First-Principles Insight into Pd-Doped C\textsubscript{3}N Monolayer as a Promising Scavenger for NO, NO\textsubscript{2} and SO\textsubscript{2}

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Abstract: The adsorption and sensing behavior of three typical industrial toxic gases NO, NO\textsubscript{2} and SO\textsubscript{2} by the Pd modified C\textsubscript{3}N monolayer were studied in this work on the basic first principles theory. Meanwhile, the feasibility of using the Pd doped C\textsubscript{3}N monolayer (Pd-C\textsubscript{3}N) as a sensor and adsorbent for industrial toxic gases was discussed. First, the binding energies of two doping systems were compared when Pd was doped in the N-vacancy and C-vacancy sites of C\textsubscript{3}N to choose the more stable doping structure. The result shows that the doping system is more stable when Pd is doped in the N-vacancy site. Then, on the basis of the more stable doping model, the adsorption process of NO, NO\textsubscript{2} and SO\textsubscript{2} by the Pd-C\textsubscript{3}N monolayer was simulated. Observing the three gases adsorption systems, it can be found that the gas molecules are all deformed, the adsorption energy (\(E_{ad}\)) and charge transfer (\(Q_{T}\)) of three adsorption systems are relatively large, especially in the NO\textsubscript{2} adsorption system. This result suggests that the adsorption of the three gases on Pd-C\textsubscript{3}N belongs to chemisorption. The above conclusions can be further confirmed by subsequent deformable charge density (DCD) and density of state (DOS) analysis. Besides, through analyzing the band structure, the change in electrical conductivity of Pd-C\textsubscript{3}N after gas adsorption was studied, and the sensing mechanism of the resistive Pd-C\textsubscript{3}N toxic gas sensor was obtained. The favorable adsorption properties and sensing mechanism indicate that the toxic gas sensor and adsorbent prepared by Pd-C\textsubscript{3}N have great application potential. Our work may provide some guidance for the application of a new resistive sensor and gas adsorbent Pd-C\textsubscript{3}N in the field of toxic gas monitoring and adsorption.

Keywords: Pd-C\textsubscript{3}N monolayer; first-principles calculation; toxic gas; adsorption

1. Introduction

Nowadays, with the progress of the economy and the acceleration of industrialization, the problem of industrial waste gases is becoming more and more serious. The industrial production process produces a large number of industrial waste gases, and these waste gases’ emission into the air will spread with the flow of the atmosphere, causing great harm to the environment and threatening the physical and mental health of the people [1,2]. NO, NO\textsubscript{2} and SO\textsubscript{2} are several typical toxic industrial waste gases. Hence, finding an effective method of detecting and adsorbing these toxic gases is of great significance to protect our living environment.

Since the typical two-dimensional (2D) material graphene was successfully synthesized, 2D nanomaterial, such as transition metal dihalogen compounds [3–5], silicene [6,7], germanene [8,9], and stanene [10,11], have attracted extensive attention in academia. The excellent properties of these 2D materials make them have broad application prospects in many areas [12–15]. Whereas, the zero-band gap characteristic of graphene limits its application in the nanoelectronics field [16,17]. Thus, researchers began to explore novel two-dimensional graphene-like materials, such as metal nitrides and carbides [18], III-V nitrides [19–21], etc. Among these new graphene-like materials, a planar honeycomb C\textsubscript{3}N...
monolayer which can be thought of as a $2 \times 2$ graphene supercell substituted by two N atoms is emerging \[22,23\]. C$_3$N is a semiconductor, and one of its characteristics compared to graphene is its indirect band gap. Owing to the substitution of N atoms, compared with graphene, the C$_3$N monolayer has higher chemical activity and carrier mobility as well as better structural stability \[24,25\]. Therefore, C$_3$N may have great application potential in gas sensing and adsorption fields \[26,27\]. Previous studies have shown that intrinsic C$_3$N is inert to many toxic gases \[28\]. The adsorption capacity of nanomaterial with transition metal (TM) doping on gas molecules can be significantly improved due to significant electron hybridization between the TM atom and gas molecule \[29–31\]. Zhu et al. \[32\] found that the InN monolayer doped with Pd has a good application prospect in detecting and removing toxic gases CO and NO. Ma et al. \[33\] found that the Au, Pt, Pd and Ni modified MoS$_2$ monolayers have good sensing performance for CO and NO gases. Therefore, the doping of Pd may enhance the adsorption capacity of C$_3$N to toxic gases NO, NO$_2$ and SO$_2$. However, so far, few research has been executed in the adsorption properties of the TM doped C$_3$N (TM-C$_3$N) monolayer for toxic gases such as NO, NO$_2$ and SO$_2$.

Based on first principles, the doping behavior of Pd on C$_3$N and the adsorption properties of Pd-C$_3$N for NO, NO$_2$ and SO$_2$ were studied in this study. Further, to study the adsorption properties and sensing mechanism of Pd-C$_3$N for three kinds of toxic gases, the $E_{ad}$, QT, DCD, DOS and band structure were analyzed. The results show that NO, NO$_2$ and SO$_2$ can be stably adsorbed by Pd-C$_3$N, which can be recognized as chemisorption. The adsorption properties and sensing mechanism of Pd-C$_3$N for toxic gases obtained in this work provide a theoretical basis for further study of the toxic gas resistive sensor and adsorbent prepared by Pd-C$_3$N.

2. Computation Methods

All the theoretical calculations on the basic density functional theory (DFT) in this paper were carried out in the dispersion-corrected DMol$^3$ package \[34,35\]. The exchange-correlation between electrons was handled by the Perdew–Burke–Ernzerhof (PBE) function under the generalized gradient approximation (GGA) to better describe the non-uniform electron density of the system which was closer to the experimental situation \[36–38\]. The DFT-D method, which was customized by Grimme, was used to understand van der Waals force and long-range interactions better \[39\]. We used DFT semi-core pseudopotential (DSSP) to handle the effects of core electron relativity and chose double numerical plus polarization (DNP) to calculate the density function of each model \[40–42\]. In terms of the setup of Monkhorst-Pack k-point mesh, $7 \times 7 \times 1$ was set for geometric optimization and $10 \times 10 \times 1$ for the calculation of static electronic structure \[43\]. The energy tolerance accuracy, maximum force, and displacement were severally set as $10^{-5}$ Ha, 0.002 Ha/Å and 0.005 Å \[44\].

A $2 \times 2 \times 1$ C$_3$N supercell with 28 C atoms and 13 N atoms was built. In order to prevent the adjacent layers from interacting with each other, the vacuum region was set to 15 Å \[45\]. The lattice constant of the fully optimized C$_3$N monolayer was calculated as 4.92 Å, which was basically consistent with the previous report (4.9 Å \[46\]). The Hirshfeld method was adopted to study the electronic behavior of atoms and molecules \[47\]. Meanwhile, charge transfer (QT) is defined to describe the electronic behavior of Pd doping and gas adsorption systems. A positive QT value means the analyte acts as an electron donator, on the contrary, a negative QT value means that the analyte acts as an electron acceptor \[48\].

3. Results and Discussions

3.1. Isolated Gas Molecules and Pd-C$_3$N Monolayer

Figure 1 displays the optimized structural models of the intrinsic C$_3$N monolayer and three gas molecules NO, NO$_2$ and SO$_2$. At the same time, Table 1 lists the geometrical parameters of the optimized three kinds of gas molecular configurations and Table 2 lists the single atom charges of gas molecules in the gas phase.
3. Results and Discussions

3.1. Isolated Gas Molecules and Pd-C\textsubscript{3}N Monolayer

Table 1. Geometrical parameters of NO, NO\textsubscript{2} and SO\textsubscript{2}.

| Gas   | Bond Length (Å) | Bond Angle (°) |
|-------|-----------------|----------------|
| NO    | N-O             | 1.164          | -              | -              |
| NO\textsubscript{2} | N-O             | 1.210          | O-N-O          | 133.487        |
| SO\textsubscript{2} | S-O             | 1.480          | O-S-O          | 119.970        |

Table 2. Single atom charges of gas molecules in the gas phase.

| Gas   | N      | O      | S      |
|-------|--------|--------|--------|
| NO    | 0.035  | -0.035 | -      |
| NO\textsubscript{2} | 0.375  | -0.188 | -      |
| SO\textsubscript{2} | -      | 0.454  | -0.227 |

According to previous report, the metal atom can be stably adsorbed by the C\textsubscript{3}N monolayer with one C atom or one N atom deficiency (simplified as VC-C\textsubscript{3}N and VN-C\textsubscript{3}N below) due to the strong electrostatic attraction where electronic localization occurs [49]. Therefore, to obtain the most stable doping structure, priority was given to the Pd atom doping at the C-vacancy or N-vacancy site on the C\textsubscript{3}N monolayer. The two optimized doping configurations are shown in Figure 2. When Pd is doped at the C-vacancy site, the length of Pd-C and Pd-N is significantly different, which are 1.979 and 2.518 Å, respectively. However, when Pd is doped at the N-vacancy site, the three Pd-C bonds have basically the same length, 2.004, 2.006 and 2.008 Å, respectively. This result shows that the doping system with Pd doping at the N-vacancy site has better central symmetry. In this paper, the stability of the doping system is evaluated by binding energy ($E_\text{b}$), and the calculation formula is as follows:

$$E_\text{b} = E_\text{Pd-C}_3\text{N} - E_\text{vacancy-C}_3\text{N} - E_\text{Pd}$$  \hspace{1cm} (1)

In the above formula, $E_\text{Pd-C}_3\text{N}$ denotes the energy of the Pd-doped system, and $E_\text{vacancy-C}_3\text{N}$ and $E_\text{Pd}$ denote the energy of the defective C\textsubscript{3}N and Pd atom, respectively. The binding energies of Pd doping at the C-vacancy site and N-vacancy site are $-4.080$ and $-5.023$ eV, respectively. This result indicates that Pd tends to be doped at the N-vacancy site, because the doping system at this time is more stable.

To further study the electronic behavior of Pd-C\textsubscript{3}N, we calculated DCD and DOS, as displayed in Figures 2 and 3, respectively. In the DCD of Figure 2, the areas with increased charge density are shown in red, while the areas with decreased charge density are shown in blue. As shown in Figure 2b, in the doping system where Pd doped is in the N-vacancy site, the charge density around Pd and C atoms decreases, while the charge density around N atoms increases. This result implies the electron-losing property of the Pd atom. In other
words, the Pd atom transfers electrons to the VN-C$_3$N monolayer. Meanwhile, the electron density between the Pd atom and C atom is very high, which suggests that a stable chemical bond in Pd-C is formed, so Pd can be stably adsorbed by VN-C$_3$N. As can be seen from the total DOS of Pd-C$_3$N, the spin up and spin down curves are highly symmetrical. This phenomenon shows that the doping system is not magnetic. Besides, the doping of Pd induces several impurity states, leading to some new peaks of total DOS after doping in the vicinity of $-5.5$, $-4.0$, $0.2$, $1.0$ and $2.0$ eV. New peaks can be observed at the top of the valence band and at the bottom of the conduction band, indicating that Pd doping contributes greatly to the states near the Fermi energy. According to Figure 3b, huge hybridization occurs between Pd 4d orbital and C 2p orbital at multiple energy levels, such as $-5.5$, $-2.7$, $-2$ and $0.2$ eV. This phenomenon confirms the previous conclusion that Pd can form a stable chemical bond with C and can be stably adsorbed by VN-C$_3$N. Through the analysis of DCD and DOS, it can be concluded that the electronic behavior of VN-C$_3$N has a significant change after doping with the Pd atom.

![Figure 2](image_url)

Figure 2. Top view of the optimized structure, side view of DCD (a) Pd doped in VC-C$_3$N, (b) Pd doped in VN-C$_3$N.

![Figure 3](image_url)

Figure 3. (a) TDOS of the VN-C$_3$N monolayer, Pd-C$_3$N monolayer, (b) PDOS of the Pd-C$_3$N monolayer, the dotted line indicates the Fermi energy.
3.2. Adsorption Analysis of Pd-C$_3$N Monolayer to NO, NO$_2$, SO$_2$

In order to fully compare various possible configurations of the three gas adsorption systems and find the most stable one for analysis, NO, NO$_2$ and SO$_2$ were placed in different directions on top of the Pd-C$_3$N monolayer. Adsorption energy ($E_{ad}$) can describe the energy change of each adsorption structure, so it can be used to assess the stability of the system after adsorption of gas. The calculation formula of $E_{ad}$ is as below:

$$E_{ad} = E_{Pd-\text{C}_3\text{N/gas}} - E_{Pd-\text{C}_3\text{N}} - E_{\text{gas}}$$

In the above formula, $E_{Pd-\text{C}_3\text{N/gas}}$ and $E_{Pd-\text{C}_3\text{N}}$ respectively represent the energy before and after the adsorption of gas by Pd-C$_3$N, and $E_{\text{gas}}$ represents the energy of the isolated gas molecule. The adsorption energies of the three gas adsorption systems are all negative, suggesting that the gas adsorption process of Pd-C$_3$N is accompanied by the release of heat. Choose the structure with the lowest $E_{ad}$, that is, the most stable configuration for subsequent works (as displayed in Figure 4). To understand the mechanism of charge transfer better, deformed charge density (DCD) is also described in Figure 4.

Meanwhile, Tables 3 and 4 show the specific characteristic parameters of the three gas adsorption systems.

![Figure 4](image_url)

**Figure 4.** The steadiest adsorption configuration of gas on the Pd-C$_3$N monolayer and the DCD of this configuration (a) NO; (b) NO$_2$ and (c) SO$_2$ adsorption systems.

In the NO adsorption system, the NO molecule is adsorbed on top of the Pd atom and perpendicular to the C$_3$N plane. When NO is adsorbed, the N-O bond elongates from 1.164 to 1.188 Å, indicating that the NO molecule has certain activity during the adsorption process. The $E_{ad}$ of the NO adsorption system is $-1.83$ eV, so the adsorption of NO by the Pd-C$_3$N monolayer can be identified as chemisorption. Meanwhile, according to the DCD in Figure 4a, the charge density near N atoms and O atoms increases. From the molecular point of view, NO has a 0.122 e negative charge, indicating the electron-receiving property of NO. During the interaction with the Pd-C$_3$N monolayer, NO obtains 0.122 e from it. According to Figure 4b,c, NO$_2$ and SO$_2$ tend to be adsorbed on one side of the Pd dopant in the Pd-C$_3$N monolayer rather than on the top. In addition, the adsorbed NO$_2$ and SO$_2$ molecules are negatively charged, which means that they both act as electron acceptors to absorb 0.407 e and 0.177 e from the Pd-C$_3$N monolayer, respectively. In the NO$_2$ adsorption...
system, the N-O bond elongates to 1.281 Å compared to the 1.210 Å in the isolated phase. At the same time, the O-N-O bond angle of the NO$_2$ molecule in the adsorption system decreases from 133.487° in the gas phase to 111.674°. This significant deformation indicates that NO$_2$ has obvious geometric activation during its interaction with the Pd dopant. Besides, the charge density near the N atom in the NO$_2$ adsorption system decreases, while the charge density near the O atom increases. In addition, the $E_{ad}$ of the NO$_2$ adsorption system is $-2.74$ eV, which indicates that NO$_2$ has an ideal chemisorption on the surface of Pd-C$_3$N, which is supported by large $Q_T$ ($-0.407$ e) and geometric deformation. In the SO$_2$ adsorption system, the S-O bond elongates from 1.480 to 1.495 Å, while the O-S-O bond angle decreases from 119.970° to 119.932°, suggesting that SO$_2$ is activated when interacting with the surface of Pd-C$_3$N. The $E_{ad}$ of the SO$_2$ adsorption system is $-1.61$ eV, $Q_T$ is $-0.177$ e, which can be used to identify the adsorption as chemisorption.

Table 3. The geometrical parameters of three gas adsorption systems.

| System          | The Length of Bond (Å) | Bond Angle (°) | Adsorption Distance (Å) |
|-----------------|------------------------|----------------|-------------------------|
| Pd-C$_3$N + NO  | N-O 1.188              |                | 1.904                   |
|                 | Pd-C 2.046, 2.046, 2.050|                |                         |
| Pd-C$_3$N + NO$_2$ | N-O 1.281              | O-N-O 111.674 | 2.202                   |
|                 | Pd-C 1.978, 1.979, 2.016|                |                         |
| Pd-C$_3$N + SO$_2$ | S-O 1.495              | O-S-O 119.932 | 2.261                   |
|                 | Pd-C 2.046, 2.044, 1.990|                |                         |

Table 4. The characteristic parameters of three gas adsorption systems.

| System          | Atom | Mulliken Charge (e) | $Q_T$ (e) | $E_{ad}$ (eV) |
|-----------------|------|---------------------|-----------|---------------|
| Pd-C$_3$N + NO  | N    | $-0.033$            | $-0.122$  | $-1.83$       |
|                 | O    | $-0.089$            |           |               |
| Pd-C$_3$N + NO$_2$ | N    | $0.270$             | $0.407$   | $-2.74$       |
|                 | O$_1$| $-0.338$            |           |               |
|                 | O$_2$| $-0.339$            |           |               |
| Pd-C$_3$N + SO$_2$ | S    | $0.457$             | $-0.177$  | $-1.61$       |
|                 | O$_1$| $-0.303$            |           |               |
|                 | O$_2$| $-0.331$            |           |               |

Previous reports have shown that $E_{ad}$ of the intrinsic C$_3$N monolayer adsorption system for NO, NO$_2$ and SO$_2$ is $-0.248$, $-0.840$ and $-0.584$ eV, respectively [28]. Comparing to the results in this study, it can be found that the adsorption capacity of Pd-C$_3$N for NO, NO$_2$ and SO$_2$ was significantly higher than that of intrinsic C$_3$N. At the same time, the adsorption process of three kinds of gas molecules by the Pd-C$_3$N monolayer is accompanied by a relatively large charge transfer, which indicates that the adsorption of gas will lead to the redistribution of electrons in the whole system and change the electronic behavior of Pd-C$_3$N. To further explore the electronic behavior of Pd-C$_3$N during the adsorption of NO, NO$_2$ and SO$_2$, DOS is analyzed in the following.

3.3. DOS Analysis of NO, NO$_2$ and SO$_2$ Adsorption Systems

DOS is an important parameter for studying the electronic behavior of the interaction between gas and the Pd-C$_3$N surface. According to Figure 5, the total DOS (TDOS) of the three adsorption systems shift to the right in different degrees compared with the Pd-C$_3$N monolayer, and some new peaks appear nearby the Fermi level. In the TDOS of
NO adsorption system, novel peaks appear in the vicinity of $-1$, $-0.1$ and 2 eV, while in NO$_2$ and SO$_2$ adsorption systems, the new peaks appear in the vicinity of $-1.5$, $-0.3$ and 0.3 eV. Besides, there are multiple activated states in the gas molecules due to the interaction between it and the surface of the Pd dopant. Then, the orbital hybridization of these activated states with Pd 4d results in new peaks in the TDOS of the three adsorption systems. In particular, the activated states of gas molecules lead to a certain degree of deformation of the states at the top of the conduction band and the bottom of the valence band, which indicates that the adsorption of gas will affect the electronic behavior of Pd-C$_3$N.

![Figure 5](image-url)

**Figure 5.** TDOS and PDOS of (a) NO, (b) NO$_2$ and (c) SO$_2$ adsorption systems, the dotted line indicates the Fermi energy.
Atomic DOS (PDOS) is shown in Figure 5. In the NO adsorption system, the N 2p and O 2p orbitals of activated NO have certain hybridization with Pd 4d orbitals at −8, −7, 0 (Fermi level) and 2.2 eV. According to the atomic DOS of the NO₂ adsorption system, the Pd 4d orbital is strongly hybridized with N 2p and O 2p orbitals around −8, −7.2 and 2 eV, resulting in a relatively large charge transfer between NO₂ and Pd-C₃N. In the atomic DOS of SO₂ adsorption system, S 2p, O 2p and Pd 4d orbital have strong hybridization at energy levels of −6.3, −2.5, −0.2 and 2 eV, indicating that there is a good orbital interaction between SO₂ and Pd dopant. The strong hybridization between the atomic orbitals of the three gas molecules and Pd 4d orbital again confirms that NO, NO₂ and SO₂ can be stably adsorbed by Pd-C₃N.

In summary, the strong interaction between three gases and Pd-C₃N during gas adsorption process significantly affects the electronic behavior of Pd-C₃N.

### 3.4. Band Structure Analysis of NO, NO₂ and SO₂ Systems

To further study the change in electrical conductivity of Pd-C₃N after adsorbing gas, we calculated and analyzed the band structure of three adsorption systems (Figure 6). In the band structure, the energy interval with zero energy state density between the conduction band and the valence band is called the band gap [50,51]. The narrower the band gap, the more easily the electron can be excited across the band gap, the higher the conductivity. According to Figure 6a, the band gap of the Pd-C₃N monolayer is 0.203 eV, which is much narrower than that of C₃N (0.44 eV [52]). Besides, the band structure of the doping system does not have an impurity state beyond the Fermi level. Thus, C₃N doped with the Pd atom still has semiconductor property. In the band structure of NO and SO₂ adsorption systems (Figure 6b,d), the new impurity level surpassing the Fermi energy appears at the top of the valence band, causing a zero band gap for both systems. Therefore, the adsorption of NO and SO₂ can be deemed to strong p-type doping for Pd-C₃N [53]. According to Figure 6, the band gap of NO and SO₂ adsorption system is 0 eV, while that of NO₂ adsorption system is 0.091 eV. It can be seen that the band gaps of these three adsorption systems are much narrower than that of Pd-C₃N. This result shows that the conductivity of Pd-C₃N is observably improved after adsorbing gas, especially after adsorbing NO and SO₂. Through calculating and analyzing the band structure of the three adsorption systems, it is helpful to further understand the sensing mechanism of the resistive chemical sensor prepared by Pd-C₃N.

![Figure 6](image-url) **Figure 6.** Energy band structure of (a) Pd-C₃N monolayer and (b) Pd-C₃N/NO, (c) Pd-C₃N/NO₂, (d) Pd-C₃N/SO₂ systems.

### 4. Conclusions

The adsorption performance and sensing mechanism of the Pd-C₃N monolayer for three kinds of industrial toxic gases NO, NO₂ and SO₂ were explored based on first principles. The DCD, DOS and band structure were considered to study the change in...
electronic behavior and conductivity of Pd-C$_3$N after adsorbing gas. The main conclusions of this study are listed as below:

1. The Pd dopant is more likely to be adsorbed on the N-vacancy site of the C$_3$N than the C-vacancy site, because the lower binding energy ($E_b = -5.023$ eV) of this doping system implies a more stable structure.

2. NO, NO$_2$ and SO$_2$ can be stably adsorbed by the Pd-C$_3$N monolayer and the adsorption can be identified as chemisorption. Besides, the adsorption energy ($E_{ad}$) of the Pd-C$_3$N/gas system is much higher than that of the C$_3$N/gas system. Among three gas adsorption systems, $E_{ad}$ and $Q_T$ of the NO$_2$ system are the largest, which indicates that Pd-C$_3$N has the strongest adsorption performance for NO$_2$.

3. Through the analysis of DOS, it is found that the gas molecules are activated during the interaction with the Pd dopant surface. The orbital hybridization of these activated states with Pd 4d give rise to new peaks in the TDOS of the three adsorption systems, which influences the electronic behavior of Pd-C$_3$N.

4. Through analyzing the band structure, it can be discovered that the band gap of Pd-C$_3$N becomes narrower after adsorbing NO, NO$_2$ and SO$_2$, which significantly improves the conductivity of Pd-C$_3$N, especially after adsorbing NO and SO$_2$.

To sum up, the calculation in this paper can offer some theoretical basis for the further study of Pd-C$_3$N as a resistive sensor and gas adsorbent for the monitoring and adsorption of typical industrial toxic gases in the environment.

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