



Article Cu_{γ} ($\gamma = 1-3$)-Modified MoS₂ Monolayer as a Gas Sensor for Detecting C₄F₇N and Its Decomposition Components

Changyun Li^{1,*}, Peigang Chen¹, Yongjin Yu¹ and Chuanyang Li²

- ¹ College of Electrical Engineering and Automation, Shandong University of Science and Technology, Qingdao 266590, China
- ² Department of Electrical Engineering, Tsinghua University, Beijing 100084, China
- * Correspondence: sdlcyee@sdust.edu.cn

Abstract: Perfluorinated isobutyronitrile (C₄F₇N) is favored in electrical engineering because it is an environmentally friendly gas-insulating medium with a low greenhouse effect. Unfortunately, under the influence of electricity and over-heating, its decomposition results in the deterioration of its insulating properties, which potentially leads to partial discharge or even gas breakdown. In this paper, the adsorption behavior of C₄F₇N gas and its toxic decomposition product, acetonitrile (C₂N₂), on MoS₂ surfaces doped with small copper clusters was investigated by calculating the adsorption energy and density of states, etc. The effects of multiple initial adsorption positions as well as externally applied electric fields were also taken into account. The results depict that the maximum adsorption energy of C₄F₇N on the Cu_{γ} ($\gamma = 1-3$)-MoS₂ surface gradually decreases with the increase in γ . The Cu₃-modified MoS₂ is most suitable for use as a resistive-based gas-sensitive sensor substrate. This paper provides the theoretical foundation for the maintenance of future power equipment with environmentally friendly insulating gas.

Keywords: first principle; C₄F₇N decomposition components; gas sensors; adsorption; applied electric field

1. Introduction

Sulfur hexafluoride (SF₆) gas, due to its excellent insulating properties such as its high dielectric strength and arc quenching performance, is mostly and widely used in Gas-insulated Switchgear (GIS), Gas-insulated Line (GIL), Gas-insulated Cabinet (GIC) and other gas-insulated power equipment in electric power transmission and distribution projects. However, SF₆ is a powerful greenhouse gas with about 23,500 times the global warming potential (GWP) of that of CO_2 [1]. The green development of global electrical engineering is an inevitable requirement in sake of environmental protection, which required that the use of SF₆ must be reduced. To meet both the high dielectric strength and environmental protection demands, C₄F₇N, with a GWP of 2090 and a dielectric strength two times higher than that of SF₆, was found by the 3M company in 2019. The first GIC using C₄F₇N gas was developed by the China Institute of Electrical Technology in the same year.

However, in the operating of electrical equipment, C_4F_7N is subjected to electrical and thermal stresses, resulting in the degradation of the insulating gas. By monitoring the composition and content of the pyrolysis product, the insulating property of C_4F_7N can be characterized. Hence, to ensure the safe and stable operation of C_4F_7N gas-insulated electric power equipment, it is necessary to detect the decomposition products of C_4F_7N in real time so as to diagnose early insulation faults. To achieve this goal, it is necessary to clarify the byproduct components of C_4F_7N and master the fundamental detection principle of each component.

G.Q. Zhang et al. investigated the partial discharge (PD) decomposition characteristics of C_4F_7N mixed with CO_2 with a pin-plate discharge test model, and the results showed



Citation: Li, C.; Chen, P.; Yu, Y.; Li, C. Cu_{γ} ($\gamma = 1-3$)-Modified MoS₂ Monolayer as a Gas Sensor for Detecting C₄F₇N and Its Decomposition Components. *Nanomaterials* **2022**, *12*, 2829. https://doi.org/10.3390/ nano12162829

Academic Editors: Fabrizio Pirri and Antonella Macagnano

Received: 11 July 2022 Accepted: 13 August 2022 Published: 17 August 2022

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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/). that the pyrolysis components of C₄F₇N mainly contained C₂F₆, C₂F₄, C₃F₆, CF₃CN and C₂N₂ [2]. X. Zhang et al. conducted a 96 h PD decomposition test on C₄F₇N/CO₂ gas mixtures using a needle-plate electrode and clarified that the characteristic decomposition components include CO, CF₄, C₂F₆, CF₃CN, C₂N₂ and COF₂ [3]. Further, they showed that the contents of CO, CF₄, C₂F₆, CF₃CN and C₂N₂ were significantly higher than those of other components. In 2017, B. Radisavljevic et al. investigated the decomposition characteristics of 9.5% C₄F₇N-9.5% O₂-81% CO₂ gas mixtures under arc discharge conditions and found that the decomposition of C₄F₇N mainly incorporated CO, CF₄, C₂F₄, CF₃CN, C₂F₅CN and C₂N₂ [4]. Furthermore, the particles produced by the decomposition of C₄F₇N under arc discharge conditions were not recoverable. Q.D. Huang et al. studied the overheated decomposition properties of a C₄F₇N/CO₂/O₂ gas mixture and found that its main decomposition product also contained C₂N₂ gas [5]. These results suggest that C₂N₂ can be used as a characteristic component of C₄F₇N decomposition that reacts to the aging state of C₄F₇N insulation under electrical and thermal faults.

 C_2N_2 is highly toxic and readily reduced to cyanide. A. Beroual and C. Preve assessed the occupational exposure limit of 10 μ L/L (8 h) with an inhalation test in rats and observed that the prolonged inhalation of C_2N_2 caused a break in the mitochondrial transfer chain of the rat cells and caused respiratory and visual irritation [6,7]. Meanwhile, it revealed that a break in the mitochondrial transfer chain of the rat cells and a strong irritation of the respiratory and visual systems, which could lead to health hazards and even death, was caused by the prolonged inhalation of C_2N_2 . Therefore, it is particularly important to ensure the safety of the operation and the maintenance of the electrical equipment using C_4F_7N as the insulating medium.

MoS₂, as a new semiconductor gas-sensitive material with a high surface area ratio and a natural semiconductor band gap [8], is broadly used in semiconductor-based micro gas-sensitive sensors as well as in the fabrication of adsorbents. However, the gas sensitivity of intrinsic MoS_2 for specific gases is often unsatisfactory, and transition metal catalyst doping is used for gas sensitivity [9,10]. Cuprum (Cu) is a relatively inexpensive transition metal catalyst compared to precious metal catalysts such as aurum (Au), argentum (Ag) and platinum (Pt). Existing studies on the gas sensitivity of Cu and its cognate elements doped with MoS_2 for specific gases demonstrate that Cu can be an excellent candidate for the MoS_2 doping of two-dimensional materials. For example, the enhancement of the gas sensitivity of C₂H₂ by Au- and Ag-doped MoS₂ was studied, and the results indicated that the doping of Au and Ag in the same main group can improve the gas sensitivity of dissolved gas C_2H_2 in insulating oil [11,12]. Furthermore, the gas sensitivity of pure and Cu-doped MoS_2 to CO and NO was discussed in document [13]. It was found that Cu doped with sulfur (S) site can significantly improve the adsorption energy for CO and NO. Furthermore, according to the Hund's rule of external electron configuration and the external electron configuration law, the external electron configuration formula of Cu is [Ar] 3d104s1. As far as transition metal elements are concerned, the outermost electron number of Cu is 1, which will make Cu atoms easily bond with the lone pair electrons of C, N and F atoms in the decomposition products of C_4F_7N , forming a strong adsorption force and achieving the purpose of capturing specific gases by gas-sensitive materials. It can be concluded that Cu may be the most ideal doping element to improve the gas sensitivity of MoS_2 to C_4F_7N and its decomposition products.

The manuscript is structured as follows: First, the DMol³ module in Materials Studio software is used to model and calculate the stable structure of Cu cluster-modified MoS₂. Second, the electronic density of states and the charge transfer amounts before and after the adsorption of C_4F_7N and C_2N_2 are compared to obtain the gas-sensitive mechanism of Cu-modified MoS₂ for the detection of C_4F_7N and its decomposition products. Third, the gas-sensitive performance of the optimal doping system under different electric fields is investigated considering the complex working conditions of power equipment. This paper investigates the adsorption mechanism of the environmentally friendly insulating gas C_4F_7N and its decomposition product C_2N_2 on the Cu cluster-modified MoS₂ surface

through theoretical calculations and lays the groundwork for the gas content monitoring of the new electrical insulation equipment using $C_4F_7N_2$.

The structure and energy optimization of the computational model was carried out based on the first principles of Density Functional Theory (DFT). We first constructed a 4 × 4 × 1 MoS₂ supercell structure. Since it is necessary to find a section for quantum mechanical adsorption calculation, the (0,0,1) section was selected in this work, and a vacuum layer with a thickness of 15 Å was established to prevent reactions between different periods. Then, the PBE function based on DFT and the GGA of the spin polarization measurement were selected to deal with the calculation problem of electron crosslinking [14]. The molecular structures of C_4F_7N , C_2N_2 and Cu clusters were optimized, and the optimal structures are shown in Figure 1. Detailed bond lengths and bond angles of C_4F_7N , C_2N_2 and Cu cluster molecules are shown in Table 1.



Figure 1. Structurally optimized molecular structures of C₄F₇N, C₂N₂ and Cu clusters. The distance is in Å.

Table 1. Bond lengths and bond angles of C₄F₇N, C₂N₂ and Cu cluster molecules.

Molecular	Bond Length (Å)	Bond Angle (°)
C_4F_7N	$\begin{array}{l} d_{(C=N)} = 1.165 \\ d_{(C-F)} = 1.349 \\ d_{(C-C)} = 1.470 \end{array}$	\angle (C-C-N) = 179.697 \angle (F-C-F) = 108.855
C_2N_2	$d_{(C-C)} = 1.376$ $d_{(C=N)} = 1.171$	∠ _(C-C-N) = 179.831
Cu ₂ Cu ₃	$d_{(Cu-Cu)} = 2.253 d_{(Cu-Cu)} = 2.313$	- ∠ _(Cu-Cu-Cu) = 55.712

The DFT-D2 method was used for dispersion correction [15], and the energy threshold, convergence force and self-consistent field were set as 1×10^{-5} Ha (1 Ha = 27.2114 eV), 2×10^{-3} Ha/Å and 1×10^{-6} eV, respectively, with a maximum displacement of 0.005 Å [16]. Since the formation of molecular orbits deforms atomic orbits to some extent, resulting in the deviation between the calculated results and the actual situation, double numerical polarization (DNP) was adopted to calculate the exchange electron pseudopotential to obtain more accurate results [17]. In orbital electronic processing, a single effective potential (DFT semicore Pseudopots (DSPP)) was used to replace the core electron to reduce the computational cost [18]. In the model surface calculation, the k point in the Brillouin region was set as $5 \times 5 \times 1$ [13].

The stability of doped structures can be measured by binding energy (E_b) [14], and it can be determined by Equation (1), as follows:

$$E_b = E_{(\mathrm{Cu})\gamma - \mathrm{MoS2}} - (E_{\mathrm{MoS2}} + E_{(\mathrm{Cu})\gamma}) \tag{1}$$

where $E_{(Cu)\gamma-MoS2}$, E_{MoS2} and $E_{(Cu)\gamma}$ represent the binding energies of $(Cu)_{\gamma}$ -MoS₂, pure MoS₂ and the Cu cluster, respectively.

The adsorption energy (E_{ads}) can be calculated by Equation (2), which is as follows:

$$E_{\rm ads} = E_{\rm (substrate+gas} - E_{\rm substrate} - E_{\rm gas}) \tag{2}$$

where $E_{\text{substrate+gas}}$ represents the total energy of the gas molecule adsorbed on the Cu_{γ} -MoS₂ surface, $E_{\text{substrate}}$ and E_{gas} are the energies of Cu_{γ} -MoS₂ and a gas molecule, respectively.

The charge amount is obtained by Mullikan [12] charge analysis. The transferred charge (Q_t) is determined by Equation (3), which is as follows:

$$Q_t = Q_{\rm ads} - Q_{\rm iso} \tag{3}$$

where Q_{ads} and Q_{iso} represent the total charge of gases after and before adsorption, respectively.

2. Results and Discussion

The adsorption energy E_{ads} proves whether the reaction can be spontaneous and indicates the strength of the adsorption reaction [19]. If $E_{ads} < 0$, the reaction releases energy, indicating that the adsorption reaction can be spontaneous. The transferred charge quantity Q_t can be used to explain the charge exchange level between the gas molecule and the substrate and then to explain the change in the conductivity of the system.

2.1. Construction of Stable Structures of Cu Clusters-Doped MoS₂

The most stable modified structure obtained by calculating the binding energy of Cu clusters doped at different positions, such as Sulfur (S), Molybdenum (Mo) and bridge positions according to Equation (1), is shown in Figure 2. The yellow atom in the diagram is S, and the cyan atom is Mo. The binding energies of the Cu clusters with MoS₂ are calculated from Equation (1) to be -1.723, -1.831 and -2.976 eV, respectively, all of which are greater than -0.6 eV [19], indicating that the structure has strong stability. Three S-Cu bonds with bond lengths of 2.261, 2.263 and 2.262 Å and a Mo-Cu bond of 2.876 Å are formed on the MoS₂ surface by single Cu atoms. Meanwhile, four S-Cu bonds with lengths of 2.302, 2.333, 2.343 and 2.322 Å are formed between Cu_2 and the S atoms of MoS₂. Interestingly, the bond length of Cu₂ increased significantly from 2.253 Å before modification to 2.380 Å, indicating that Cu-Cu is activated, which is strong evidence of its stability in binding to MoS₂. Similarly, Cu₃ breaks a Cu-Cu bond upon binding to MoS₂, forming six S-Cu bonds with bond lengths of 2.303, 2.360, 2.323, 2.326, 2.308 and 2.357 Å, respectively. Further, the electronic density of states (DOS) and partial density of states (PDOS) distributions for $(Cu)_{\gamma}$ -MoS₂ and pure MoS₂ are obtained, which are shown in Figure 3.



Figure 2. Three stable structures of MoS₂ modified by Cu clusters: (**a**) Stable structure of Cu-modified MoS₂; (**b**) Stable structure of Cu₂-modified MoS₂; (**c**) Stable structure of Cu₃-modified MoS₂.



Figure 3. Electron density of states and partial density of states before and after the modification of MoS₂ by Cu clusters.

As shown in Figure 3, the electron density distribution of MoS₂ changes significantly after the Cu_{γ} ($\gamma = 1, 2, 3$) modification, which is reflected in the significant leftward shift of the DOS diagram compared to the intrinsic MoS₂, resulting in a decrease in the electron energy level. Based on the PDOS diagram of Cu-MoS₂ in Figure 3, it can be seen that the electron densities of Cu-3d and S-3p peak simultaneously and are close to -6, -4 and -2 eV, indicating that strong orbital hybridization between the two has been formed. The two orbit peaks of S-3p and Mo-4d at 2 eV overlap. The aforementioned facts reasonably explain the bond forming between the Cu and S atoms in Cu-MoS₂.

As far as the Cu₂-MoS₂ system is concerned, the electron density increases near the Fermi level (E = 0 eV), which indicates that there is an increase in conductivity for the Cu₂-modified system. In terms of electron orbit analysis, the Cu-3d, Mo-4d and S-3p orbits have strong orbital hybridization around -1.5 eV. The electron density contribution from the Cu-4s orbit is responsible for the elevated electron density near the Fermi level. The PDOS diagram of the Cu₃-MoS₂ system shows that the Cu-3d, Mo-4d and S-3p orbits reach a simultaneous maximum in electron density at -3.5 eV, which accounts for the bonding of Cu to S atoms.

2.2. Adsorption on the Cu-MoS₂ Monolayer

Figure 4 shows the four different conformations of C_4F_7N and C_2N_2 adsorbed on the Cu-MoS₂ surface, and the candidates are labeled as X11, X12, X21 and X22, respectively. The magnitudes of the adsorption energies of the four systems calculated with Equation (2) are as follows: $E_{ads}(X21) = -1.080 \text{ eV} > E_{ads}(X11) = -1.011 \text{ eV} > E_{ads}(X22) = -0.632 \text{ eV}$ $> E_{ads}(X12) = -0.235$ eV. According to the calculated adsorption energy, the adsorption strength of the Cu-MoS₂ system is slightly greater than that of C_4F_7N for C_2N_2 , and both of them are spontaneous adsorption. Here, only X11 and X21, which have larger adsorption energies, are taken as examples for further analysis. The minimum adsorption distance between C_4F_7N and C_2N_2 on the Cu-MoS₂ surface is 1.856 A, and the electron density distribution after adsorption is shifted to the left, as shown in Figures 4 and 5a. The electron difference density (EDD) plots for X11 and X21 are shown in Figure 5b,c, where the red region indicates electron loss and the blue region indicates electron enrichment. The C and N atoms of CN^{*} of C₄F₇N in X11 are surrounded by the red region, indicating electron loss, and the Cu atoms are surrounded by the blue electron cloud, indicating electron gain by the Cu atom. In contrast, the red region in X21 is distributed around the two CN* of C_2N_2 , which demonstrates an overall loss of electrons and a transfer of electrons to the substrate.



Figure 4. Four stable structures of Cu-modified MoS₂ for C_4F_7N and C_2N_2 adsorption obtained after structural optimization: (a) X11: Stable structure of C_4F_7N adsorbed on Cu-MoS₂ surface; (b) X12: Stable structure of C_4F_7N adsorbed on Cu-MoS₂ surface; (c) X21: Stable structure of C_2N_2 adsorbed on Cu-MoS₂ surface; (d) X22: Stable structure of C_2N_2 adsorbed on Cu-MoS₂ surface.



Figure 5. (a) DOS and PDOS plots of X11 and X21; (b) EDD plots for X11 (c) EDD plots for X21.

For X11, the C-2p and N-2p orbits near -9.5 and -4 eV have a clear overlap of orbit peaks with the Cu-3d orbit, forming a strong orbital hybridization, as shown by the DOS and PDOS distributions in Figure 5a. The orbital overlap of Cu-3d with N-2p near the Fermi energy level reasonably explains the bonding of the N atom of CN* to the Cu atom in C₄F₇N. Based on the amount of transferred charge charge of X11 (0.176e), C₄F₇N is positively charged after adsorption, indicating that it acts as an electron donor transferring electrons to the substrate, which results in an increase in the conductivity of the substrate. Similarly, for the X21 system, the orbital hybridization of C-2p, N-2p and Cu-3d is mainly at -8 and -4.5 eV. Unlike C₄F₇N, the orbital hybridization of N-2p and Cu-3d after the adsorption of C₂N₂ on the Cu-MoS₂ surface is mainly concentrated near the -5 eV, which is closer to the Fermi energy level, and this is the reason why the surface interaction between C₂N₂ and Cu-MoS₂ is stronger than that of C₄F₇N. The transferred charge of C₂N₂ is 0.024e, again acting as an electron donor to the substrate.

2.3. Adsorption on the Cu_2 -MoS₂ Monolayer

The four stable structures of C₄F₇N and C₂N₂ adsorbed on the Cu₂-MoS₂ surface are shown in Figure 6. They are named as X31, X32, X41 and X42, respectively. According to Equation (2), the calculated magnitudes of the adsorption energies are as follows: $E_{ads}(X41) = -1.572 \text{ eV} > E_{ads}(X31) = -0.956 \text{ eV} > E_{ads}(X42) = -0.6-0.662 \text{ eV} > E_{ads}(X32) = -0.184 \text{ eV}$. Here, only X41 and X31, which have a higher adsorption energy, are taken for further analysis. Figure 7 shows the DOS and PDOS of X41 and X31 after adsorption. Based on

the DOS diagram shown in Figure 7a, the variation in the density of electron states from -2 to -4 eV after the adsorption of C_2N_2 is more pronounced than that of C_4F_7N , which reasonably indicates that the adsorption of C_2N_2 with the Cu_2 -MoS₂ surface is stronger than that of C_4F_7N . In detail, with the PDOS diagram shown in Figure 7, the X31 structure has orbital hybridization present at -8 and -6 eV for C-2p, N-2p and Cu-3d. The X41 system has orbital hybridization at -6 and -5 eV for C-2p, N-2p and Cu-3d, and it is close to the Fermi energy level. The transferred charge of C_2N_2 in the X41 system is -0.186eafter adsorption by the Cu₂-MoS₂ surface, which acts as an electron acceptor, and electrons are transferred from the substrate to the C2N2 molecule, resulting in a decrease in the substrate conductivity. The transferred charge (0.134e) and adsorption energy of the system of X31 are both reduced compared to the system of X11. The EDD plots for X31 and X41 are shown in Figure 7b,c. The N atom of the CN* of C₄F₇N in X31 is surrounded by a red region, indicating electron loss, while the Cu atom is surrounded by a blue electron cloud, indicating electron gain from the Cu atom. The red region in X41 is distributed around the CN^* of C_2N_2 , which proves its loss of electrons and the transfer of electrons to the two Cu atoms.



Figure 6. Four stable structures of Cu₂-modified MoS₂ for C₄F₇N and C₂N₂ adsorption obtained after structural optimization: (a) X31: Stable structure of C₄F₇N adsorbed on Cu₂-MoS₂ surface; (b) X32: Stable structure of C₄F₇N adsorbed on Cu₂-MoS₂ surface; (c) X41: Stable structure of C₂N₂ adsorbed on Cu₂-MoS₂ surface; (d) X42: Stable structure of C₂N₂ adsorbed on Cu₂-MoS₂ surface.



Figure 7. (a) DOS and PDOS plots of X31 and X41; (b) EDD plots for X31; (c) EDD plots for X41.

2.4. Adsorption on the Cu₃-MoS₂ Monolayer

The three stable structures of the two gases adsorbed on the Cu_3 -MoS₂ surface, C_4F_7N and C_2N_2 , are shown in Figure 8 and are named X51, X52 and X61, respectively. The

adsorption energies are listed as follows: $E_{ads}(X61) = -1.09 \text{ eV} > E_{ads}(X51) = -0.770 \text{ eV} > -0.7$ $E_{ads}(X52) = -0.239$ eV. For X51, the C₄F₇N gas molecule undergoes a large change in shape after adsorption. This is demonstrated by the reduction in the bond angle of C-C \equiv N from 179.697° to 146.642° before adsorption and the shortest distance for adsorption of 1.974 A. The PDOS diagram, shown in Figure 9a, shows that the C-2p, N-2p and Cu-3d orbital hybridization is mainly concentrated in the -4 to -7.5 eV range. From the calculated adsorption energy magnitude, it is learned that the adsorption energy of the X51 system is less than -0.6 eV, which means that chemisorption can no longer be constituted. In contrast, the degree of change in the structure of X61 after C₂N₂ adsorption is more pronounced compared to that of X51. In detail, the bond angle of C_2N_2 of C-C=N drops sharply from 179.931° before adsorption to 128.543° and forms a "ring" structure with the Cu₃ cluster. At the same time, orbital hybridization exists at -5.5 to -7 eV and at -3.5 eV for C-2p, N-2p and Cu-3d. According to the EDD diagram shown in Figure 9b,c, it can be seen that the distribution of the electron cloud around the C_4F_7N molecule in X51 is not obvious, indicating a relatively small amount of charge transfer. The blue region in X61 is distributed around C in the CN* above C_2N_2 , which proves that it has gained electrons.



Figure 8. Three stable structures of Cu₃-modified MoS₂ for C₄F₇N and C₂N₂ adsorption obtained after structural optimization: (a) X51: Stable structure of C₄F₇N adsorbed on Cu₂-MoS₂ surface; (b) X52: Stable structure of C₄F₇N adsorbed on Cu₃-MoS₂ surface; (c) X61: Stable structure of C₂N₂ adsorbed on Cu₃-MoS₂ surface.



Figure 9. (a) DOS and PDOS plots of X51 and X61; (b) EDD plots for X51; (c) EDD plots for X61.

From Figure 10, it can be seen that the maximum adsorption energy of Cu_{γ} -MoS₂ for C_4F_7N shows a decreasing trend as the value of the Cu cluster γ ($\gamma = 1, 2, 3$) increases. The transferred charge is 0.003e, tending to 0, which has less of an effect on the conductivity

of the substrate. At this point, Cu_{γ} -MoS₂ can still satisfy the chemisorption for C_2N_2 with good selectivity. Therefore, Cu_3 small clusters modified with MoS₂ can avoid main gas interference and be used as a sensitive substrate for the detection of C_2N_2 -resistive gas sensors.



Figure 10. Maximum adsorption energies of C_4F_7N and C_2N_2 on Cu_γ ($\gamma = 1-3$)-MoS₂ surfaces and charge transfer in the corresponding systems.

2.5. Externally Applied Electric Field

This is investigated by applying positive and negative polar electric fields perpendicular to the X61 system. The effect of the externally applied electric field on the adsorption energy and charge transfer of X61 is shown in Figure 11. In Figure 11, 1 a.u is equal to 51.36 V/Å. As can be seen from Figure 11, the application of either a positive or negative electric field is detrimental to the adsorption energy, resulting in a reduction in the adsorption energy. However, when a positive polar electric field is applied, the electrons due to the electric field force cause the electrons gained by the C_2N_2 gas molecules to increase with the increase in the electric field value. In general, although the adsorption energy and the magnitude of the transferred charge are influenced by the applied electric field, they still meet the detection requirements.



Figure 11. The effect of an applied electric field on the adsorption energy and the amount of charge transfer in the X61 system.

2.6. Band Strcture and Recovery Time of C₂N₂-Cu₃/MoS₂

We calculated the change in the band gap values before and after the adsorption of C_2N_2 gas on the Cu_3/MoS_2 surface are shown in Figure 12. In this case, the Brillouin zone scan path was set to G-M-K-G during the calculation of the bandgap map. The calculated band gap value of the adsorbed C_2N_2 gas molecules is 1.201 eV, which is 10.5% higher than the band gap value of 1.087 eV of the Cu_3-MoS_2 system before adsorption, which is consistent with our previous finding that C_2N_2 acts as an electron acceptor and thus leads to a decrease in the conductivity of the Cu_3-MoS_2 system. Meanwhile, we calculated from Equation (4) that the desorption time of C_2N_2 at 370 K is 645 s, which can have good recovery characteristics.



Figure 12. Band structure: (a) Band structure of Cu₃/MoS₂; (b) Band structure of C₂N₂-Cu₃/MoS₂.

The general formula for calculating the recovery time of a gas-sensitive substrate is defined as [20,21]:

$$\tau = \frac{e^{-E_{\rm ads}/KT}}{v_0} \tag{4}$$

where v_0 is the apparent frequency (here, we take 10^{12} s^{-1}); E_{ads} is the adsorption energy; *K* is the Boltzmann constant (8.62 × 10^{-5} eV/K); *T* is the temperature (K).

3. Synthesis of Cu Clusters-Doped MoS₂ Gas-Sensitive Materials

In this paper, Cu-containing cluster-doped MoS₂ gas-sensitive materials were synthesized at the experimental level. The specific synthesis process is shown in Figure 13. The analytical pure grade drugs involved in the synthesis of this paper were purchased from Shanghai Aladdin. For the synthesis of MoS₂ nanosheets, 100 mL of thioglycolic acid (HSCH₂CO₂H, TA) was first placed in a 250 mL volumetric beaker, and sodium molybdate (Na₂MoO₄) was added to the above beaker in a 1:3 molar ratio with TA, sealed and stirred for 30 min at room temperature using a magnetic stirrer. For the preparation of the Cu-containing powder, 12 g of Cu(NO₃)₂·3H₂O was first dissolved in 100 mL of distilled water and stirred for 15 min before adding potassium hydroxide (KOH) solution dropwise; the solution gradually became darker in color, and after warming and stirring at 60 °C (333 K), the solution turned black and was left to stand for 12 h to obtain a solid-liquid layered solution. The upper layer of the solution was removed with a dropper, and the solid was centrifuged in a centrifuge at 10,000 r/min, put into an oven, dried at 80 °C for 12 h and ground to obtain Cu powder.



Figure 13. Flow chart of the Cu-containing cluster-doped MoS₂ synthesis.

For the synthesis of Cu-containing cluster-doped MoS_2 , the gas-sensitive material was mainly obtained by mixing the abovementioned synthesized Cu-containing powder as well as MoS_2 nanosheets in a 1:9 molar ratio into isopropanol (C_3H_8O), stirring for 8 h using a magnetic stirrer and then drying. The synthesized MoS_2 and the microscopic appearance of the Cu-containing cluster-doped MoS_2 are shown in Figure 14. The scanning electron microscope (SEM) image in Figure 14 shows that the MoS_2 exhibits a sheet-like structure with a smooth surface. In contrast, the doped MoS_2 nanosheets have many tiny clusters attached to them, resulting in a Cu-containing cluster-doped MoS_2 composite structure.



(c)

(**d**)

Figure 14. Microscopic patterns of MoS_2 nanosheets and Cu-containing cluster-doped MoS_2 : (a) Microscopic representation of MoS_2 nanosheets at a 20 μ m scale; (b) Microscopic representation of MoS_2 nanosheets at a 5 μ m scale; (c) Cu-containing cluster-doped MoS_2 at a 20 μ m scale; (d) Cu-containing cluster-doped MoS_2 at a 5 μ m scale.

4. Conclusions

In this paper, the adsorption mechanism of C_4F_7N and its electrothermal aging decomposition characteristic component C_2N_2 on Cu_{γ} ($\gamma = 1-3$)-MoS₂ are investigated based on

the DFT theory by calculating the DOS, the PDOS and the adsorption energy. The following conclusions are obtained.

The maximum adsorption energy of a single Cu atom modified with MoS₂ is -1.011 and -1.080 eV for C₄F₇N and C₂N₂, respectively. Due to the close proximity of the two values, the selectivity requirements for detection may not be met at this point. However, as the number of doped copper atoms increases, the adsorption energy of the doped system for C₄F₇N gradually decreases, reaching a minimum value of -0.770 eV at $\gamma = 3$. In comparison, the magnitude of the adsorption energy of C₂N₂ is significantly higher than that of C₄F₇N at -1.09 eV. The calculated band gap value of the C₂N₂ gas molecules after adsorption increased by 10.5% compared to the Cu₃-MoS₂ system before adsorption. This indicates that a more significant decrease in conductivity occurred after adsorption. Moreover, the desorption time of C₂N₂ at 370 K is 645 s, which can have good recovery characteristics. Small clusters of Cu₃-modified MoS₂ are therefore suitable as detection gas-sensitive substrates for the detection of the toxic gas C₂N₂.

When an electric field of positive and negative polarity is applied to Cu₃-MoS₂, the adsorption energy of C₂N₂ on the surface of Cu₃-MoS₂ decreases with the increase in the electric field, but it is still greater than -0.6 eV, which still meets the detection requirements. When a negative polarity electric field is applied, Q_t increases as the electric field increases due to the force of the electric field. The conclusions of this paper provide theoretical guidance for the selection of gas-sensitive materials for the decomposition products of C₄F₇N.

Author Contributions: Conceptualization, C.L. (Changyun Li); methodology, P.C.; software, Y.Y.; validation, C.L. (Changyun Li); formal analysis, P.C.; investigation, P.C.; resources, P.C.; data curation, P.C.; writing—original draft preparation, C.L. (Chuanyang Li); writing—review and editing, visualization, P.C.; supervision, C.L. (Changyun Li); project administration, C.L. (Changyun Li); funding acquisition, C.L. (Changyun Li). All authors have read and agreed to the published version of the manuscript.

Funding: Key R & D Program of Shandong Province (2019GGX102049).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author, [C.L. (Changyun Li)], upon reasonable request.

Acknowledgments: The software materials used in this work were provided by the China University of Petroleum (East China).

Conflicts of Interest: The authors declare no conflict of interest.

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