



Article Si-Doped Nitrogenated Holey Graphene (C₂N) as a Promising Gas Sensor for O-Containing Volatile Organic Compounds (VOCs) and Ammonia

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Abstract: Two-dimensional (2D) crystalline materials have been regarded as promising sensor materials due to their large specific surface area, high sensitivity, and low cost. In the present work, based on the density functional theory (DFT) method, the sensor performance of novel silicon (Si)-doped nitrogenated holey graphene (SiC₂N) toward five typical VOCs (HCHO, CH₃OH, C₃H₆O, C₆H₆, and C₂HCl₃) and ammonia were systematically investigated. The results demonstrated that Si doping could effectively decrease the band gap of C₂N and simultaneously provide active sites for gas adsorption. Through comprehensive analyses of adsorption energies and electronic properties, the SiC₂N was found to exhibit high selectivity for O-containing VOCs (HCHO, CH₃OH, and C₃H₆O) and NH₃ via a covalent bond. Moreover, after the HCHO, CH₃OH, C₃H₆O, and NH₃ adsorption, the band gap of SiC₂N greatly decreases from 1.07 eV to 0.29, 0.13, 0.25, and 0.12 eV, respectively, which indicated the enhancement the conductivity and enabled the SiC₂N to be a highly sensitive resistive-type sensor. In addition, the SiC₂N possesses a short recovery time. For instance, the recovery time of HCHO desorbed from SiC₂N is 29.2 s at room temperature. Our work anticipates a wide range of potential applications of Si-doped C₂N for the detection of toxic VOCs and ammonia, and supplies a valuable reference for the development of C₂N-based gas sensors.

Keywords: volatile organic compounds (VOCs); ammonia; nitrogenated holey graphene (C₂N); silicon (Si) doping; density functional theory (DFT)

1. Introduction

Along with the improvement of residential air tightness, the issues related to indoor air pollution have aroused increasing critical attention. Volatile organic compounds (VOCs) and ammonia are identified as the main indoor contaminants that are mainly emitted from building and furnishing materials [1]. Long-term exposure to these harmful gases can cause severe health problems such as headaches, respiratory tract irritation, nervous system injury, and even cancer such as leukemia, etc. [2,3]. Given the increasing health hazard, the environmental monitoring of exposed VOCs is desired.

Over time, researchers have devoted continuous efforts to develop novel and highperformance capture agents for gaseous contaminants detection [4–6]. Two-dimensional (2D) and nonmetal materials, such as graphene, graphdiyne, phosphorene, carbon nitrides, etc., have been widely used in interdisciplinary regions, such as gas sensors [7–15], spintronics [16,17], photo- or electro- catalysis [18,19], and so on, due to their large specific surface area, unique electronic properties, and low cost. Additionally, such 2D materials that act as sensor materials exhibited high sensitivity in minute concentrations. For instance, the



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Copyright: © 2023 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/). graphene/polyaniline nanocomposite proposed by Wu et al. [9] exhibited high sensitivity for ammonia molecules at ppm level. In addition, Ahmad's group [12] reported that the detection limit of black phosphorus toward NO₂ was as low as 5 ppb. Very recently, a novel 2D nitrogenated holey graphene (C_2N) was synthesized by Mahmood's group [20] through a bottom-up wet-chemical reaction. The newly synthesized C_2N possesses a high specific surface area and uniformly distributed pores and is deemed a potential candidate for gas detection. Previous computational works manifested that C_2N -based materials can be used in the detection of some toxic gases such as NI₃ [21], H₂S [22], and so on [23,24]. However, the pristine C_2N exhibited finite adsorption ability, low selectivity, and low sensitivity toward VOCs and ammonia (NH₃) [25–27]. Can the sensor performance of C_2N toward VOCs and ammonia be regulated through appropriate functionalization strategies?

Previous studies have demonstrated that heteroatom doping can not only offer active sites for gas adsorption but also promote the charge transfer between gases and substrate, thereby effectively enhancing the sensor performance of materials. For instance, metal oxides doped with Sc [28] and Ag [29] atoms exhibited enhanced sensor performance toward VOCs in contrast with their pure phase. Additionally, it has been reported that B [30], N [31], and Li [32] atoms doping could effectively enhance the selective recognition of carbon-based materials toward VOCs and ammonia. In addition, previous theoretical studies have reported that metal (e.g., Al and Ti)-doped C_2N were potential sensing materials for certain VOCs [27,33]. At present, it remains curious if nonmetal-modified C_2N is an efficient sensor material for VOCs. Silicon (Si), as one of the most earth-abundant elements, is non-toxic and environmentally friendly. Ren and coworkers [34] have prepared Si-doped metastable ε -phase WO₃ as a gas sensor for acetone (C₃H₆O). It was found that Si element doping could not only provide abundant target-receptor sites for target gases but also enhance the charge transfer performance of WO_3 . The synthesized Sidoped ε -WO₃-based detector exhibited high sensitivity (a detection limit of 10 ppb) and outstanding selectivity for C_3H_6O . In addition, Guntner and coworkers found that the sensor response of MoO_3 toward NH_3 increased twice via Si doping when compared to its pristine phase [35]. Very recently, the DFT method has been utilized by Singsen et al. [36] to investigate the chemical detection performance of Si-doped green phosphorene (Si-GreenP) for biotoxin volatile organic compounds. The results demonstrated that the Si-GreenP presented enhanced adsorption ability (almost ~five times greater than pure GreenP) and selectivity toward formaldehyde (HCHO) and C_3H_6O . Additionally, considerable changes have been found in the band gap and work function of Si-GreenP after gas adsorption, suggesting its excellent sensitivity as a gas sensor. Given these advances, Si-doped C_2N may be a potential gas sensor for VOCs and NH₃. However, at present, the understanding of electronic characteristics and potential sensor performance of Si-doped C₂N remain in its infancy and needs further exploration.

In the current work, the dispersion corrected density functional theory was implemented to investigate the electronic properties of Si-doped nitrogenated holey graphene (SiC₂N) as well as its sensor ability for typical VOCs (HCHO, methanol (CH₃OH), C₃H₆O, benzene (C₆H₆), and trichloroethylene (C₂HCl₃)) and NH₃. Firstly, the detailed doping modes of SiC₂N and the inherent regulation of the Si atom on the electronic structures of C₂N were exhaustively discussed. Next, we systematically analyzed the adsorption performance and selectivity of pure C₂N and SiC₂N toward various VOCs and NH₃. It was found that after Si doping, the capture ability and selectivity of C₂N toward O-containing VOCs and NH₃ were dramatically improved. In addition, the SiC₂N possessed high sensitivity and appropriate recovery time as a resistive-type sensor. These explorations aim to contribute a theoretical basis to existing knowledge and provide new insights for the design and development of high-performance C₂N-based sensing materials used for VOCs and ammonia detection.

2. Materials and Methods

The 2 \times 2 supercell of C₂N was used as the basic computational model in the present work. A vacuum space of 20 Å in the z-direction was employed to avoid the interlayer interaction. All the spin-polarized density functional theory calculations were executed by using the Vienna ab initio simulation package (VASP) code [37]. The Perdew–Burke– Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was adopted to treat the exchange-correlation energies and potentials [38]. The interactions between core ions and valence electrons were depicted with the projector augmented wave (PAW) pseudopotential [39] with the cutoff energy set to 500 eV. Additionally, the D3 vdw correction proposed by S. Grimme was performed for the consideration of van der Waals interactions [40,41]. The convergence criteria for the total energy and the Hellmann–Feynman force were 10^{-5} eV and 0.01 eV/Å, respectively. The 3 \times 3 \times 1 and 7 \times 7 \times 1 Monkhorst– Pack grids were utilized for the geometric optimizations and electronic characteristics, respectively. In addition, the electronic structure calculations with HSE06 functional [42] were also carried out for partial systems with the Monkhorst–Pack grids of $7 \times 7 \times 1$ to obtain accurate band structure and band-gap values. The formation energies for the Si atom doping process were calculated by the following equation:

$$E_{form} = E(\operatorname{SiC}_2 N) - E(\operatorname{C}_2 N) - \mu(\operatorname{Si})$$
(1)

where the $E(SiC_2N)$ and $E(C_2N)$ were the total electronic energies of SiC₂N and pristine C₂N, respectively. The $\mu(Si)$ represented the potential energy of Si atoms, which was adopted as the cohesive energy of each Si atom in the Si-bulk (-4.63 eV).

The adsorption energies (E_{ad}) of SiC₂N toward gases were obtained by Formula (2):

$$E_{ad} = E(SiC_2N_gas) - E(SiC_2N) - E(gas)$$
⁽²⁾

where the $E(SiC_2N_gas)$ and $E(SiC_2N)$ donated the total electronic energies of SiC_2N_gas and SiC_2N , respectively. Additionally, the E(gas) were the energies of isolated VOCs and NH₃. In addition, the conductivity and adsorption of Gibbs free energies were found within the VASPKIT code [43]. Moreover, the Atomistix ToolKit (ATK) package was performed to investigate the transport properties of the SiC₂N-based systems [44].

3. Results and Discussion

3.1. Geometric Configurations and Electronic Properties of Si-Doped C₂N

Firstly, the incorporation configurations and formation energies of Si-doped C_2N (Si C_2N) were comprehensively investigated. As shown in Figure 1a, there are five distinct sites, including the C atom, N atom, and interstitial space (I1, I2, and I3) for Si doping; the optimized configurations are shown in Figure S1. The computational results demonstrate that the Si atom is more favorable to anchor on the I1 site with the formation energy of -1.51 eV. This configuration was filtered out and displayed in Figure 1b. The negative formation energy indicates that the doping process is exothermic, which provides significant feasibility in terms of experimental synthesis of Si-doped C_2N . Herein, the doping density of the Si atom is at a relatively low level of 1.37 at%. Then, we only focus on this configuration. The stability of SiC₂N was further validated by the ab initio molecular dynamics simulations (AIMD) [45] at 300 and 500 K for 10 ps, respectively. As shown in Figure S2, the geometric structure of SiC₂N is well preserved at room temperature and even at 500 K, indicative of the high thermodynamic stability of SiC₂N.





Figure 1. (a) The 2 × 2 supercell of C_2N as well as the possible doping sites for Si atom; (b) the optimal doping configuration of Si-doped C_2N ; (c) the band structure and (d) partial density of states of pure C_2N calculated with HSE06 functional; (e) the band structure, CBM and VBM distribution of Si-doped C_2N calculated with HSE06 functional, with the isosurface value of 0.0015 e/Bohr³; and (f) the partial density of states of Si-doped C_2N calculated with HSE06 functional.

Then, the band structures and partial density of states (PDOS) plots were investigated with the HSE06 functional in Figure 1c–f to obtain accurate electronic characteristics of intrinsic C₂N and SiC₂N. Firstly, as shown in Figure 1c,d, the pristine C₂N exhibits a semiconductor feature with a direct band gap of ~2.41 eV, which is quite consistent with previous studies [46]. As shown in Figure 1e, after Si doping, the band gap of SiC₂N considerably decreases to 1.07 eV, which is conducive to electron transmission. Additionally, the Si doping yields a new state on the VBM, which is mainly localized around the Si atom. More notably, from the PDOS plot of SiC₂N, we can observe that the VBM mainly consists of active p_z electrons, which ensure high activity of SiC₂N for gas adsorption. In addition, strong hybridization can be observed between Si and N atoms, signing strong covalent characters. Herein, the band structures of pure C₂N and SiC₂N were also calculated with the PBE functional, as displayed in Figure S3a,b. Additionally, the obtained band gap values for C₂N and SiC₂N with the PBE functional are 1.65 and 0.60 eV, respectively. To sum up, Si doping can effectively regulate the electronic structure of C₂N, which will be beneficial for electron transmission and gas adsorption.

The electron localization function (ELF) map of SiC₂N is presented in Figure 2a. The ELF map has been deemed a useful tool to directly ascertain the bonding nature and the degree of electron localization [47,48]. In general, the region with an ELF value > 0.5 signs covalent interaction and high electron localization [49]. Firstly, topographical analysis of ELF manifests that the formed Si-N exhibits a covalent feather. In addition, the highly localized electrons are located on the Si atom, which is susceptible to interaction with the incoming gas molecules. In addition, the charge density difference (CDD) plot of SiC₂N between the Si atom and C₂N was also analyzed in Figure 2b, from which we can see remarkable charge transfer between the Si atom and the substrate. Additionally, the Bader charge result demonstrates that the Si atom donates 1.28 e to the C₂N.



Figure 2. (a) Electron localization function (ELF) diagram of Si-doped C_2N ; (b) the charge density difference of SiC₂N between the Si atom and C_2N . The cyan and magenta regions denote the charge accumulation and depletion, respectively, and the isosurface value is 0.002 e/Bohr³.

3.2. Adsorption of Gases on Pristine C₂N

In this section, the adsorption behavior of gaseous pollutants on pristine C₂N was investigated. Four typical and toxic VOCs (HCHO, CH₃OH, C₃H₆O, C₆H₆, and C₂HCl₃) and NH₃ were selected as the target adsorbates. Various initial adsorption configurations were constructed to determine the most stable structures of C₂N_gas systems. According to previous studies, the gases preferred to adsorb on the large hole site of C₂N (see Figure S3c) due to its copious π -electrons; thus, it was chosen as the adsorption site for VOCs and NH₃ [24,50,51]. For volatile organic compounds, the adsorption models were established by laying the pollutants in parallel to vertical positions on the hole site. In the vertical scenarios, the interaction sites of VOCs were also considered. For NH₃, only the interaction sites of NH₃ (N and H) were taken into account. The initial binding configurations, the optimized structures, and the adsorption energies of gases on pristine C₂N were recorded in Figures S4–S7.

The optimal binding configurations were filtered out and depicted in Figure 3, and the corresponding adsorption energies were listed in Table 1. As displayed in Figure 3, the HCHO, C_6H_6 , and C_2HCl_3 molecules tend to adsorb on the C_2N sheet in a vertical orientation, in which their C-H bonds point toward the large hole of C₂N. The vertical distances (named as D_v) between the HCHO, C_6H_6 , and C_2HCl_3 molecules and the substrate are 1.03, 1.46, and 1.66 Å, respectively, while the CH_3OH and C_3H_6O molecules prefer to lie flat on the C_2N surface with vertical distances of 1.41 and 1.85 Å, respectively. When it comes to the NH₃ molecule, the NH₃ is adsorbed on the surface of C_2N with its two H atoms downwards; the D_v between NH₃ and C₂N is 1.29 Å. Notably, scrutinizing the binding configurations of C_2N_{gas} systems, there are no obvious chemical bonds between them, which portends weak interaction. Moreover, the adsorption energy of -0.50 eVis always used to distinguish physical and chemical adsorption [52]. As summarized in Table 1, the E_{ad} of C₂N for HCHO, CH₃OH, C₃H₆O, C₆H₆, C₂HCl₃, and NH₃ molecules are -0.47, -0.53, -0.44, -0.38, -0.48, and -0.38 eV, respectively, demonstrating physisorption or weak chemisorption. Their relatively weak interaction ascribes to the van der Waals affinity of π -electrons in C₂N toward VOCs (or NH₃). Additionally, it can be seen that the adsorption energies of pure C_2N toward these gases are at a comparable level, indicating poor selectivity.

Then, the electronic properties of C_2N_gas systems, including PDOS and Bader charge, were investigated to further comprehend the interaction behavior between C_2N and contaminants. The density of states of gases before and after adsorption, the partial density of states of gases, and C_2N in the adsorption systems were displayed in Figure S8. On the one hand, there are tiny state variations in the DOS of gas molecules after the adsorption process. On the other hand, the gas molecules hybridize with C_2N at a low degree. Additionally, as recorded in Table 1, only thimbleful charge transfers can be observed in C_2N_gas systems. The density of states and Bader charge results further prove the relatively weak interaction between C_2N and VOCs (or NH₃).



Figure 3. The optimal binding configurations of (a) C_2N_HCHO ; (b) $C_2N_CH_3OH$; (c) $C_2N_C_3H_6O$; (d) $C_2N_C_6H_6$; (e) $C_2N_C_2HCl_3$, and (f) $C_2N_NH_3$. (Silvery: C atom, Blue: N atom, Red: O atom, Cyan: Cl atom, and Pink: H atom).

Table 1. The adsorption energies (E_{ad}) and Bader charge transfer (Δq) in C₂N_gas and SiC₂N_gas systems. The minus sign in Δq represents the electron reduction of gases.

	E_{ad} (eV)	Δq (Gas)		E_{ad} (eV)	Δq (Gas)
C ₂ N_HCHO	-0.47	0.017	SiC ₂ N_HCHO	-1.04	0.388
C ₂ N_CH ₃ OH	-0.53	0.019	SiC ₂ N_CH ₃ OH	-0.90	0.057
$C_2N_C_3H_6O$	-0.44	0.005	SiC2N_C3H6O	-0.60	0.134
$C_2N_C_6H_6$	-0.38	0.003	SiC ₂ N_C ₆ H ₆	-0.36	-0.016
$C_2N_2HCl_3$	-0.48	0.001	SiC ₂ N_C ₂ HCl ₃	-0.41	0.017
$C_2N_NH_3$	-0.38	-0.004	SiC ₂ N_NH ₃	-1.21	-0.046

3.3. Adsorption of Gases on SiC_2N

3.3.1. Binding Configurations and Adsorption Energies

The adsorption behavior of VOCs and NH_3 on Si-doped C_2N was probed in this section. Herein, the Si and hole sites were selected as the adsorption sites for gas molecules (see Figure S3d). Similarly, various binding configurations of SiC_2N_gas systems were examined in Figures S9-S20 to search for the optimal adsorption structures. The most energetically favorable binding configurations of SiC_2N_2 as systems are depicted in Figure 4, and the corresponding adsorption energies are displayed in Table 1. Combining the binding configurations and adsorption energies, we can see that Si doping can effectively promote the adsorption of HCHO, CH_3OH , C_3H_6O , and NH_3 . Firstly, as shown in Figure 4a, the HCHO molecule prefers to interact with SiC₂N in a parallel pattern, in which the Si atom and the N atom of the C_2N skeleton act as dual adsorption sites for HCHO. Stable Si-O (1.67 Å) and N-C (1.52 Å) bonds are formed between HCHO and SiC₂N, which ultimately leads to appreciable adsorption energy of -1.04 eV. In the CH₃OH, C₃H₆O, and NH₃ adsorption systems, the O atoms in hydroxyl and ketone groups, as well as the N atom of NH_3 , are chemically active to interact with the dopant Si atom. The newly formed Si-O (or Si-N) bond lengths in SiC₂N_CH₃OH, SiC₂N_C₃H₆O, and SiC₂N_NH₃ systems are 1.82, 1.85, and 1.91 A, respectively, which are quite close to the sum covalent radii of Si and O (N) atoms (1.84 for Si-O and 1.86 for Si-N). These results indicate the formation of covalent bonds between Si and O (or N) atoms. Additionally, the obtained adsorption energies of

SiC₂N for CH₃OH, C₃H₆O, and NH₃ are -0.90, -0.60, and -1.21 eV, respectively, which are much higher than that of pristine C₂N, whereas the C₆H₆ and C₂HCl₃ still tend to physically adsorb on the hole site of SiC₂N, accompanied by small adsorption energies of -0.36 and -0.41 eV, respectively. There is no noticeable enhancement in the C₆H₆ and C₂HCl₃ adsorption after Si doping. Overall, from both structural and energetical perspectives, doping the Si atom can remarkably boost the selective adsorption performance of SiC₂N for target O-containing VOCs (HCHO, CH₃OH, and C₃H₆O) and NH₃. Additionally, the outstanding capture capacity and selectivity may enable the SiC₂N to be a potential semiconductor material for the environmental monitoring of gaseous pollutants.



Figure 4. The optimal binding configurations of (a) SiC_2N_HCHO ; (b) $SiC_2N_CH_3OH$; (c) $SiC_2N_C_3H_6O$; (d) $SiC_2N_C_6H_6$; (e) $SiC_2N_C_2HCl_3$, and (f) $SiC_2N_NH_3$. Bonds are in Å. (Silvery: C atom, Blue: N atom, Yellow: Si atom, Red: O atom, Cyan: Cl atom, Pink: H atom).

It should be noted that as a sensor material, the SiC₂N should be insensitive to main ambient gases (N₂ and O₂). Thus, the adsorption of these two ambient gases on the Si site of SiC₂N was also evaluated in Figure S21. The computational results reveal that the adsorption of N₂ on the SiC₂N can be summarized as a weak van der Waals interaction ($E_{ad} = -0.12$ eV), indicating that the nitrogen almost does not interfere with VOC and NH₃ detection. However, the O₂ has a stronger interaction with Si-doped C₂N with the adsorption energy of -2.05 eV, which will cause the Si site to be occupied and thereby decrease the sensor performance. Therefore, it is advisable to utilize appropriate O₂ filters or control the detection environment to minimize the interference of O₂ in actual application [35].

3.3.2. Interaction Mechanism

Then, the electronic characteristics, including PDOS, ELF, and CDD, were probed within the PBE method to give a deep mechanistic understanding of the interaction between SiC_2N and O-containing VOCs (or NH₃). The density of states of gases before and after adsorption, the partial density of states of working Si (or N) atoms in SiC_2N , and the O (or N) in gases for SiC_2N_HCHO , $SiC_2N_CH_3OH$, $SiC_2N_C_3H_6O$, and $SiC_2N_NH_3$ systems were shown in Figure 5. In the cases of HCHO adsorption, first, it can be seen that the localized electronic states of isolated HCHO split into small continuous energy states, which can be regarded as the electron redistribution caused by the strong interaction. Additionally, in the SiC_2N_HCHO system, the dopant Si atom and the N atom of C_2N act

as dual adsorption sites for HCHO. The O atom of HCHO highly hybridizes with the Si at -10.69~-6.60, -5.14~-4.45, and -1.35~-0.73 eV, respectively. In addition, obvious orbital overlaps between the N atom of SiC2N and the C atom of HCHO can be observed at -14.60~-5.79 eV. These results confirm the formation of intense Si-O and N-C covalent bonds. Furthermore, as depicted in Figure 5b–d, in the SiC₂N_CH₃OH, SiC₂N_C₃H₆O, and $SiC_2N_NH_3$ systems, the orbitals of CH_3OH , C_3H_6O , and NH_3 molecules are also divided into several small states. Additionally, there are obvious electron hybridizations between the Si atom and the O (or N) of gaseous molecules, likewise indicating their exquisite covalent interaction. Herein, one can see that the hybrid degree between Si and the O of C_3H_6O is weaker compared with that in the other three systems, which explains the relatively weak adsorption capacity of SiC_2N toward C_3H_6O . In comparison, the electronic state deformations of the C_6H_6 and C_2HCl_3 in the adsorption process are negligible. Additionally, there are a few orbital overlaps between C_6H_6 (or C_2HCl_3) and SiC_2N in $SiC_2N_C_6H_6$ and $SiC_2N_C_2HCl_3$ systems (see Figure S22). The DOS results further demonstrate the high selective adsorption performance of SiC₂N toward O-containing VOCs and NH₃.



Figure 5. The density of states of gases before and after adsorption, and the partial density of states of working Si (or N) atom in SiC₂N and the O (or N) in gases for (a) SiC₂N_HCHO, (b) SiC₂N_CH₃OH, (c) SiC₂N_C₃H₆O, and (d) SiC₂N_NH₃ systems.

As discussed above, the bonding nature can be intuitively determined by ELF diagrams. The ELF plots of SiC₂N_HCHO, SiC₂N_CH₃OH, SiC₂N_C₃H₆O, and SiC₂N_NH₃ systems are given in Figure S23. It can be seen that the Si-O (or Si-N) bonds exhibit covalent bonding characteristics. Additionally, it can be seen that the covalent degree of Si-O bond in SiC₂N_C₃H₆O is lower than the Si-O (or Si-N) in other adsorption systems, which is corroborated mutually in the previous adsorption energies and DOS results. The ELF diagrams of SiC₂N_C₆H₆ and SiC₂N_C₂HCl₃ were not analyzed since there is no obvious chemical bonding between SiC₂N and C₆H₆ (or C₂HCl₃). Moreover, the CDD diagrams of the adsorption systems with regard to SiC₂N and gas molecules are presented in Figure S24. Significant charge transfer can be observed between the SiC₂N substrate and O-containing VOCs (or NH₃). The amounts of charge transfer in various adsorption systems were recorded in Table 1. It can be seen that the charge transfer from the SiC₂N monolayer to HCHO, CH₃OH, and C₃H₆O is calculated to be 0.388, 0.057, and 0.134 e, respectively. Additionally, in the SiC₂N_NH₃ system, the NH₃ molecule donates 0.046 e to the SiC₂N sheet. The remarkable charge transfer demonstrates the intense covalent bonding between O-containing VOCs (or NH₃) and SiC₂N, while the charges of C₆H₆ and C₂HCl₃ are almost unchanged after being adsorbed on SiC₂N.

3.4. Sensor Explanation of Si-Doped C₂N Sheet

3.4.1. Sensor Performance of SiC_2N

The potential of SiC₂N as resistive or work function (Φ)-type sensors was assessed in this section. Firstly, the operation of sensor materials is mainly based on the conductance variations after capturing target analytes. Additionally, the conductivity (σ) of semiconductor materials is quite related to its band gap, and the relationship between the σ and E_g is expressed as follows [53,54]:

$$\sigma \propto \exp(-\frac{E_g}{2kT}) \tag{3}$$

where the E_g , k, and T donate the band gap, Boltzmann constant (8.62 × 10⁻⁵ eV/K), and temperature, respectively. The band structures of SiC₂N_gas systems with the HSE06 functional were depicted in Figure 6. One can see that the adsorption of O-containing VOCs and NH_3 inspires dramatic declines in the band gap of SiC₂N. The band gaps of SiC₂N_HCHO, SiC₂N_CH₃OH, SiC₂N_C₃H₆O, and SiC₂N_NH₃ systems considerably decrease to 0.29, 0.13, 0.25, and 0.12 eV, respectively, which will result in an evident increase in conductivity, while the band gap of SiC_2N is almost unchanged after the adsorption of C_6H_6 and C_2HCl_3 . The band structures of SiC_2N_gas systems calculated by the PBE functional were displayed in Figure S25. In general, the PBE method underestimates the band-gap values; qualitatively, the PBE results are quite consistent with the HSE06 results. Herein we further calculated the electrical conductivity (σ) of SiC₂N and the adsorption systems at 300 K in Figure 7 with the PBE functional. It can be observed that the adsorption of O-containing VOCs and NH₃ generates remarkable changes in conductivity; their peaks of conductivity occur at lower values of the chemical potential. In addition, one can see that the conductivity of the carrier near or at the chemical potential is 0 V, which is consistent with the PBE band structure results (see Figure S25) and further confirms the narrower band gaps of the adsorption systems, while the adsorption of C_6H_6 and C_2HCl_3 has a negligible influence on the conductivity of SiC_2N . These results indicate that the Si-doped C₂N possesses both high sensitivity and selectivity for O-containing VOC and NH₃ detection. Furthermore, the current–voltage of the SiC₂N_NH₃ system was found as an example to ensure the effect of gas adsorption on the conductivity of SiC_2N . The I–V curves for pure SiC₂N and SiC₂N_NH₃ systems are shown in Figure 7g, in which the applied voltage ranges from 0 to 1.0 with the increment of 0.2 V. For pure SiC₂N, there is no apparent current flow at 0 and 0.2 V owing to the band gap of SiC_2N . The current appears when the applied voltage reaches 0.4 V, and then the current gradually increases along with the applied voltage. Additionally, the adsorption of NH₃ remarkably enhances the electrical conductivity of the SiC_2N sheet. Firstly, due to the quite small band gap of the SiC₂N_NH₃ system, there is an obvious current in the SiC₂N_NH₃ system even at a small applied voltage of 0.2 V. In addition, it can be observed that the current flows in the $SiC_2N_NH_3$ system are evidently stronger in contrast with the pure SiC_2N when using the applied voltage of 0~1 V. Additionally, the difference in the conductivity is most significant at the applied voltage of 0.4 V. One can see that at the applied voltage of 0.4 V, the current flowing through SiC₂N_NH₃ system is 18.76 μ A, which is almost six times higher than pure SiC₂N (3.27 μ A), which predicts that the SiC₂N sheet possesses highest sensitivity



toward NH_3 at 0.4 V. Overall, the current–voltage curve further proves the high sensitivity toward ammonia.

Figure 6. Band structures of (a) SiC_2N_HCHO , (b) $SiC_2N_CH_3OH$, (c) $SiC_2N_C_3H_6O$, (d) $SiC_2N_C_6H_6$, (e) $SiC_2N_C_2HCl_3$, and (f) $SiC_2N_NH_3$ systems calculated by the HSE06 functional.



Figure 7. (**a**–**f**) The electrical conductivity (σ) as a function of chemical potential for SiC₂N and adsorption systems; (**g**) the I–V curves of SiC₂N and SiC₂N_NH₃ system at the voltage of 0–1 V.

The sensitivity of SiC_2N toward O-containing VOCs and ammonia was further investigated. The sensitivity was calculated by the following equation [55]:

$$S = (\sigma_2 - \sigma_1) / \sigma_1 \tag{4}$$

where the σ_2 and σ_1 donate the electrical conductance of SiC₂N_gas and SiC₂N systems, respectively. Additionally, according to the relationship between the σ and E_g in Equation (3), the *S* can be written as follows:

$$S = \exp[-(E_{g2} - E_{g1})/2kT] = \exp(-\Delta E_g/2kT)$$
(5)

where the E_{g2} and E_{g1} are the band gap of SiC₂N_gas and SiC₂N systems, respectively. The sensitivity of SiC₂N toward O-containing VOCs and ammonia at 300, 350, and 400 K were summarized in Figure 8. It can be seen that the sensitivity of SiC₂N toward O-containing VOCs and NH₃ is high ($8.17 \times > 10^4$) within the normal working temperature range (300–400 K). In addition, the sensitivity of some other sensor materials reported in previous studies is summarized in Table S1 [36,54–60]. The sensitivity of SiC₂N toward O-containing VOCs and NH₃ is comparable to or higher than some well-established gas sensors such as Si-GreenP toward acetone (~10⁸ at room temperature) [36], vacancy-doped black phosphorus toward CO₂ (1254%, 298 K) [56], Rh-BN toward SO₂ (4.79 × 10⁷, 298 K) [54], and so on, showing superior sensor ability.



Figure 8. The sensitivity of SiC₂N to O-containing VOCs and NH₃.

We also assess the performance of SiC₂N as a Φ -type sensor in Figure S26 [61,62]. However, the relatively small Φ changes (-6.63%~-8.28%) after O-containing VOC and NH₃ adsorption may cause the SiC₂N to suffer from low sensitivity in the realistic application. The detailed descriptions were displayed in SI. Therefore, by comparison, the Si-doped C₂N is more suitable as a resistive-type sensor for O-containing VOC and NH₃ detection.

The recovery time is another vital factor for gas-sensor materials in practical application, and it can be improved by increasing the working temperature or applying ultraviolet (UV) light. The recovery time was determined by the following [63]:

$$\mathbf{r} = \boldsymbol{\omega}^{-1} \exp(-\frac{E_{\mathrm{ad}}}{kT}) \tag{6}$$

where the ω , E_{ad} , k, and T were the attempt frequency (10¹²/s), adsorption energies for target gases, and Boltzmann constant as well as temperature, respectively. The calculated recovery time of SiC_2N_gas systems at the temperature of 300, 400, and 450 K was summarized in Figure 9a. It can be found that the recovery time of $SiC_2N_C_3H_6O$ is only 1.19×10^{-2} , while the SiC₂N_HCHO, SiC₂N_CH₃OH, and SiC₂N_NH₃ systems require a relatively long time $(1.30 \times 10^3 \sim 2.09 \times 10^8 \text{ s})$ at room temperature. Nevertheless, when using a working temperature of 400 K, the recovery time of SiC₂N_HCHO and SiC₂N_CH₃OH systems can significantly decrease to 12.6 and 2.17×10^{-1} s, respectively. As the temperature continues to rise to 450 K, the SiC₂N_NH₃ system likewise presents a short recovery time of 3.53×10^1 s. It can be seen that only the detection of NH₃ needs a relatively high recovery temperature of 450 K; nevertheless, it is acceptable. The calculated recovery time without UV of O-containing VOCs is shorter than some well-established sensor materials. For example, the recovery time for detecting HCHO of SiC₂N is 12.6 s at 400 K, which is lower than Au-modified indium–gallium–zinc oxide (13 s at 523 K) [64], A-site cation deficiency in LaFeO₃ (13 s at 478 K) [65], In₂O₃ (40 s at 438 K) [66], SnO₂ (7 s at 488 K) [67], and ZnO/SnO₂ (9 s at 498 K) [68]. Moreover, we also estimated the adsorption Gibbs free energies of gases on SiC_2N at the temperature of 300~400 K, as shown in Figure 9b. The adsorption Gibbs free energies were calculated by the following:

$$\Delta G_{ad} = G(\text{SiC}_2\text{N}_{gas}) - G(\text{SiC}_2\text{N}) - G(\text{gas})$$
(7)

where the $G(SiC_2N_gas)$ and $G(SiC_2N)$ donated the Gibbs free energies of SiC_2N_gas and SiC_2N , respectively. Additionally, the G(gas) was the Gibbs free energies of isolated VOCs and NH₃. It can be seen that only the NH₃ exhibits a relatively large ΔG_{ad} of -0.43~-0.61 eV at 300~400 K. The ΔG_{ad} for O-containing VOCs on SiC₂N is quite small, indicating that the entropy effect involving the temperature is conducive to the desorption of gases. In addition, according to previous reports, the recovery time can be further shortened by exposure to UV light ($\omega = 10^{16}/s$) due to the elimination of the desorption barrier [69,70]. Additionally, UV light has been widely used to reduce recovery time. Aasi and coworkers have reported that the desorption of indole from Pd-decorated MoS₂ needs a recovery time of 1.28×10^5 s, whereas, under UV light, the recovery time can greatly decrease to 12.8 s. Herein, the recovery time of SiC₂N_gas systems under UV light at 300, 350, and 400 K is shown in Figure 9c. It can be seen that, under exposure to UV light, the SiC₂N_HCHO, SiC₂N_CH₃OH, and SiC₂N_C₃H₆O possess short recovery times of 29.2, 0.13, and 1.19×10^{-6} s, respectively, at room temperature. Even for the SiC₂N_NH₃ system, when using UV light, the recovery time can be effectively shortened to 26.2 s at 350 K. In a word, the apparent changes in conductivity and acceptable recovery time offer significant advantages for SiC₂N as a resistive-type sensor in the detection of O-containing VOCs and NH₃.



Figure 9. (a) Recovery time of the SiC₂N for VOC and NH₃ detection under visible light; (b) the adsorption Gibbs free energies of VOCs and ammonia on SiC₂N; and (c) recovery time of the SiC₂N for VOC and NH₃ detection under UV light.

Moreover, we also investigated the co-adsorption of gases on the sensor performance of SiC₂N, and the results were recorded in Figures S27–S30 and Table S2. It was found that the coverage and co-adsorption of different gases have little effect on the sensitivity but slightly increase the recovery time. Therefore, in the real application, the environment with low gas concentration is more favorable for the utilization of SiC₂N. A detailed description is displayed in the Supporting Information. Furthermore, we also investigated the sensor performance of the other two nonmetal B- [71] and P-doped C₂N [72] for VOCs and ammonia, the results were recorded in Figures S31–S34 and Table S3. The weak affinity of P-doped C₂N towards VOCs and NH₃ manifests its poor sensor performance. And although BC₂N also presents high sensivitity for O-containing VOCs and ammonia, the BC₂N_gas systems need a long recovery time or high operation temperature. Therefore, comparing B- and P-doped C₂N, the SiC₂N is more suitable as a sensor for VOCs and ammonia.

3.4.2. The Effect of Si Doping Density

In this section, we further increase the doping density of the Si atom to evaluate the effect of doping density on the sensing performance. Two other Si doping densities were taken into consideration, including moderate and high Si doping density. In the case of moderate Si doping density, two Si atoms were incorporated into a 2×2 supercell of C_2N with a Si doping density of 2.70 at%. As shown in Figure S35a,b, there are two possible doping modes for Si₂C₂N. In one case, the two Si atoms are scattered in two different interstitial spaces (labeled as Si₂C₂N_a), and in another one, the Si atoms are gathered in one interstitial space (labeled as Si₂C₂N_b). Additionally, the former configuration is proved to be more energetically favorable ($E_{form} = -2.98$ eV), which is chosen as the computational model for Si₂C₂N. In addition, the Si doping density was further increased to 5.26 at%, and the optimized configuration of Si₄C₂N was shown in Figure S35c. Herein, we first analyze the effect of Si density on the electronic characteristics of Si-doped C₂N in Figure S35d–g. It can be seen that the band gaps of Si-doped C₂N decrease with the Si density. Moreover, similar to SiC₂N, the VBM of Si₂C₂N and Si₄C₂N is composed of active p_z electrons, which also guarantee the high activity of Si₂C₂N and Si₄C₂N.

Then, we further assess the doping density of Si atoms on the sensing performance of Si-doped C₂N toward O-containing VOCs and ammonia. Firstly, the adsorption of HCHO, CH₃OH, C₃H₆O, and NH₃ on Si₂C₂N was investigated. Since the two dopant Si atoms can both serve as the adsorption sites for gases, the adsorptions of single and two gaseous pollutants on Si₂C₂N were both taken into consideration. The optimized adsorption configurations are displayed in Figure S36. It can be seen that the adsorption energies of Si_2C_2N and Si_4C_2N toward O-containing VOCs and ammonia are slightly larger than that of SiC_2N , and the adsorption energies gradually increase with the Si doping density. In addition, the band gaps of Si-doped C2N after the adsorption of O-containing VOCs and ammonia are summarized in Table 2. For Si_2C_2N , similar to SiC_2N , a single molecule of O-containing VOCs or ammonia adsorption can cause remarkable band gap changes. It can be seen after a CH₃OH, C₃H₆O, and NH₃ molecule adsorption that the band gaps of Si₂C₂N_CH₃OH, Si₂C₂N_C₃H₆O, and Si₂C₂N_NH₃ systems considerably decrease to 0.02, 0.03, and 0.07 eV. Additionally, the band gap of Si₂C₂N_HCHO approaches 0 eV, indicating the high sensor performance of Si_2C_2N . The quantities of the adsorbed gases have little effect on sensing performance (see Table S4).

Furthermore, for Si_4C_2N , the adsorption configurations of gases on Si_4C_2N were presented in Figures S37 and S38, and the band gap, as well as band gap changes in $Si_4C_2N_gas$ systems, are also recorded in Table 2. Since the intrinsic band gap of Si_4C_2N is quite small (~0.27 eV), after the adsorption of O-containing VOCs and ammonia, the band gap values are very close to 0 eV. The band gap changes are smaller in contrast with SiC₂N and Si₂C₂N systems, which results in low sensitivity. In addition, since Si doping density also affects adsorption energies, it can be seen that the recovery time is slightly increased along with the Si doping density (see Table 2). Therefore, taking careful consideration of sensitivity and recovery time, low or moderate Si doping densities are more favorable for Si-doped C_2N as a resistive-type sensor.

	E_g (eV)	τ (UV Light)	τ (UV Light)	τ (UV Light)
SiC ₂ N_HCHO	0.11	$2.92 imes 10^1$	$3.59 imes 10^{-2}$	$1.26 imes 10^{-3}$
SiC ₂ N_CH ₃ OH	~0	$1.30 imes10^{-1}$	$3.94 imes10^{-4}$	$2.17 imes10^{-5}$
SiC2N_C3H6O	0.07	$1.19 imes10^{-6}$	$2.49 imes10^{-8}$	$3.61 imes 10^{-9}$
SiC ₂ N_NH ₃	~0	$2.09 imes10^4$	$8.59 imes10^{0}$	$1.74 imes10^{-1}$
Si ₂ C ₂ N_HCHO	~0	$6.68 imes10^4$	$2.26 imes 10^1$	$4.15 imes10^{-1}$
Si ₂ C ₂ N_CH ₃ OH	0.02	$1.37 imes 10^2$	$1.30 imes10^{-1}$	$4.01 imes10^{-3}$
$Si_2C_2N_C_3H_6O$	0.03	$1.79 imes 10^{-5}$	$2.38 imes10^{-7}$	$2.75 imes 10^{-8}$
Si ₂ C ₂ N_NH ₃	0.02	$6.80 imes10^5$	$1.56 imes 10^2$	$2.37 imes10^{0}$
Si ₄ C ₂ N_HCHO	~0	$2.21 imes 10^7$	$2.84 imes10^3$	$3.22 imes 10^1$
Si ₄ C ₂ N_CH ₃ OH	~0	$4.46 imes 10^3$	$2.37 imes10^{0}$	$5.45 imes 10^{-2}$
$Si_4C_2N_C_3H_6O$	~0	$5.70 imes 10^{-5}$	$6.26 imes10^{-7}$	$6.56 imes10^{-8}$
$Si_4C_2N_NH_3$	~0	$4.78 imes10^7$	5.41×10^3	$5.75 imes 10^1$

Table 2. The band gap and recovery time of $Si_nC_2N_gas$ systems based on the PBE functional.

4. Conclusions

In summary, the sensor performance of Si-doped nitrogenated holey graphene (C_2N) for five kinds of representative VOCs (HCHO, CH₃OH, C₃H₆O, C₆H₆, and C₂HCl₃) and NH₃ were systematically evaluated by the first-principle calculations. Firstly, the formation energies and AIMD simulations proved the incorporation of Si atom into C₂N was thermodynamically stable. The Si doping not only induced a considerable decrease (~1.34 eV) in the band gap of C_2N , but also provided an adsorption site for gaseous pollutants. Compared with the inherent physical or weak chemical adsorption of C_2N toward gases, the SiC₂N exhibited high capture capacity and selectivity for O-containing VOCs and NH₃ through intense strong covalent bonds. Furthermore, the potential of SiC₂N as resistiveand work-function-type sensors were checked. The band gap of SiC₂N dramatically decreases after capturing O-containing VOCs and NH₃. The band gap of SiC₂N_HCHO, SiC₂N_CH₃OH, SiC₂N_C₃H₆O, and SiC₂N_NH₃ systems are 0.29, 0.13, 0.25, and 0.12 eV, respectively, which leads to great enhancement in the conductivity of the system. In comparison, the changes in work function were relatively tiny (-6.63% - 8.28%), demonstrating that the SiC_2N is more suitable to act as a resistive-type sensor. In addition, the SiC_2N was found to possess an acceptable recovery time in detecting O-containing VOCs and NH₃. When using UV light, the SiC₂N_HCHO, SiC₂N_CH₃OH, and SiC₂N_C₃H₆O possess short recovery times of 29.2, 0.13, and 1.19×10^{-6} s, respectively, at room temperature. Additionally, the recovery time of $SiC_2N_NH_3$ is 26.2 s at 350 K. In conclusion, our findings demonstrate that the Si-doped C_2N is a promising candidate for the environmental detection of O-containing VOCs and ammonia.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/cryst13050816/s1. Figure S1: Optimized structures of (a) SiC₂N_C, (b) SiC₂N_N, (c) SiC₂N_{I1}, and (d) SiC₂N_{I2}, and (e) SiC₂N_{I3} systems; Figure S2: Variations of temperatures and energies against the time for AIMD simulations of SiC₂N at (a) 300 and (b) 500 K; Figure S3: The band strucures of (a) C₂N and (b) SiC₂N with PBE method; the adsorption sites of (c) C₂N and (d) SiC₂N for VOCs and ammonia; Figure S4: The initial adsorption configurations of HCHO, CH₃OH, and C₃H₆O molecules on the hole site of pristine C₂N; Figure S5: The initial adsorption configurations of C₆H₆, C₂HCl₃, and NH₃ molecules on the hole site of pristine C₂N; Figure S7: The optimized adsorption configurations in Figure S5; Figure S8: The density of states of gases before and after adsorption; the partial density of states of C₂N and (f) C₂N_AHCHO, (b) C₂N_CCH₃OH, (c) C₂N_AC₃H₆O, (d) C₂N_AC₆H₆, (e) C₂N_ACHCl₃, and (f) C₂N_AHCHO, (b) C₂N_ACH₃OH, (c) C₂N_AC₃H₆O, (d) C₂N_AC₆H₆, (e) C₂N_AC₄HCl₃, and (f) C₂N_AHCHO, (b) C₂N_ACH₃OH, (c) C₂N_AC₃H₆O, (d) C₂N_AC₄H₆O, (e) C₂N_AC₄HCl₃, and (f) C₂N_AN_A systems; Figure S9: The initial adsorption configurations of HCHO molecule on the Si

and hole sites of SiC₂N; Figure S10: The initial adsorption configurations of CH₃OH molecule on the Si and hole sites of SiC₂N; Figure S11: The initial adsorption configurations of C₃H₆O molecule on the Si and hole sites of SiC₂N; Figure S12: The initial adsorption configurations of C_6H_6 molecule on the Si and hole sites of SiC₂N; Figure S13: The initial adsorption configurations of C₂HCl₃ molecule on the Si and hole sites of SiC₂N; Figure S14: The initial adsorption configurations of NH_3 molecule on the Si and hole sites of SiC₂N; Figure S15: The optimized adsorption configurations of SiC₂N_HCHO systems based on the initial configurations in Figure S9; Figure S16: The optimized adsorption configurations of SiC₂N_CH₃OH systems based on the initial configurations in Figure S10; Figure S17: The optimized adsorption configurations of $SiC_2N_C_3H_6O$ systems based on the initial configurations in Figure S11; Figure S18: The optimized adsorption configurations of $SiC_2N_{-}C_6H_6$ systems based on the initial configurations in Figure S12; Figure S19: The optimized adsorption configurations of SiC₂N_C₂HCl₃ systems based on the initial configurations in Figure S13; Figure S20: The optimized adsorption configurations of SiC₂N_NH₃ systems based on the initial configurations in Figure S14; Figure S21: The optimal binding configurations of N_2 and O_2 on SiC₂N; Figure S22: The density of states of gases before and after adsorption, the partial density of states of SiC₂N and gases for (a) $SiC_2N_C_6H_6$ and (b) $SiC_2N_C_2HCl_3$ systems; Figure S23: The electron localization function (ELF) diagrams of (a) SiC₂N_HCHO, (b) SiC₂N_CH₃OH, (c) SiC₂N_C₃H₆O, and (d) SiC₂N_NH₃ systems, in which partial atoms are hidden for better reading; Figure S24: The charge density difference between gases and SiC₂N in (a) SiC₂N_HCHO, (b) SiC₂N_CH₃OH, (c) SiC₂N_C₃H₆O, (d) SiC₂N_C₆H₆, (e) SiC₂N_C₂HCl₃, and (f) SiC₂N_NH₃ systems; Figure S25: Band structures of (a) SiC₂N_HCHO, (b) SiC₂N_CH₃OH, (c) SiC₂N_C₃H₆O, (d) SiC₂N_C₆H₆, (e) SiC₂N_C₂HCl₃, and (f) SiC₂N_NH₃ systems within PBE method; Figure S26: (a) The work function and (b) work function changes in SiC₂N and SiC_2N_gas systems; Figure S27: The adsorption configurations of two or three same gases on the SiC_2N sheet; Figure S28: The adsorption configurations of two kinds of gases on the SiC_2N sheet; Figure S29: The adsorption configurations of three kinds of gases on the SiC_2N sheet; Figure S30: The band structures of the two-molecule adsorption system; Figure S31: The optimal configuration, band structure, and partial density of states of BC_2N and PC_2N ; Figure S32: The optimal adsorption configurations of VOCs and ammonia on BC₂N; Figure S33: The optimal adsorption configurations of VOCs and ammonia on PC₂N; Figure S34: The band structure of BC₂N_HCHO, BC₂N_CH₃OH, $BC_2N_C_3H_6O$, and $BC_2N_NH_3$ systems; Figure S35: The optimized configurations of (a) $Si_2C_2N_a$, (b) Si₂C₂N_b, and (c) Si₄C₂N; the band structure of (d) Si₂C₂N and (f) Si₄C₂N; the partial density of states of (e) Si₂C₂N and (g) Si₄C₂N; Figure S36: The optimized configurations of HCHO, CH₃OH, C_3H_6O , and NH_3 on Si_2C_2N ; Figure S37: The optimized configurations of HCHO and CH_3OH on $Si_4C_2N_i$; Figure S38: The optimized configurations of C_3H_6O and NH_3 on Si_4C_2N . Table S1: The sensitivity of some other sensor materials reported in previous studies; Table S2: The adsorption energies and recovery times of gas co-adsorption on SiC_2N sheet; Table S3: The recovery time of BC_2N_gas systems under UV light; Table S4: The band gap and recovery time of $Si_nC_2N_gas$ systems based on the PBE functional.

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