron density for F and Cl atoms adsorption on PG and VG.

doped graphene. And the adsorption energy for Al on graphene was computed to evaluate the stability of AlG, which is -3.3 eV. Hence, the high stability of Al doped graphene suggests that AlG sheet is the most promising candidate for capturing F and Cl in our work. Here, we used the LST/QST [52] and NEB methods to further evaluate the thermodynamic stability of F and Cl atoms on PG, VG and AlG, all the three

possible diffusion pathways on these surfaces are shown in Fig. 7a and specially, four possible pathways as shown in Fig. 7b for Cl atom adsorbed on AlG due to the bigger atomic radius and strong interaction between Cl and Al atoms, and the results are shown in Table 3, where the diffusion barrier represents the energy difference between the energy of transition state (TS) and of the initial structure (IS) before

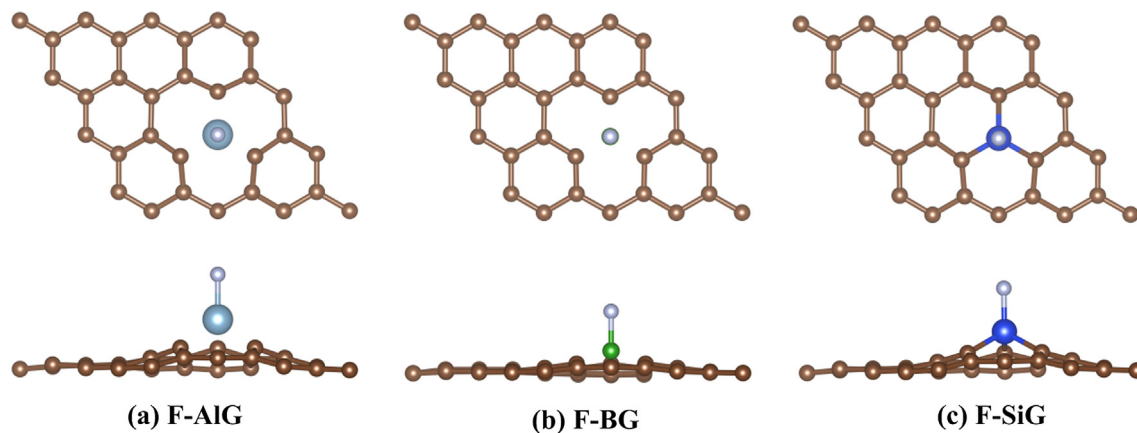


Fig. 3. The optimized stable configuration of F adsorption on (a) AlG, (b) BG and (c) SiG.

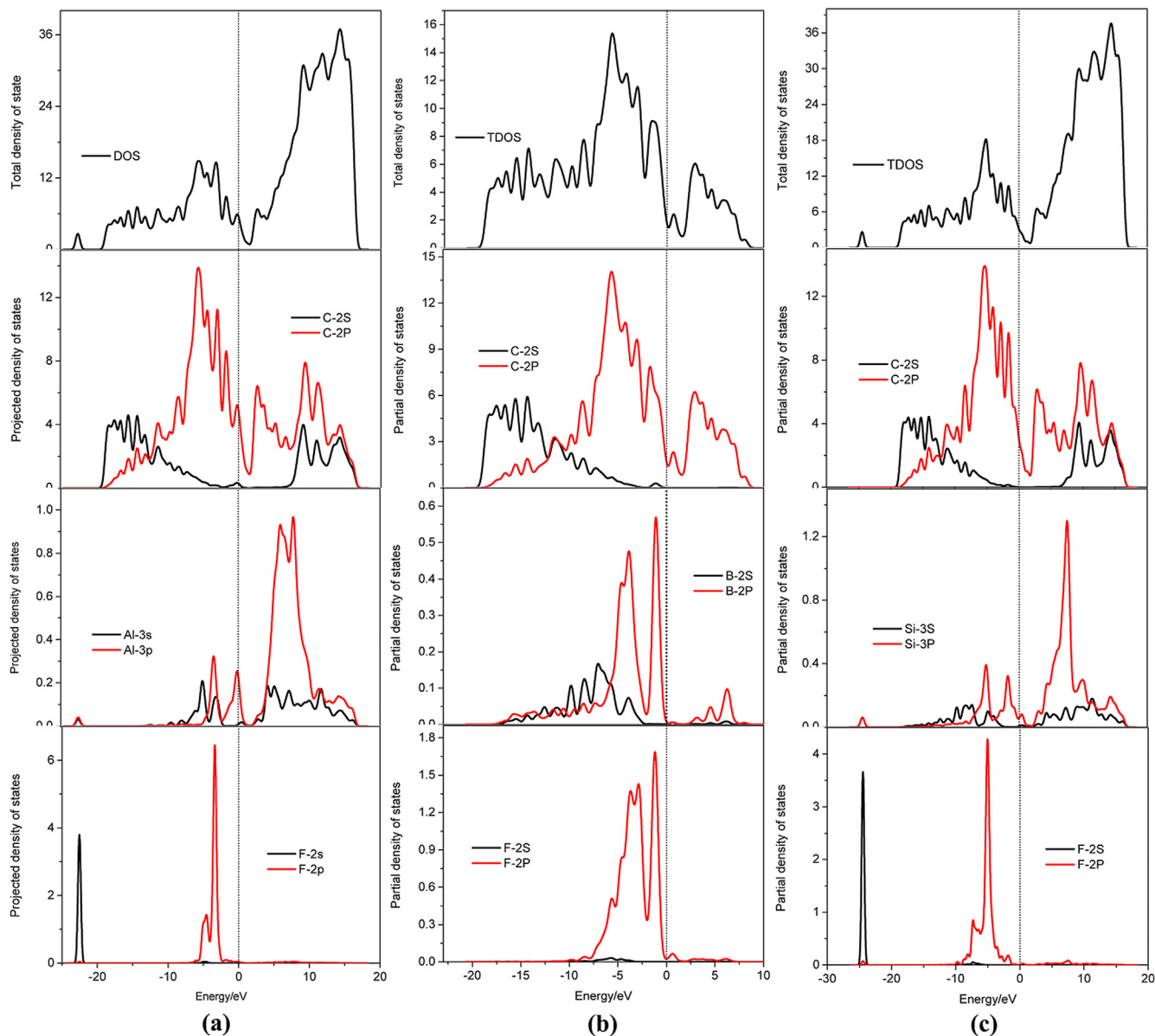


Fig. 4. The PDOS of atom for F adsorption on (a) AlG, (b) BG and (c) SiG, the dotted line represents the Fermi level.

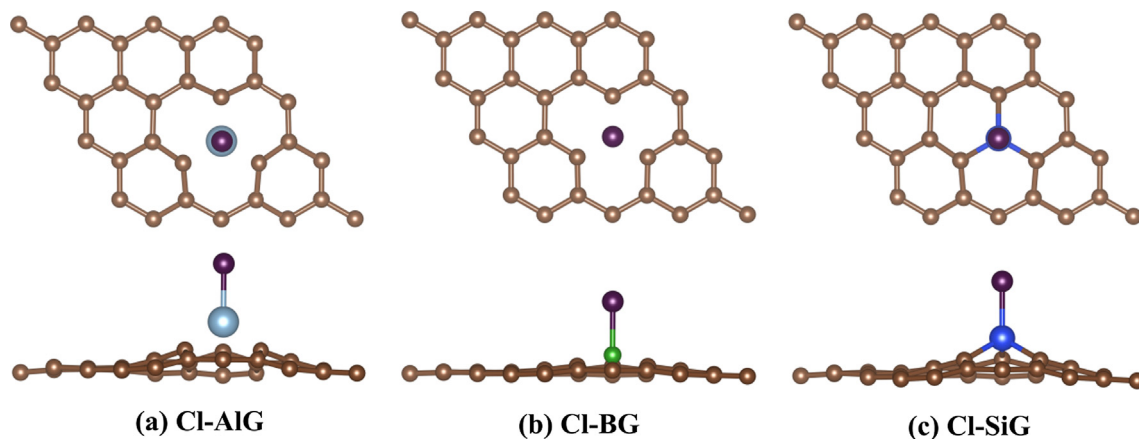


Fig. 5. The optimized configurations for Cl atom adsorbed on (a) AlG, (b) BG and (c) SiG.

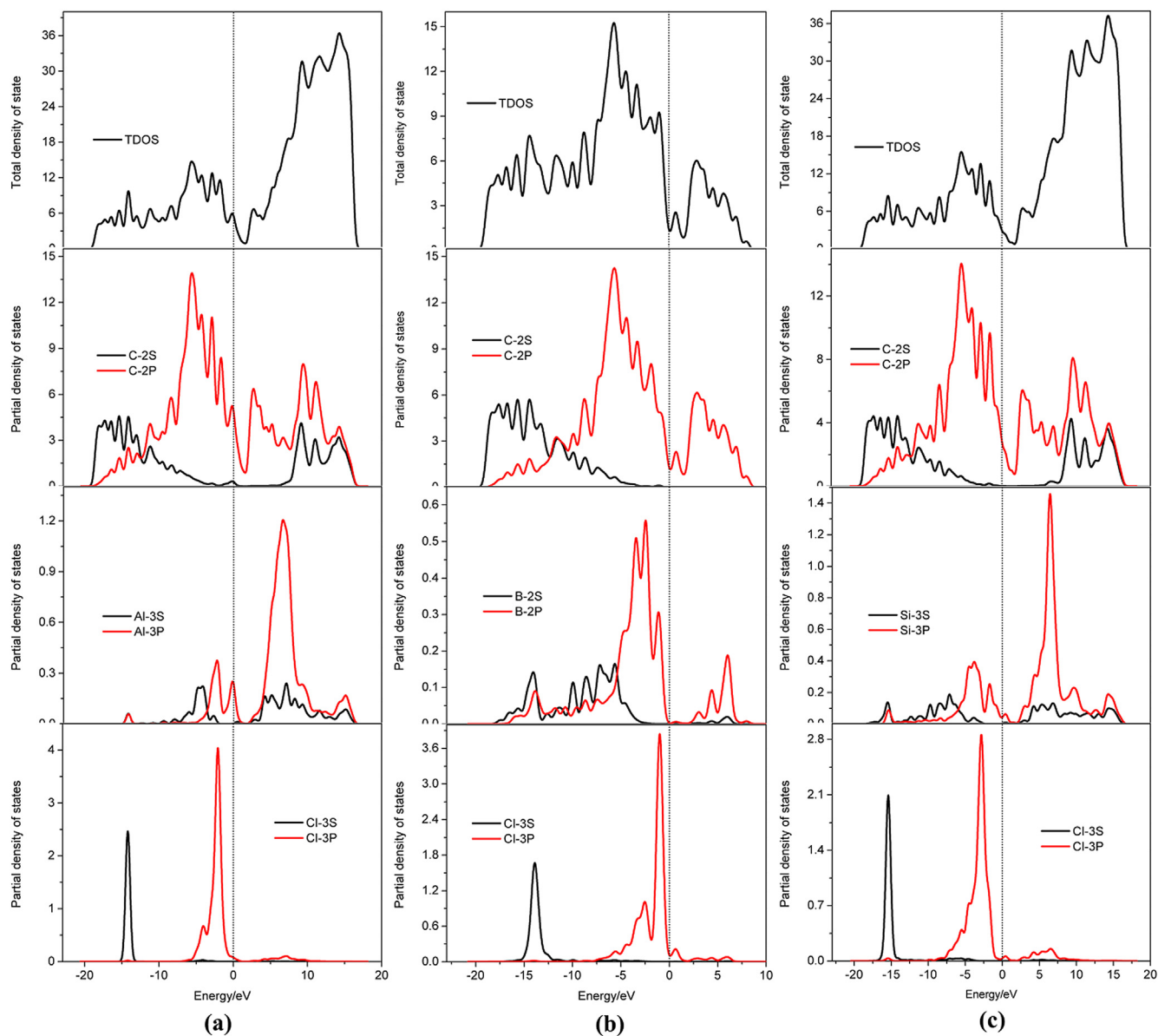


Fig. 6. The PDOS of atom for Cl adsorption on (a) AlG, (b) BG and (c) SiG, the dotted line represents the Fermi level.

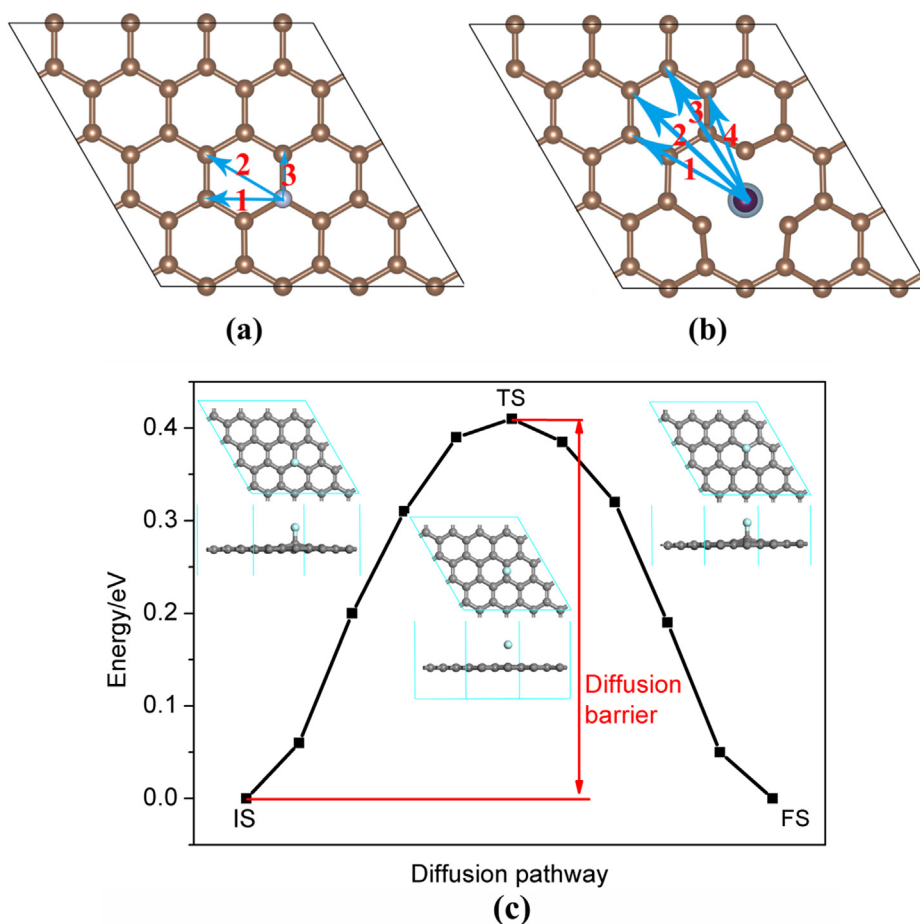


Fig. 7. The diffusion pathways for (a) F and Cl atoms on PG and defective graphene, (b) is special for Cl atom on Al-doped graphene; (c) Diffusion pathway of F atom on pristine graphene along path 3. The diffusion energy barrier is the energy difference between TS and IS, the energy of IS is set to be 0.

diffusion. In order to better understand the diffusion process and the change of diffusion barrier, the detailed diffusion pathway of F atom on PG surface along path 3 is adopted in Fig. 7c as an example, the corresponding configurations of IS, TS and FS are inserted. Fig. 7c shows that the energy of TS is 0.41 eV higher than IS, which is in line with the previous report [50]. From the diffusion barriers listed in Table 3, it is found that the diffusion barrier for pathways 1 and 3 are close to 0.4 eV, but the barrier for pathway 2 is 0.6 eV owing to the longer diffusion distance and involving more C atoms in the diffusion process. When a vacancy is introduced in graphene, the diffusion barriers are substantially increased for three pathways as compared to PG. It can be concluded that F atom prefers to diffusion along the pathways 3 with a lower barrier of 1.73 eV. For the possible pathways 1 and 2, the barriers are 3.15 eV and 2.82 eV, indicating that the vacant defect can significantly improve the thermodynamic stability of F atom adsorbed on graphene. On Al-doped graphene surface, the energy barriers for the possible pathways will further increase compared to PG and VG. The energy barriers for pathways 1 and 2 are 3.87 eV and 3.24 eV, respectively, hence, the F atom prefers to diffusion along the pathway 2. The higher energy barriers indicate that the adsorption of F atom on graphene has the stronger thermodynamic stability. However, the diffusion for pathway 3 could not happen, which can be attributed to the strong interaction between F atom and Al atom so that the F atom diffused back to the initial site automatically during the geometry optimization. This phenomenon also occurs when Cl atom adsorption on VG and AlG.

It can be seen from Table 3, the small energy barriers of Cl atom diffusion on PG surface suggest the low thermodynamic stability of Cl adsorbed on PG. After introducing a vacant defect, the diffusion for

pathways 1 and 3 will not happen because of the strong interaction between Cl atom and vacant graphene, but Cl atom prefers to diffusion along pathway 2 with a strong energy barrier of 0.61 eV, indicating the vacancy can improve the adsorption performance of Cl atom. For the system of Cl adsorption on AlG, combining the Fig. 7b we can know that the stronger interaction between Cl atom and Al-doped graphene. The diffusion for pathways 1 and 4 also not occur, and the diffusion barriers for pathways 2 and 3 are 3.27 eV and 3.11 eV, respectively. Therefore, the system of Cl adsorbed on AlG has a stronger thermodynamic stability than that adsorbed on PG and VG, suggesting the AlG can effectively capture Cl atom.

3.6. Adsorption in H₂O environment

To realize the purpose that removing F and Cl elements from aqueous system, the influence of H₂O molecules during the capture of F or Cl atom onto graphene could take into account. In this regard, some simulations including H₂O adsorption on PG (defective graphene) and F/Cl-H₂O co-adsorption on AlG were carried out, Fig. 8 shows the optimized configurations. The results show that the H₂O prefers to adsorb on the hollow site of PG with two H atoms point down to graphene and the adsorption energy reaches -0.2 eV, which is very close to the previous value of -0.221 eV [53]. The adsorption energies are -0.57 eV, -2.987 eV, -0.195 eV and -1.085 eV for H₂O-VG, H₂O-AlG, H₂O-BG and H₂O-SiG systems, respectively, which are less than the adsorption energy of F/Cl adsorption on these graphene-based materials, suggesting that F/Cl element will preferentially adsorb on these graphene-based materials in water environment. In addition, previous studies [54,55] have shown that the co-adsorption phenomenon occurs

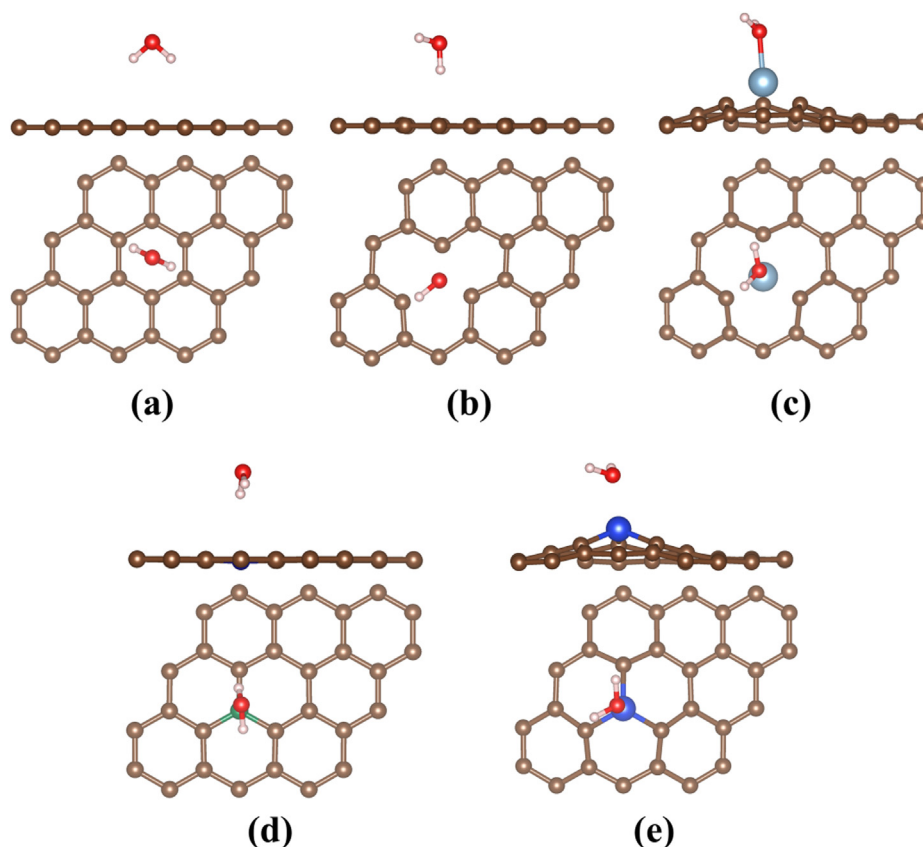


Fig. 8. The optimized configurations for H₂O adsorption on (a) PG, (b) VG, (c) AlG, (d) BG and (d) SiG.

on graphene surface. To get further insights into the effects of H₂O molecule on capturing F and Cl atoms, the co-adsorption of F or Cl atom onto AlG in the presence of one H₂O molecule was explored, and the F or Cl atom and H₂O molecule are adsorbed on the same dopant site. The stable co-adsorption configurations are shown in Fig. 9, the bond length of Al–F and Al–Cl are 1.699 Å and 2.159 Å, which are very close to the free H₂O cases (bond length of Al–F and Al–Cl are 1.679 Å and 2.123 Å, respectively), suggesting the slight weakening in the adsorption strength in the presence of H₂O molecule.

Otherwise, the adsorption energy of F or Cl atom adsorbed on AlG but after H₂O uptake (E_{ads-af}) is considered in our work, which can be defined by:

$$E_{ads-af} = E_{ads} - E_{ads(AlG-H_2O)}$$

where E_{ads} represents the total adsorption energy of the whole F/Cl–H₂O–AlG system, $E_{ads(AlG-H_2O)}$ is the adsorption energy of H₂O onto AlG. In this framework, the E_{ads-af} for F/Cl adsorbed on AlG–H₂O are –4.2 eV and –3.77 eV, respectively. The result suggests that the adsorption systems are still stable in H₂O environment.

The charge populations for these co-adsorption systems are shown in Fig. 9, the net charge transition from Al atom to F and Cl atom are 0.25e and 0.18e, which are fewer than that in the free H₂O cases. Despite this, the charge transition is larger than that in the PG cases, indicating that the stronger interaction between F/Cl and Al atom in the H₂O cases. Fig. 10 shows the PDOS of co-adsorption systems, it can be found that the H₂O-s,p orbitals hybridize with the Al-s,p orbitals at 3–10 eV and –9 to –3 eV, which indicates that the Al-doped graphene

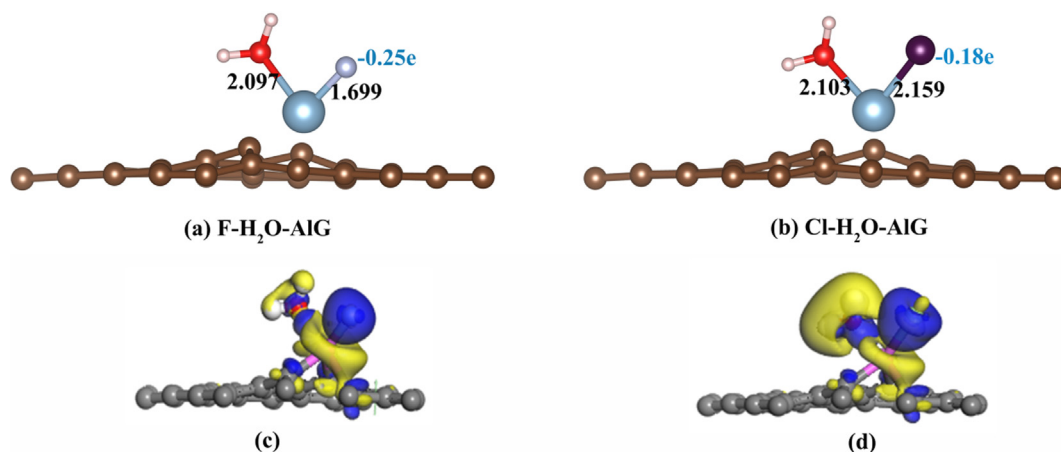


Fig. 9. Optimized stable structures of (a) the co-adsorption system of F atom and H₂O molecule; (b) the co-adsorption system of F atom and H₂O molecule; (c) and (d) are the electron density difference for F and Cl adsorbed on H₂O–AlG system.

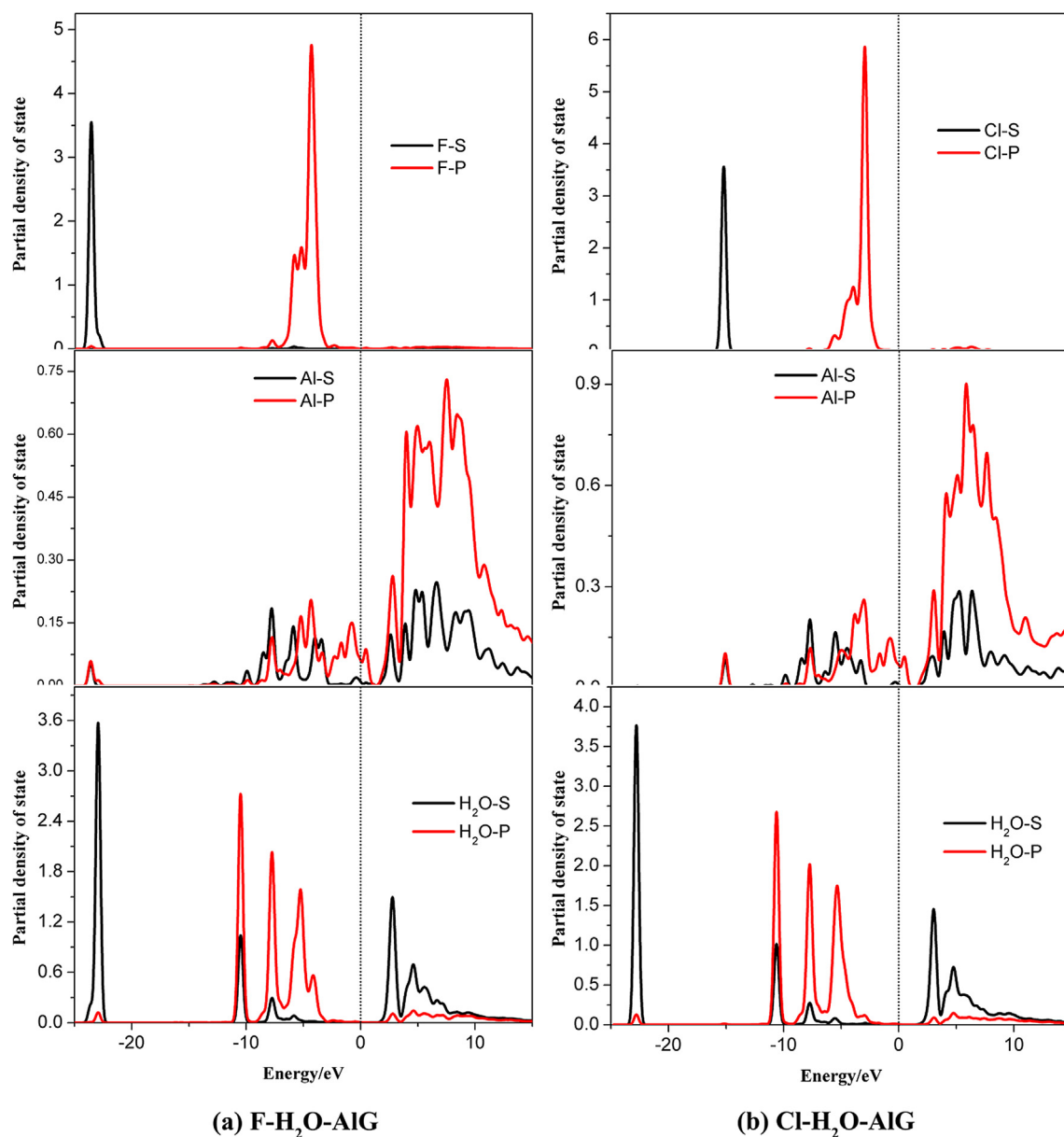


Fig. 10. Partial density of states (PDOS) plots of the (a) F-H₂O-AlG and (b) Cl-H₂O-AlG co-adsorption systems. The vertical dotted line indicates the Fermi level.

can effectively improve the adsorption performance of H₂O molecule, the result great matches with the previous study. Although it is observed that the strong hybridization between the p orbital of F (Cl) atom and the p orbital of Al atom in the range of -7 to -3 eV (-6 to -1.5 eV), and the peaks overlap for F-s (Cl-s) orbital with the Al-s,p orbitals also is occurred at about -23.5 eV (-15 eV). These results are close to the PDOS of F and Cl atoms in the free H₂O cases, suggesting the pre-adsorption of H₂O molecule has little impact on the adsorption of F and Cl. The charge density difference ($\Delta\rho(r)$) is adopted to visualize the electron transfer and the bonding characteristics between F/Cl atoms and the Al-graphene membrane. Fig. 8c and d show the 3D charge density difference of F/Cl-H₂O-AlG systems. The blue area and yellow areas represent the accumulation and depletion electrons, respectively. The results show that a large charge accumulation occurs between F or Cl atoms and Al atom. It also can be found that the obvious charge depletion area near the Al atom, confirming that the charge transfers from Al atom to F or Cl atom. The analysis of charge density difference is in agreement with the PDOS and charge population, suggesting the Al-doped graphene is a perfect candidate for

adsorbing F and Cl elements in H₂O environment.

4. Conclusions

We have conducted a study on the adsorption behavior of F and Cl atoms on pristine and defective graphene surfaces (including vacancy and the doped of Al, B and Si) by density functional theory calculations. According to the adsorption energy, charge population and PDOS, the F atom has more favourable adsorption energies than Cl on the top site of graphene. The Cl atom exhibits a slight physical adsorption behavior on PG surface. Defects in graphene, such as vacancy and dope, increase the adsorption energy significantly, thus the adsorption performance of graphene for F or Cl atom is greatly improved. Among these adsorption systems, the Al-doped graphene has the strongest adsorption ability for F and Cl atoms with the most negative adsorption energy of -7.37 eV and -4.85 eV, respectively. On the other hand, the diffusion barriers for F and Cl atoms on graphene surfaces increase with the introduce of vacancy and doped atoms, suggesting the vacant defect can strength the thermodynamic stability of the adsorption systems and the Al-doped

atom can further strengthen the thermodynamic stability. When the adsorption occurs in H₂O environment, although the Al-doped graphene increases the interaction between H₂O molecule and AlG, there are few impacts on the adsorption of F and Cl atoms. In the H₂O cases, the adsorption energy of F and Cl atoms are -4.2 eV and -3.77 eV, and the obvious charge accumulation near to F or Cl atom, indicating the strong interaction between F/Cl atom and AlG. This will localize the F or Cl atom on Al-doped graphene and therefore maintain the thermodynamic stability for adsorbing F and Cl elements in H₂O environment.

CRedit authorship contribution statement

Chaohong Guan: Methodology, Data curation, Writing - original draft. **Xiaojun Lv:** Conceptualization, Software. **Zexun Han:** Data curation. **Chang Chen:** Validation. **Zhenming Xu:** Software, Supervision. **Qingsheng Liu:** Supervision, Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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