The Investigation of Adsorption Behavior of Gas Molecules on FeN₃-Doped Graphene

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1. Introduction

The air pollution caused by the emission of poison gases has attracted global attention in recent years. For example, the gases, such as C₃H₂, H₂S, SO₂, SO₃, and O₂, can harm the health of human beings in our daily life. Among these gases, SO₂ and SO₃ are the general inducement of acid rain [1]; H₂S is a kind of combustible gas with no colour [2]; C₃H₂ is a gas with a little poison for cells in the human body [3]; the gas sensor can be used to detect inflammable and poison gases and has been applied extensively into areas including industry and fire control [4]. Based on this basic model, many works have also been performed on the gas capture and catalysis [2, 3, 5–8]. The commonly used adsorbates mainly include metals, metal oxides, and graphene-based materials. The graphene-based single-atom catalysts (SAC-gra) have been extensively applied into gas sensor due to the merits including low cost, high conductivity, perfect chemical stability, big specific surface area, and high mechanical strength [9–11]. Most importantly, the electric properties of substrates can be changed under the influence of molecule adsorption, which mainly originates from the charge transfer between molecules and the substrates [12]. Thus, graphene is a promising candidate in gas sensor [13–15]. In some experimental works, the graphene has been made into some devices of gas sensors with high sensitivity [16, 17], which has great significance for establishing early warning systems.

The transition metals (TMs) and N atoms are commonly used dopants in graphene-based SAC, which play an important role in catalytic reactivity [18–23]. The Fe SAC based on N-doped graphene has been proved to possess remarkable reactivity in pioneering works [24]. Thus, the N-coordinated SAC-gra has been extensively investigated by
scientists to find out the effective catalysts for electric catalysts [25–27]. For example, the first-principle investigation of N\textsubscript{2} adsorption on FeN\textsubscript{3}-doped graphene (FeN\textsubscript{3}-gra) has been performed and the results demonstrate that the catalyst can activate N\textsubscript{2} to N\textsubscript{2}H\textsubscript{4} with high efficiency [28]. Liu et al. have also investigated the degradation of CH\textsubscript{4}O to H\textsubscript{2}O and CO\textsubscript{2} on FeN\textsubscript{3}-gra, indicating that the desorption process of the reaction products is advantageous in this system [29]. However, the reports on the gases, including C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}S, SO\textsubscript{2}, SO\textsubscript{3}, and O\textsubscript{2}, are limited on FeN\textsubscript{3}-gra.

Herein, we have performed calculations based on density functional theory (DFT) on FeN\textsubscript{3}-gra, including geometric configurations, stability, and origin of magnetic. In addition, the adsorption of gas molecules, including C\textsubscript{2}H\textsubscript{2}, H\textsubscript{2}S, SO\textsubscript{2}, SO\textsubscript{3}, and O\textsubscript{2}, has also been studied on FeN\textsubscript{3}-gra. The calculations are mainly focused on the change of configurations, charge density, and spin states influenced by the interaction between gas molecules and substrates. The intrinsic mechanism has also been analyzed via density of states (DOS). Our results may pave the way for development of gas sensor on both experimental and theoretical aspects.

2. Computational Methods

In this work, the first-principle calculations are carried out based on density functional theory (DFT) in the Vienna ab initio simulation package (VASP). Exchange and correlation potential is illustrated by the projector augmented wave (PAW) [30, 31] and the generalized gradient approximation (GGA) in format [32–34]. The interaction of the van der Waals (vdW) is employed with DFT-D3 [35]. Other geometric and physical parameters are described in detail in our previous work [36]. The charge transfer characteristics between FeN3-gra and the catalysts are evaluated by the Bader charge [37].

The binding energy of single Fe atom (\(E_b[\text{Fe}]\)) in Fe/N\textsubscript{3}-gra is expressed as

\[ E_b[\text{Fe}] = E[\text{Fe}] + E[d - \text{Fe}/N_3 - \text{gra}] - E[\text{Fe}/N_3 - \text{gra}], \]  

where the \(E[\text{Fe}/N_3 - \text{gra}], E[d - \text{Fe}/N_3 - \text{gra}], \) and \(E[\text{Fe}]\) denote total energy of Fe/N\textsubscript{3}-gra, Fe/N\textsubscript{3}-gra with Fe vacancy, and single Fe atom in vacuum, respectively.

The adsorption energy of gas molecules \(E_{ad}[\text{gas}]\) on Fe/N\textsubscript{3}-gra is expressed as

\[ E_{ad}[\text{gas}] = E[\text{gas}] + E[\text{Fe}/N_3 - \text{gra}] - E[\text{gas} - \text{Fe}/N_3 - \text{gra}], \]  

where the \(E[\text{gas} - \text{Fe}/N_3 - \text{gra}], E[\text{Fe}/N_3 - \text{gra}], \) and \(E[\text{gas}]\) denote total energy of gas adsorbed Fe/N\textsubscript{3}-gra, Fe/N\textsubscript{3}-gra surface, and single gas molecules in vacuum, respectively.

In addition, the electron density difference is visualized via VESTA3 [38].

3. Results and Discussion

3.1. The Configuration and Electric Properties of FeN\textsubscript{3}-gra.

The configuration of FeN\textsubscript{3}-gra after full optimization is shown in Figure 1. The length of Fe-N bonds is 1.87 Å. The uplift height of Fe atom above graphene plane is about 1.47 Å, which can serve as an appropriate adsorption site [28]. In order to verify the stability of the configuration, the binding energy of Fe atom in the FeN\textsubscript{3}-gra is also calculated with a value of 4.97 eV, which is larger than the cohesive energy of Fe. This may indicate that the N atoms can bind Fe tightly enough to prohibit the aggregation of Fe atoms into clusters. Therefore, the FeN\textsubscript{3}-gra possesses strong geometric stability, which is beneficial for application in gas adsorbate. Table S1 has summarized the data of bond length, the uplift height of Fe, charge, binding energies, and magnetic moments. The values calculated generally agree with the pioneering works, indicating the accuracy of our results [39].

It is worth noting that the charge transfer (CT) between Fe and N atoms in FeN\textsubscript{3}-gra is 0.96 e (Bader charge). However, the CT between Fe and adjacent C atoms in Fe-doped graphene with no N doping (Fe-gra) is only 0.69 e [40]. Thus, N doping can lead to the formation of covalent bonds between Fe and the substrate. Besides, the N doping can also increase the magnetic moment from 0 (Fe-gra) to 3.17 μB (FeN\textsubscript{3}-gra), which further leads to a half-occupied state of the system [41, 42]. In order to verify the magnetic character of FeN\textsubscript{3}-gra, the DOS has been calculated, showing an asymmetrical distribution between up and down spin, leading to a high magnetic moment (see Figure 2). There exists a strong overlap between Fe-3d states and total dos (TDOS) of FeN\textsubscript{3}-gra. This may indicate that the magnetic moments are mainly contributed by the 3d states, which can be enhanced via the hybridization between Fe and N atoms. In order to further clarify the character of magnetism, we have also displayed the density of spin in Figures 1(c) and 1(d). The distribution of spin mainly concentrates on the Fe site, which agrees with the DOS.

3.2. The Adsorption Behavior of C\textsubscript{2}H\textsubscript{2} and H\textsubscript{2}S.

The optimal adsorption configurations of gas molecules are confirmed after comprehensive calculation of different adsorption orientations (see Figure S1).

We first focus our study on the adsorption of C\textsubscript{2}H\textsubscript{2} and H\textsubscript{2}S on FeN\textsubscript{3}-gra. For C\textsubscript{2}H\textsubscript{2} adsorption, the C-C bond distributes nearly parallel to the FeN\textsubscript{3}-gra surface (see Figure S2). The bond angle and bond length of C\textsubscript{2}H\textsubscript{2} have changed dramatically after adsorption, which is mainly caused by the strain around Fe dopant. The adsorption energy and adsorption distance are 2.23 eV and 1.93 Å (see Table S2), which agrees with the situation on Mn-doped graphene [43]. The Fe dopant can also promote the charge transfer between gas molecules and substrates (see Table S2): the C\textsubscript{2}H\textsubscript{2} and H\textsubscript{2}S all act as electron acceptor and are negatively charged with 0.43e and 0.07e, respectively (see Figure S3). For H\textsubscript{2}S adsorption, H\textsubscript{2}S tends to adsorb on the top site of FeN\textsubscript{3}-gra with an adsorption energy of 1.19 eV, which agrees with the pioneering works [22, 40]. The bond length and bond angle of H\textsubscript{2}S are similar as adsorbed on FeN\textsubscript{3}-gra and Fe-gra. Therefore, the N doping has nearly no influence on the adsorption behavior of H\textsubscript{2}S (see Table S3) [22].
In order to clarify the adsorption behavior of C$_2$H$_2$ and H$_2$S on FeN$_3$-gra, we have also calculated the partial density of state (PDOS). As shown in Figure 3(a), the distribution of Fe-3d states has become delocalized after C$_2$H$_2$ adsorption and hybridized with C$_2$H$_2$’s orbitals dramatically near Fermi level. In addition, the spin states have also changed significantly with an increased magnetic moment of 3.02 $\mu$B (see Table S2), which agrees with the spin density (see Figure S1 (a)). Therefore, the regulation of DOS near Fermi level can significantly change the electric and magnetic properties of FeN$_3$-gra, which is beneficial for the application in spintronic devices.

In comparison, the hybridization between H$_2$S and FeN$_3$-gra is much less than C$_2$H$_2$ situation, leading to a weaker adsorption ability of H$_2$S. The Fe in FeN$_3$-gra can form chemical bonds with H$_2$S (see Figure S3 (b)), which agrees with PDOS analysis. Similar to C$_2$H$_2$, the spin states of H$_2$S/FeN$_3$-gra complex has changed significantly for both up and down spins compared to bare FeN$_3$-gra (see Figure 3(b)), leading to a total magnetic moment of 3.24 $\mu$B. The increased spin state originates from the charge transfer from FeN$_3$-gra to H$_2$S, leading to a decreased electric energy of H$_2$S. The spin states are strongly localized on Fe site in FeN$_3$-gra (Figure S1 (b)).
The changed band gap is particularly interesting, which is beneficial for the application in the gas sensor for H\textsubscript{2}S.

3.3. The Adsorption Properties of SO\textsubscript{2} and SO\textsubscript{3}. The adsorption configurations of SO\textsubscript{2} and SO\textsubscript{3} after full optimization are displayed in Figures S2 (c) and S2 (d). Table S1 displays the adsorption energies, charge transfer, adsorption distance between gas molecules and FeN\textsubscript{3}-gra, adsorption height, and magnetic moments. For SO\textsubscript{2} adsorption, SO\textsubscript{2} tends to bind Fe atom with O atoms (see Figure S2 (c)), which agrees with the situation of Ti-doped graphene [44, 45]. Unlike H\textsubscript{2}S, the N doping can effectively enhance the adsorption of SO\textsubscript{2} with an increased adsorption energy of 0.25 eV. The length of Fe-O bond is 1.97 Å, and the angle of SO\textsubscript{2} has decreased to 98.1° after adsorption. Compared to free SO\textsubscript{2} molecule, the S-O bond has enlarged about 0.11 Å, indicating a decreased density of S-O bonds. In comparison, SO\textsubscript{3} exhibits an enhanced adsorption strength than SO\textsubscript{2} with an adsorption energy of 3.30 eV (\(E_{\text{ad}}[\text{SO}_2] = 1.25\) eV). This adsorption strength is much larger than the results reported in the pioneering works on Fe-gra [40, 45]. Thus, the enhanced effect of N doping exhibits much favorable effect for SO\textsubscript{3} compared to SO\textsubscript{2} situation. The SO\textsubscript{3} binds FeN\textsubscript{3}-gra bidentately with two O atoms with Fe, and the corresponding Fe-O bond length is 1.88 Å. One O-S bond in SO\textsubscript{3} distributes parallel to FeN\textsubscript{3}-gra surface. Compared to free SO\textsubscript{3}, the bond angle (length) of O-S-O (S-O) in SO\textsubscript{3} has decreased (increased) from 120° (1.44 Å) to 44.2° (1.46 Å) and 108.7° (1.63 Å). These results have demonstrated that the N doping can effectively enhance the adsorption of SO\textsubscript{2} and SO\textsubscript{3}.

In order to clarify the adsorption of SO\textsubscript{2} and SO\textsubscript{3} on FeN\textsubscript{3}-gra, we have also analyzed electric properties including the charge transfer, DOS, and density of spin during the interaction between FeN\textsubscript{3}-gra and SO\textsubscript{2}/SO\textsubscript{3} (see Table S2). The SO\textsubscript{2} and SO\textsubscript{3} are negatively charged with 0.73 e and 1.09 e, respectively. In order to describe the process of charge transfer visually, we have also calculated the charge density difference (CDD) (see Figures S3 (c) and S3 (d)). The CDD demonstrated that the charge mainly accumulates on O atoms in SO\textsubscript{2}/SO\textsubscript{3} and Fe atom in FeN\textsubscript{3}-gra. Larger charge transfer may cause significant change of conductivity, which is beneficial for improved sensitivity for gas sensing [46, 47].

In order to clarify the change of electric properties in detail, we have analyzed the DOS to investigate the
adsorption properties of SO$_2$ and SO$_3$ (see Figure 4). The DOS of gas molecules has experienced dramatic change caused by the strong interaction between FeN$_3$-gra and SO$_2$/SO$_3$. The DOS of SO$_2$ ranging from -1.5 to 0 eV has become delocalized after adsorption on FeN$_3$-gra. In addition, the magnetic moment of FeN$_3$-gra has decreased from 3.17 to -1$\mu$B due to the no magnetic character of SO$_2$ and SO$_3$. The spin mainly concentrates on SO$_2$ and Fe atom with identical spin direction (see Figure S1 (c)). There exists a significant overlap between Fe-3d states and SO$_2$ at energy $E_{F}$.
range of -1.0 eV and 1.5 eV (Figure 4(a)). This can also be reflected from the charge overlap in Figure S3 (c), indicating the strong chemical interaction between Fe-3d and SO₂. These characters can also illustrate that a delocalized DOS distribution of SO₂ may contribute to enhance the adsorption strength. About SO₂, the TDOS ranging from -3 to 0 eV has increased and shifted to lower energy level after SO₂ adsorption. Similar to SO₂, the adsorption of SO₃ can also induce decreased magnetic moments (see Table S2). The formation of spin states of SO₂ near Fermi level can hybridize dramatically with Fe. The spin states mainly concentrate on Fe site as shown in Figure S1 (d). As shown in Table S3, the occupied states in SO₃ can lead to increased length of S-O bond, which is verified from charge transfer in Figures S3 (c) and S3 (d). Above all, the analysis of electric and magnetic properties can pave the way for FeN₃-gra application in gas sensor and spintronic device.

3.4. The Adsorption Properties of O₂. In addition, O₂ is also an important gas that is frequently present in the atmosphere. We thus investigated the adsorption behavior of O₂ at the end of this article. The most stable configuration of O₂ adsorption after optimization is shown in Figure S4. Other information, including the adsorption height, binding distance, charge transfer, adsorption energy, and magnetic moment, is displayed in Table S2. As shown in Figure S4, O₂ can adsorb on FeN₃-gra parallelly with an adsorption energy of -3.03 eV, which is similar to pioneering research [29]. This result has proceeded about 1.5 times of the adsorption energy on FeSV-gra [48]. In addition, the FeN₃-gra substrate can activate O₂ more effectively than FeSV-gra with a bond length of 1.42 Å of O-O bond, compared to the 1.39 Å on FeSV-gra. This character may originate from the enhanced interaction between O₂ and FeN₃-gra.

In order to clarify the O₂ adsorption on FeN₃-gra, we have also calculated the electric properties, including charge transfer, DOS, and spin density. The O₂ has been negatively charged with -0.77 e by the substrate, indicating the strong interaction between O₂ and FeN₃-gra. In other words, O₂ can act as an electron acceptor. These characters can also be reflected from the charge density difference (Figure S4 (c)): There exists a strong overlap between the charge distribution of O₂ and FeN₃-gra, indicating a covalent bond. In addition, O₂ has been magnetized after adsorption on FeN₃-gra as shown in Figure 5: The spin density distributes both on O₂ and FeN₃-gra. This may derive from the significant hybridization between O₂ and Fe-3d orbitals (Figure 5(a)).

4. Conclusions

In conclusion, we have investigated a series of gas molecules, including C₂H₂, H₂S, SO₂, SO₃, and O₂, on FeN₃-gra. These molecules can interact strongly with FeN₃-gra. Particularly, FeN₃-gra can adsorb SO₂/SO₃ and O₂ much strongly than Fe-gra, which mainly originates from N doping. The strong interaction may induce dramatic change of electric conductivity of FeN₃-gra, leading to a high sensitivity for gas sensing. Besides, the adsorbed gas molecules can modulate the magnetic property of FeN₃-gra effectively. Thus, our results can provide theoretical basement for applications of gas sensing and spintronic devices.

Data Availability

The data underlying the results presented in the study are available within the manuscript and supplementary materials.

Conflicts of Interest

All the authors declare no conflict of interest.

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Supplementary Materials

The supporting information is available free of charge on the Hindawi website publications at DOI. Table S1: the comparison of parameters between our work and the pioneering studies for FeN₃-gra substrate: the length of Fe-N bond (d /Å), the uplift height of Fe (h/Å), binding energy of Fe (Eₜ/ eV), charge transfer between Fe and graphene (CT/e), and the magnetic moment of the system (M/μB). Table S2: the parameters of gas molecules, including C₂H₂, H₂S, SO₂, and SO₃, adsorbed FeN₃-gra: the length of Fe-N bond (d /Å), the uplift height of Fe (h/Å), the binding energy of Fe (Eₜ/ eV), the adsorption energy of gas molecules (Eₜ/ eV), the charge transfer between gas molecules and FeN₃-gra (CT/e), and the magnetic moment of the system (M/μB). Table S3: the geometric configurations of different systems: the length (d/Å) and angle (θ/) of various bonds in the gas molecules in separated and adsorbed states. Figure S1: the spin density of gas molecules, including (a) C₂H₂, (b) H₂S, (c) SO₂, and (d) SO₃, on FeN₃-gra (spin up (yellow) and spin down (cyan); isosurface value: 0.01 e/Bohr³). Figure S2: the adsorption configurations of gas molecules, including (a) C₂H₂, (b) H₂S, (c) SO₂, and (d) SO₃, on FeN₃-gra. Figure S3: the charge density difference (CDD) of (a) C₂H₂-FeN₃-gra, (b) H₂S-FeN₃-gra, (c) SO₂-FeN₃-gra, and (d) SO₃-FeN₃-gra. GN. The accumulation and depletion of electrons are represented by the yellow and cyan regions, respectively (isosurface value: 0.003 e/Bohr³). Figure S4: (a) the adsorption configuration of O₂ on FeN₃-gra. (b) The spin density of FeN₃-gra with O₂ adsorbed on it (spin up (yellow) and spin down (cyan); isosurface value: 0.01 e/Bohr³). (c) The charge density difference of FeN₃-gra with O₂ adsorbed on it. The accumulation and depletion of electrons are represented by the yellow and cyan regions, respectively (isosurface value: 0.003 e/Bohr³). (Supplementary Materials)
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