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Density Functional Theory Study on the Influence of Cation and Anion Elements Doping on the Surface of Ti_3C_2 on the Adsorption Performance of Formaldehyde

Qianyu Guo¹, Baikang Zhu², Zhouhao Zhu¹, Mengshan Chen³ and Jian Guo^{2,*}

- ¹ School of Naval Architecture and Maritime, Zhejiang Ocean University, Zhoushan 316022, China; y1129655895@163.com (Q.G.); zhuzhouhao98@foxmail.com (Z.Z.)
- ² School of Petrochemical Engineering & Environment, Zhejiang Ocean University, Zhoushan 316022, China; zszbk@126.com
- ³ National Engineering Research Center for Marine Aquaculture, Marine Science and Technology College, Zhejiang Ocean University, Zhoushan 316022, China; mengshanchen0@163.com
- * Correspondence: 025125@zjou.edu.cn

Abstract: Based on the generalized gradient approximation of density functional theory, the geometric structure and electronic properties of the intrinsic Ti_3C_2 and Cu-, Pt-, Co-, Si-, F-, Cl- or Br-doped Ti_3C_2 are optimized, and the adsorption process of HCHO on the surface of the intrinsic Ti_3C_2 and doped Ti_3C_2 is calculated. The effects of adsorption energy, stability, DOS and doping on bond length were discussed. The results show that the adsorption energy of the intrinsic Ti_3C_2 crystal plane at the top site is the strongest, at -7.58 eV. The optimal adsorption sites of HCHO on various doping systems are Cu-Top, Pt-Top, Co-Top, Si-Hollow, Cl-Hollow, F-Bridge and Br-Hollow, respectively. Among the doped elements, anion (F, Cl, Br) doping at each adsorption site generally reduces the formaldehyde adsorption activity of the substrate; cationic doping (Cu, Pt, Co, Si) enhances the adsorption activity of the substrate for formaldehyde at most of the adsorption sites, indicating that the modification effect of anions on Ti_3C_2 is not as good as that of cations. The adsorption capacity of Si-doped Ti_3C_2 for formaldehyde was significantly improved. Compared with the intrinsic Ti_3C_2 crystal plane at the same adsorption site, the adsorption activity of HCHO was improved, and the highest adsorption energy was -8.09 eV.

Keywords: Ti₃C₂; adsorption; formaldehyde; density functional theory

1. Introduction

Energy shortage and environmental pollution are two major global challenges facing mankind today [1]. Air pollution is closely related to human health and has attracted considerable attention in the past few years. Formaldehyde has many uses in industry. Commonly used boards, paints, carpets and wallpapers in interior decoration release formaldehyde. The incomplete combustion of fuel and tobacco leaves also releases formaldehyde. In medicine, formaldehyde is often used as an antiseptic and disinfectant. The main ways humans are exposed to formaldehyde are inhalation through the respiratory tract, ingestion through the mouth and contact through the skin. Formaldehyde poisoning can cause congestion, inflammation of the conjunctiva, skin allergies, nasopharyngeal discomfort, cough, acute and chronic bronchitis and other respiratory diseases. It can also cause nausea, vomiting and gastrointestinal disorders. Therefore, removing formaldehyde is a necessary measure to reduce air pollution and protect human health.

At present, to deal with toxic and harmful gases, the adsorption method and the catalytic oxidation method are mainly used. Su Yuetan et al. used density functional theory chemical calculation methods to study the adsorption performance of formaldehyde molecules on C_2N and Al-modified C_2N . The results show that the modification



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). of Al atoms changes the nearby electronic structure, thereby changing the chemical and physical behaviors of the modified Al atoms, making them act as a bridge connecting the formaldehyde molecules and the C_2N layer, which enhances the adsorption capacity [2]. Hong-ping Zhang et al. studied the influence of doped Ti or N atoms on the interaction of these gases with graphene through density functional theory calculations. The analysis show that doped Ti atoms can greatly improve the interaction between gas molecules and graphene [3]. Zhijian Liu et al. found that the doping of N atoms into the graphene plane can significantly increase the adsorption strength of formaldehyde by adjusting the charge of the metal atoms. According to the analysis of geometric structure, electron transfer and density of states (DOS), the adsorption of formaldehyde belongs to a stable chemisorption, which is a combined action of electron transfer and hybridization effect [4]. Zhenzhong Zhang et al. used density functional theory to calculate the influence of Pd modification on the sensitivity of ZnO nanotubes to formaldehyde (HCHO) gas, and the results indicated that electron donation and back-donation processes between the reactants and the ZnO surface were the main reasons for the enhanced adsorption to formaldehyde [5]. Xi Zhou et al. studied the adsorption of formaldehyde (HCHO) molecules on pure nanotube and Pd-doped, Si-doped single-walled carbon nanotubes (SWCNT) by density functional theory (DFT) method; the results show that conductivities of CNTs with HCHO molecule adsorption according to their energy gaps between HOMO and LUMO in frontier molecular orbital are, in decreasing order, Pd-doped CNT, Si-doped CNT and pure CNT [6]. Navaratnarajah Kuganathan et al. studied the effect of graphene and graphene doped with B, Si and N surfaces to remove Pb atoms by using density functional theory calculations, and the results showed that the bonding of Si-doped graphene surfaces was significantly enhanced [7]. Hao Luo et al. used first-principles calculations to study the adsorption of NO₂ and NH3 gas molecules on Al, Si and P-doped single-layer MoS₂. The results showed that Al-, Si- and P-doped single-layer MoS₂ increased the NO₂ and NH₃ structural stability [8]. B. Zhao et al. used first-principles calculations to explore the interaction between H₂O molecules and a single-layer MoS₂ surface doped with B and Si atoms, and the results showed that the introduction of impurity, in the form of B/Si atoms, can destroy the single-layer MoS_2 (001) surface. The chemical insensitivity of this product promotes the capture of H_2O molecules [9]. Xiaoli Jiang et al. stated in the article that, due to the synergy of different dopants, proper anion-cation double doping can greatly promote the performance of OER electrocatalysts [10]. Wenpei Kang et al. found that, for the possible kinetic mechanism, the ultra-fast pseudo capacitance contribution and higher adsorption energy caused by anion doping may promote its high-rate sodium storage capacity [11]. Yinlong Zhu et al. revealed the effect of Cl-anion doping in perovskite on the improvement of OER performance; the results demonstrate that proper Cl doping at the oxygen site of LaFeO₃ (LFO) perovskite can induce multiple favorable characteristics for catalyzing the OER, including rich oxygen vacancies, increased electrical conductivity and enhanced Fe-O covalency. [12]. Zaheer Ahmed Ujjan et al. found that nonmetal doping via S and Cl significantly enhanced the photocatalytic properties of ZnO towards methylene blue (MB), due to the high density of active sites and the decreased charge recombination rate of electron-hole pairs [13]. These fruitful studies showed that doping with various elements can change the overall electronic structure of the material, thereby achieving the purpose of improving the material properties [2–19].

Zhou Junhui et al. used the first-principles calculation method to study the adsorption and catalytic oxidation performance of formaldehyde molecules on the surface of singleatom catalysts (monolayer MXene-Ti₃C₂ modified with Ti atoms). Ti₃C₂ can automatically dissociate into CO molecules, and two H atoms and activated O atoms form two *OH groups [20]. Yang Jianhui et al.'s research on the surface adsorption activity of Ti₃C₂ is helpful in understanding their surface characteristics. First-principles calculation studies have shown that Ti₂C and Ti₃C₂ have strong adsorption activities for O, OH and F [21]. Studies by Yujuan Zhang et al. have shown that Ti₃C₂ nanosheets can provide ideal recyclable materials for indoor formaldehyde removal and, at the same time, promote formaldehyde desorption at higher temperatures [22]. Qui Thanh Hoai Ta et al. used density functional theory calculations to show that Si atoms may promote the NO₂ adsorption process. The results of this work may highlight the potential of Si@TiO₂/Ti₃C₂T_X heterostructures as multifunctional nanomaterials [23].

The research results of many scholars have shown that Ti_3C_2 MXene material is a potential adsorption material for harmful gases, and the performance of detecting, capturing and catalyzing organic vapor pollutants can be improved by doping it with various anions or cations [20–31].

2. Calculation Method and Structural Model

The calculation is done using the Vienna Ab-initio Simulation Package (VASP 5.5.4) software based on density functional theory [32]. Among them, the energy exchange correlation energy function uses the PBE (Perdew–Burke–Ernzerh) function of generalized gradient approximation (GGA) [33], and the interaction potential between valence electrons and ions uses the conjugated plane wave pseudopotential method to describe it.

The model used in the study is the Ti₃C₂ (001) surface, with a $3 \times 3 \times 1$ expanded cell as the substrate for doping and adsorption [20,21]. The surface was simulated using multiple atomic layers plus a 15 Å vacuum layer. The 15 Å vacuum layer ensures that there is no interaction between adjacent plates in the z-axis direction. The lattice parameter is $3a0 \times 3a0 \times 20$, where a0 is the lattice length obtained by energy optimization. The calculated a0 is 0.311 nm, which is in good agreement with the results of previous studies [34,35].

In the selection of the doping position, the doping of Cu atoms is used as the verification, because the Ti_3C_2 (001) of the 5-layer structure is symmetrical on the upper and lower sides, and only the upper 3 layers are required to be verified. On the Ti_3C_2 (001) surface of the 5-layer structure, one Ti atom was replaced by Cu atom in the first and third layers, and one C atom was replaced by Cu atom in the second layer. After structure optimization, it was found that the energies of doping in layers 1 to 3 were -387.96 eV, -257.50 eV, and -383.81 eV, respectively. When the first layer was doped, the energy was lower and the structure was more stable. Furthermore, based on many studies, the first layer of the Ti_3C_2 (001) plane is generally selected for doping.

The cutoff energy used for structural optimization and calculations was 500 eV. When the structure is optimized, the next three layers of atoms are fixed. The atomic relaxation uses a conjugate gradient algorithm to optimize atomic positions with a maximum relaxation step of 500. In terms of the iterative loop convergence criterion for electrons, EDIFF is set to 1×10^{-5} eV. The value of K-point is $3 \times 3 \times 1$ [21]. After the structure optimization is completed, the electronic structure information of each system is calculated to discuss the adsorption stability and adsorption mechanism of each adsorption system.

The adsorption energy of HCHO molecule is calculated by the following formula:

$$E_{ads} = E_{total} - E_{doping \ atom/slab} - E_{HCHO}$$
(1)

In the formula: E_{total} represents the total energy of the system after adsorption; $E_{doping atom/slab}$ represents the energy of the intrinsic Ti_3C_2 surface before adsorption or the Ti_3C_2 surface after doping, and E_{HCHO} represents the energy of the free gas molecule HCHO. E_{ads} is a negative value, indicating that energy is released during the adsorption process, and the more negative its value, the stronger the adsorption.

3. Results and Discussion

3.1. The Adsorption Characteristics of HCHO on the Surface of Ti_3C_2

In order to find the best adsorption site on the Ti_3C_2 surface, three possible preliminary adsorption methods were designed in the study, as shown in Figure 1. The first method of adsorption is to adsorb formaldehyde molecules perpendicularly to the titanium atoms in the center of the Ti_3C_2 surface; the second method is to place formaldehyde molecules in parallel on the gaps between the three titanium atoms; the third method of adsorption is to Top Hollow Bridge

adsorb formaldehyde molecules on the gap between the three titanium atoms. The plane is vertically adsorbed on the bridge between two titanium atoms.

Figure 1. The adsorption configuration of HCHO at different sites on the surface of Ti_3C_2 .

It is found from Table 1 that, when formaldehyde is adsorbed on the top site on the Ti_3C_2 surface, the two C–H bonds change from 1.12 Å to 1.41 Å and 1.41 Å after adsorption, which is larger than the sum of the covalent radii of C and H (1.09 Å). There is a tendency to dissociate, and its adsorption energy is -7.58 eV. When formaldehyde is adsorbed at the hollow site, the C–O bond length of formaldehyde is reduced by 0.12 Å compared to the bond length when it is not adsorbed, while the two C–H bonds increase by 0.30 Å, indicating that the C–O bond is strengthened after formaldehyde is adsorbed on the Ti_3C_2 surface, while the C–H bond is activated and its adsorption energy is -7.54 eV. When formaldehyde is adsorbed on the bridge site, the formaldehyde is decomposed into oxygen atoms and methylene groups (–CH₂), and the oxygen atoms are adsorbed between the three titanium atoms of the substrate. The two C–H bonds increase by 0.06 Å, and the two C–H bonds do not change a lot, and the adsorption energy is -5.42 eV. By comparing the three adsorption methods, it is found that the system energy is the lowest when formaldehyde is adsorbed at the top site, and the adsorption energy produced is also the largest, which is the best adsorption method for formaldehyde on the intrinsic Ti_3C_2 crystal surface.

Table 1. System energy, adsorption energy and related parameters of the three forms of formaldehyde adsorption on the intrinsic Ti_3C_2 surface.

Adsorption Method	r _{C-O} /Å	$r_{C-H}^1/\text{\AA}$	$r_{C-H}^2/\text{\AA}$	E _{total} /eV	E _{ads} /eV
Тор	1.09	1.41	1.41	-421.32	-7.58
Hollow	1.10	1.42	1.41	-421.29	-7.55
Bridge	-	1.18	1.18	-419.16	-5.42

In order to further understand the mechanism of formaldehyde adsorption and dissociation on Ti_3C_2 surface, this paper analyzes the electronic structure of the most stable adsorption position from the charge density distribution [36]. As shown in Figure 2, the yellow area around the atom indicates that the charge density of the bond area increases, and the blue area indicates that the charge density of the bond area decreases. In addition, the differential charge analysis method is used to calculate the charge of each atom in the adsorption system. It can be seen from Figure 2 that, when formaldehyde is stably adsorbed at each adsorption site on the Ti_3C_2 surface, electron transfer occurs between the oxygen atom and the hydrogen atom. The oxygen atom loses electrons, while the two hydrogen atoms gain electrons, causing the two hydrogen atoms to have a tendency to be catalytically decomposed. When formaldehyde is adsorbed on the top and hollow sites, the C atom of formaldehyde and the Ti atom of the substrate generate Ti–C bonds during the electron transfer process. When formaldehyde is stably adsorbed at the bridge site, the carbon and oxygen atoms in the adsorption system lose part of their electrons, the charge density of the Ti–O bond area decreases, and the Ti–O bond is formed.



Figure 2. Side and top views of the differential charge density plots of the stable adsorption configuration of HCHO on the Ti_3C_2 surface. (Isosurface value is 0.002 e/Å³).

3.2. The Adsorption of Formaldehyde by Element-Doped Ti_3C_2

3.2.1. Doping System Structure Optimization

Replacing the central titanium atom on the Ti_3C_2 surface with Cu, Pt, Co, Si, F, Cl or Br, obtained after structure optimization: Cu- Ti_3C_2 surface, Pt- Ti_3C_2 surface, Co- Ti_3C_2 surface, Si- Ti_3C_2 surface, Cl- Ti_3C_2 surface, F- Ti_3C_2 surface and Br- Ti_3C_2 surface, as shown in Figure 3.



Figure 3. (a) Intrinsic Ti_3C_2 relaxation side view, (b) Cu-doped Ti_3C_2 configuration relaxation side view, (c) Pt-doped Ti_3C_2 configuration relaxation side view, (d) Co-doped Ti_3C_2 configuration relaxation side view, (e) Si-doped Ti_3C_2 configuration relaxation side view, (f) F-doped Ti_3C_2 configuration relaxation side view, (g) Cl-doped Ti_3C_2 configuration relaxation side view, (h) side view of the relaxation of the Br-doped Ti_3C_2 configuration.

After the structures of Cu-Ti₃C₂ surface, Pt-Ti₃C₂ surface and Co-Ti₃C₂ surface are optimized, and the three neighboring carbon atoms around the top doping atom all move to the center of the doping atom. For example, Cu–C bond's length is shortened from 2.08 Å to 2.02 Å; the surface dopant insertion energy of the three is -386.14 eV, -389.03 eV and -383.61 eV, respectively. The Pt-doped surface has the lowest energy and is the most stable, followed by the Cu-doped. The Cl-Ti₃C₂ surface, the F-Ti₃C₂ surface and the Br-Ti₃C₂ surface doped with non-metal anions, after the structure optimization, the top dopant atoms protrude above the surface, and the surface dopant insertion energy is -385.11 eV, -385.52 eV, and -384.91 eV; the energy of the three as well as the optimized structure is similar, and the change trend is the same, indicating that non-metal anion doping may have a consistent aspect for the modification of Ti₃C₂ substrate. The surface of Si-Ti₃C₂ doped with non-metallic cations is relatively special, and the structural change is consistent with the former cation doping. The three C atoms around Si atoms on the surface of Si-Ti₃C₂ move to the center of the Si atom, and the Si–C bond length is 2.07 Å is shortened to 1.94 Å, and its surface dopant insertion energy is -388.34 eV.

3.2.2. Adsorption Characteristics of Doped System to HCHO

In order to study the influence of metal atoms and non-metal atom doping on the adsorption of formaldehyde molecule and to compare it with the intrinsic Ti_3C_2 , an adsorption site consistent with Figure 1 was adopted, and three possible adsorption methods were designed for the top site, bridge site and gap site. Ti_3C_2 was doped with Cu, Pt, Co, Si, F, Cl and Br atoms to optimize the structure. The bond length changes of HCHO in different adsorption systems and the adsorption energy of HCHO are shown in Table 2. The comparison of the adsorption energy of each adsorption system is shown in Figure 4.

Adsorption Site	Adsorption of Basal	E _{total} /eV	E _{substrate} /eV	r _{C-O} /Å	$r^1_{C-H}/{\rm \AA}$	$r_{C-H}^2/{ m \AA}$	E _{ads} /eV
Тор	Ti_3C_2	-421.32	-391.61	1.09	1.41	1.41	-7.58
	Cu-Ti ₃ C ₂	-416.26	-386.09	1.10	1.42	1.43	-8.04
	Pt-Ti ₃ C ₂	-416.23	-389.03	-	1.13	1.11	-5.07
	Co-Ti ₃ C ₂	-412.73	-389.96	-	1.13	1.11	-0.64
	Si-Ti ₃ C ₂	-418.21	-388.34	1.09	1.38	1.43	-7.74
	F-Ti ₃ C ₂	-415.40	-385.52	-	1.10	1.13	-7.75
	Cl-Ti ₃ C ₂	-413.81	-385.11	-	1.10	1.12	-6.57
	Br-Ti ₃ C ₂	-413.23	-384.92	-	1.10	1.12	-6.18
Hollow	Ti ₃ C ₂	-421.28	-391.61	1.10	1.42	1.41	-7.54
	Cu-Ti ₃ C ₂	-414.88	-386.09	1.10	1.30	1.28	-6.66
	Pt-Ti ₃ C ₂	-414.03	-389.04	-	1.11	1.13	-2.86
	$Co-Ti_3C_2$	-411.83	-389.95	-	1.11	1.11	0.25
	Si-Ti ₃ C ₂	-418.56	-388.34	1.10	1.43	1.43	-8.09
	F-Ti ₃ C ₂	-412.09	-385.53	1.55	1.10	1.10	-4.43
	Cl-Ti ₃ C ₂	-414.62	-385.12	-	1.11	1.12	-7.37
	Br-Ti ₃ C ₂	-413.23	-384.92	-	1.13	1.10	-6.18
Bridge	Ti ₃ C ₂	-419.16	-391.61	-	1.18	1.18	-5.42
	Cu-Ti ₃ C ₂	-413.67	-386.09	-	1.18	1.18	-5.45
	Pt-Ti ₃ C ₂	-413.84	-389.03	1.90	1.10	1.09	-2.68
	$Co-Ti_3C_2$	-412.33	-389.95	-	1.13	1.11	-0.25
	Si-Ti ₃ C ₂	-415.92	-388.34	-	1.18	1.18	-5.45
	F-Ti ₃ C ₂	-415.57	-385.52	-	1.11	1.13	-7.92
	Cl-Ti ₃ C ₂	-414.16	-385.11	-	1.10	1.13	-6.92
	Br-Ti ₃ C ₂	-408.43	-384.92	-	1.09	1.09	-1.38

Table 2. Energy and adsorption energy of different adsorption systems.



Figure 4. Comparison of the formaldehyde adsorption energy of various doping systems.

As it can be seen from Table 2, among all metal cations (Cu, Pt, Co), copper doping had the best modification effect on Ti_3C_2 , improving the adsorption effect of the Ti_3C_2 substrate on formaldehyde at the top and bridge sites, and the adsorption energy increased by 0.46 eV and 0.03 eV, respectively. In the hollow position, it decreased by 0.8802 eV. Among the nonmetallic anions (F, Cl, Br), fluorine doping had the best modification effect on Ti_3C_2 and improved the adsorption capacity of the Ti_3C_2 substrate to formaldehyde at the top and bridge sites by 0.17 eV and 2.50 eV, respectively, and decreased by 3.11 eV at the hollow site. Among all the doped elements, only silicon doping significantly increased the adsorption energy of formaldehyde at the three adsorption sites on Ti_3C_2 substrate and the adsorption energy at the top. Hollow and bridge sites increased by 0.17 eV, 0.55 eV and 0.03 eV, respectively. In addition, only chlorine-doped Ti_3C_2 improved by 1.50 eV at the bridge site, while Ti_3C_2 doped with other elements had poor effects at all adsorption sites. Based on the judgment of adsorption energy, it can be known that Cu, Si and F have better modification effect on Ti_3C_2 substrate. Further research can be carried out by doping Ti_3C_2 with these three elements.

When formaldehyde adsorbed stably on the top position of the Cu-doped Ti_3C_2 surface, the two H–C bond lengths increased by 0.01 Å and 0.02 Å, respectively, and the C–O bond lengths increased by 0.01 Å. When formaldehyde adsorbed stably on the bridge site of Cu-doped Ti_3C_2 , formaldehyde decomposed into oxygen atoms and methylene group (–CH2). When formaldehyde adsorbed at the hollow position on Cu-doped Ti_3C_2 , the H–C bond length was shortened by 0.12 A and 0.14 A, respectively, and the C–O bond length was basically unchanged. When formaldehyde was stably adsorbed on the surface of F-doped Ti_3C_2 , it decomposed into oxygen atoms and methylene group (-CH₂) at two positions (top and bridge) where the adsorption energy increased. At the hollow site, the H–C bond lengths of formaldehyde were shortened by 0.32 A and 0.31 A, respectively, and the C–O bond lengths increased by 0.45 Å. When formaldehyde was stably adsorbed on the top position of the Si-doped Ti_3C_2 surface, one H–C bond was shortened by 0.03 A, and the other H–C bond increased by 0.02 Å, and the C–O bond length was basically unchanged. When formaldehyde was stably adsorbed at hollow sites on the Si-doped Ti_3C_2 surface, the H–C bond lengths increased by 0.01 Å and 0.02 Å, respectively, and the C–O bond length length was basically unchanged. When formaldehyde adsorbed stably on the bridge site of Si-doped Ti_3C_2 , formaldehyde was catalyzed to decompose into methylene (–CH₂).

In order to study the adsorption mechanism of metal atom doping and non-metal atom doping on formaldehyde, the density of states and differential charges of the metal cation Cu atom, non-metal anion F atom and non-metal cation Si atom doping system were calculated.

Differential charge density can be used to analyze the electron rearrangement of the system after adsorption [37], as shown in Figure 5. Yellow represents electron enrichment, and blue represents electron reduction. It can be seen that, in the Cu-Ti₃C₂-HCHO system, an oxygen atom loses part of its electrons at three adsorption sites, and a copper atom and two hydrogen atoms gain part of their electrons, and formaldehyde and the substrate produce electron transfer. Formaldehyde is mainly chemisorbed at the top and hollow sites, and decomposed at the bridge sites. In the Si-Ti₃C₂-HCHO system, oxygen also loses some of its electrons and the substrate occurs between the top and bridge sites. At the bridge site, formaldehyde is also decomposed and oxygen atoms are adsorbed on the substrate. At each adsorption site of the F-Ti₃C₂-HCHO system, an oxygen atom loses some electrons and a fluorine atom gains some electrons. The F atom moves from the center of the Ti₃C₂ surface up to the surface and bonds with the Ti atom.



Figure 5. Differential charge density diagram of HCHO at different adsorption sites on Cu-Ti₃C₂, Si-Ti₃C₂ and F-Ti₃C₂ surfaces. (Iso Ti₃C₂surface value is 0.002 e/Å³).

In order to further understand the change of Ti_3C_2 doped with Cu, Si and F elements, the density of states of intrinsic Ti_3C_2 and doped Ti_3C_2 were compared and analyzed. It can be seen from Figure 6 that Cu-, Si- and F-doped elements significantly changed the electronic structure of the intrinsic Ti_3C_2 crystal plane. Compared with the intrinsic state density of Ti_3C_2 , the peak of the state density of Cu- and Si-doped Ti_3C_2 -adsorbed formaldehyde shifted to the lower-energy region by 0.2 eV~0.5 eV as a whole and the peak also decreased, indicating that the introduction of Cu or Si elements made the adsorption of Ti_3C_2 substrate for formaldehyde tend to be more stable. The overall peak of the state density of formaldehyde adsorbed by F-doped Ti_3C_2 migrated to the high-energy region, about 0.2 eV~0.5 eV, and decreased as well, indicating that the stability of the Ti_3C_2 substrate was reduced by F. The results of state density analysis showed that, compared with intrinsic Ti_3C_2 , F-doped Ti_3C_2 adsorbed formaldehyde at the top and bridge sites and its adsorption energy increased, but the overall structure was not stable enough, which was also reflected in the structure optimization and differential charge. The adsorption energy of formaldehyde on the Cu-doped Ti_3C_2 hollow site decreased compared with the intrinsic Ti_3C_2 , but the structural system tended to be stable. Si-doped Ti_3C_2 not only enhanced the adsorption energy region, so its system structure was the most stable among all of the doping systems studied.



(a) The total state density of HCHO adsorbed by intrinsic Ti₃C₂ and Cu- Ti₃C₂, Si- Ti₃C₂ and F-Ti₃C₂ at the top site.



(**b**) The total state density of HCHO adsorbed by intrinsic Ti₃C₂ and Cu-Ti₃C₂, Si-Ti₃C₂ and F-Ti₃C₂ at the hollow site.



(c) The total state density of HCHO adsorbed by intrinsic Ti3C2 and Cu-Ti₃C₂, Si-Ti₃C₂ and F-Ti₃C₂ at the bridge site.

Figure 6. The state density of each adsorption system.

Figure 7 compares electron local density maps of formaldehyde adsorption by intrinsic Ti_3C_2 and Cu-, Si- or F-doped Ti_3C_2 . Electron localization function (ELF) is often used to determine the chemical bonding properties among atoms, and its value ranges from 0 to 1; when the electrons are completely localized or there are no electrons, the ELF is 0; when the ELF is 0.5, it indicates that a charge distribution similar to an electron gas is formed among atoms, which is a typical metallic bond; when the electrons are completely localized, that is, when the ELF is 1, the typical covalent bonding among atoms is shown [38]. Figure 7 shows that a small amount of Cu, Si or F doping has little effect on the chemical bond environment of Ti_3C_2 , and the electrons of Ti atoms are completely delocalized, which shows that the main effect of doping Cu, Si or F is to improve the adsorption and decomposition of formaldehyde, rather than direct strong adsorption of formaldehyde. Taken together, these theoretical studies suggest that Cu, Si and F additions enhance the electron delocalization of formaldehyde.



(c) Bridge site adsorption of formaldehyde.

Figure 7. Electron localization function.

4. Conclusions

The adsorption of formaldehyde on Ti_3C_2 and Cu-, Pt-, Co-, Si-, F-, Cl- and Br-doped Ti_3C_2 was studied by density functional theory. The results show that, in the metal cations, Cu, Pt and Co, only the same Cu element at the two adsorption sites improved the adsorption capacity of the Ti_3C_2 substrate for formaldehyde. Among the nonmetallic anions Cl, F and Br, only F improved the adsorption capacity of the substrate to formaldehyde

at the two adsorption sites. In addition, non-metallic cation Si doping enhanced the adsorption performance of formaldehyde on the substrate at three adsorption sites, and the system structure was the most stable. In general, cationic doping is better than anionic doping. These conclusions provide a theoretical reference for designing new formaldehyde gas-detection materials.

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