First-Principles Exploration of Hazardous Gas Molecule Adsorption on Pure and Modified Al$_{60}$N$_{60}$ Nanoclusters

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Abstract: In this work, we use the first-principles method to study in details the characteristics of the adsorption of hazardous NO$_2$, NO, CO$_2$, CO and SO$_2$ gas molecules by pure and heteroatom (Ti, Si, Mn) modified Al$_{60}$N$_{60}$ nanoclusters. It is found that the pure Al$_{60}$N$_{60}$ cluster is not sensitive to CO. When NO$_2$, NO, CO$_2$, CO and SO$_2$ are adsorbed on Al$_{60}$N$_{60}$ cluster's top, edge, and edge sites respectively, the obtained configuration is the most stable for each gas. Ti, Si and Mn atoms prefer to stay on the top sites of Al$_{60}$N$_{60}$ cluster when these heteroatoms are used to modify the pure clusters. The adsorption characteristics of above hazardous gas molecules on these hetero-atom modified nanoclusters are also revealed. It is found that when Ti-Al$_{60}$N$_{60}$ cluster adsorbs CO and SO$_2$, the energy gap decreases sharply and the change rate of gap is 62% and 50%, respectively. The Ti-modified Al$_{60}$N$_{60}$ improves the adsorption sensitivity of the cluster to CO and SO$_2$. This theoretical work is proposed to predict and understand the basic adsorption characteristics of AlN-based nanoclusters for hazardous gases, which will help and guide researchers to design better nanomaterials for gas adsorption or detection.

Keywords: environment and health; first-principles physics; DFT; electronic structure; hazardous gas

1. Introduction

In recent years, industrial and fossil-fuel motor exhaust gases and the flue gas from the burning of garbage and straw crops in some areas have come to harm humans and the environment. These gases accumulate in the air and undergo a series of complex chemical reactions with the dust, small particles, bacteria, etc. in the air to form small agglomerated particles. When their concentration reaches a certain level and is further affected by weather, smog could appear. These hazardous gases include nitrogen dioxide (NO$_2$), carbon monoxide (CO), nitric oxide (NO), carbon dioxide (CO$_2$) and sulfur dioxide (SO$_2$), etc. Some of these gases are irritating and toxic gases which are the main source of acid rain. Some have strong oxidizing properties and are strong combustion aids and some gases can cause greenhouse effects. They harm people’s health and pollute the environment, thus the adsorption
and detection of these gases are of great significance to environmental protection and human health. From the perspective of materials, it is very important to find material substrates with high sensitivity to these gases. At present, nanoclusters, nanosheets, nanotubes and other low-dimensional nanomaterials are regarded to be potential candidates for these applications [1–3].

AlN is a kind of semiconducting material with excellent physical and chemical properties and its unique nanostructures have attracted the attentions of gas sensing researchers [4–11]. The electronic properties of nanomaterials can be improved by atomic modification or doping [12–15]. For example, Rezaei-Sameti et al. studied the adsorption characteristics of pure, B-, As-doped AlN nanotubes for CO adsorption [16]. The results showed that doping with B and As atoms was conducive to CO gas adsorption and effectively improved the sensitivity of AlN nanotubes to CO gas. Saedi et al. [17] considered the adsorption of H2S, COS, CS2 and SO2 gases by Al12N12 nanoclusters using density functional theory and it had been revealed that the Al12N12 nanocluster was a promising SO2 gas and electronic sensor and a CS2 gas electronic sensor, while they had different effects on conductivity. The theoretical investigations of AlN-based low-dimensional nanomaterials in this field are not only interesting to unveil some physics in the area but also of significance to move forward the field.

Based on previous research on AlN nanoclusters [18], in this work we have investigated the adsorption behaviors of NO2, NO, CO2, CO, and SO2 molecules on the large Al60N60 cluster. We select more stable adsorption sites to study their adsorption characteristics and electronic structures. Beside the pure cluster, some heteroatoms such as Ti, Si and Mn are also used to modify the Al60N60 nanocluster as substrates, for each of which the most stable sites are respectively considered to adsorb the above five gases and the sensitivity of each modified cluster to the gas molecules are also studied systematically.

2. Theoretical Methods

In this work, the first-principles method based on Density Functional Theory (DFT) [19,20] is used. The Vienna ab-initio simulation package [21–23] is employed to optimize the geometry structures and calculate the energetics and electronic structures of various gas adsorption on pure and hetero-atom modified nanoclusters. The projector augmented wave (PAW) [21] pseudopotentials are used to describe the ion-electron interactions. The exchange correlation potentials are treated by the Perdew-Burke-Ernzerhof (PBE) functional within the framework of the generalized gradient approximation [24]. Due to the van der Waals interaction between the atomic cluster and the gas molecule, we have used DFT-D2 method of Grimme [25] to make the correction. The plan wave basis set with an energy cut-off of 520 eV has been used. The Brillouin zone is sampled using the Monkhorst-Pack method and the supercell approach is used for structural optimizations and electronic structure calculations. The conjugate gradient algorithm is used to optimize the geometry structures and the convergence criterion of the atomic force is less than 0.02 eV/Å. The charge transfer between Al60N60 nanocluster and hazardous gas molecules were analyzed by the Bader charge analysis using the previous method [26–28]. In order to avoid interaction between clusters in x, y and z directions, all the models are separated by the vacuum space of 20 Å. The following formula is utilized to calculate the adsorption energies:

\[ E_{\text{ad}} = E_{\text{cluster+gas}} - E_{\text{cluster}} - E_{\text{gas}} \]  

where \( E_{\text{cluster+gas}} \) represents the total energy of the cluster (pure or hetero-atom modified) after gas molecule adsorption, \( E_{\text{cluster}} \) and \( E_{\text{gas}} \) represent the energies of the bare cluster and gas molecule respectively.

3. Results and Discussion

3.1. Adsorption of NO2, NO, CO2, CO and SO2 by Pure Al60N60 Nanocluster

Firstly, we have systematically considered the adsorption of NO2, NO, CO2, CO and SO2 on the surface of pure Al60N60 nanoclusters, the structure of which had been revealed by us in an earlier study. There are different adsorption positions (we designate them as the edge, side and top position in this
work) on the surface of clusters, and these three positions have four, two and two different adsorption sites, respectively. In Figure 1, Figure 1a shows the four adsorption sites at the edge position: edge.a (N-site) and edge.b (Al-site) have four coordination, edge.c (N-site) and edge.d (Al-site) have three coordination. Figure 1b shows the adsorption sites of the side position: side.a and side.b are the sites at the concave N atom and the Al-N bond, respectively. Figure 1c illustrates the two sites at the top position: top.a and top.b are the sites at the center and the Al-N bond, respectively. The NO₂, NO, CO₂, CO and SO₂ molecules are horizontally or vertically placed in front of the edge and side sites and are horizontally placed directly above the top two sites for adsorption. Here, the readers may ask why we don’t adopt the cluster model with passivated heteroatoms or functional group such as H, O, OH, etc. in this study, since the cluster may react in air or solution. There are mainly two reasons: one is that the real cluster structure after passivation in air or solution would be very complicated, i.e., it is hard to define what kinds of heteroatoms or functional group (H, O, OH, etc.) passivate which specific sites of the cluster. It may be argued that this can be run through in every possible “combination”, but the computational time and cost would be huge considering that only for one model there will be 14 different adsorption configurations for each kind of gas molecule (more details will be in the following paragraph) and we have five different gas molecules to investigate in total. The other is that in our intrinsic cluster model, most surface Al/N atoms have three or four coordinations and the Al-N bonds are almost saturated, similar case also exists in other research [17]. Thus in this fundamental study we employ the current model to explore the intrinsic adsorption properties of Al₆₀N₆₀ nanocluster.

![Figure 1](image-url)

**Figure 1.** Various adsorption sites (shown in red letters) at each position (a) edge, (b) side or (c) top of pure Al₆₀N₆₀ cluster.

Based on the above model, there are 14 different adsorption configurations for each kind of gas molecule. We have systematically studied the adsorption characteristics of each gas at various sites, as shown in Table 1. The subscripts h and p represent the horizontal and perpendicular adsorption of gas molecules at each site. From the data of adsorption energy, it can be seen that compared with other four gases, the adsorption energy absolute values of pure Al₆₀N₆₀ cluster towards CO are generally smaller. The adsorption energies of NO₂, NO, CO₂ and CO are relatively high at edge.a site. In addition, it is also found that when these five gas molecules are adsorbed at the top position, the adsorption energy value obtained at the Al-N bond site is high. When NO₂ and CO₂ are adsorbed at the side sites and SO₂ is adsorbed at the edge.c sites, and side.a sites, the adsorption energy values are more than 10 eV. Therefore, we have studied the adsorption details of these five gases at these sites. The optimized configurations corresponding to the higher energy values are shown in Figure 2. It can be seen from the Figure 2 that when the adsorption energy values are large, the corresponding optimized configurations have obvious shrinkage deformation such as NO₂ adsorption at the side.a sites, and side.b sites, CO₂ adsorption at the side.a and side.b sites, and SO₂ adsorption at the edge.c sites.
When the pure Al atom at the edge of cluster, and the charge density of O atom after bonding is spindle-shaped. The optimized configurations corresponding to the higher energy values are shown in Figure 2. It can be seen from the Figure 2 that when the adsorption energy values are large, the adsorption at the edge.ch and side.ap. When NO$_2$ is adsorbed at the edge.a$_h$ site, the structure of the edge position is obviously deformed. From the optimized model structure, it can be seen that when the gas molecules are located at the edge and side sites, the structure is prone to deform.

**Table 1.** The adsorption energies of various gas molecules adsorbed on different sites of pure Al$_{60}$N$_{60}$ nanocluster.

| Sites | $E_{ad}$ (eV) | $a_h$ | $a_p$ | $b_h$ | $b_p$ | $c_h$ | $c_p$ | $d_h$ | $d_p$ | $a_h$ | $a_p$ | $b_h$ | $b_p$ | $a$ | $b$ |
|-------|---------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----|-----|
| Edge  | $E_{ad}$+NO$_2$ | −4.77 | −4.41 | −3.39 | −2.98 | −2.88 | −4.22 | −3.17 | −18.21 | −0.22 | −10.77 | −2.79 | −0.31 | −3.52 |
|       | $E_{ad}$+NO   | −2.02 | −2.60 | −2.01 | −1.99 | −2.01 | −1.97 | −1.58 | −0.17 | −0.81 | −1.38 | −0.83 | −0.36 | −0.38 |
|       | $E_{ad}$+CO$_2$| −2.36 | −0.12 | −0.11 | −0.09 | −0.17 | −0.28 | −0.90 | −0.37 | −0.35 | −10.04 | −10.04 | −0.25 | −0.29 | −0.30 |
|       | $E_{ad}$+CO   | −0.99 | −1.47 | −0.97 | −0.97 | −0.09 | −0.75 | −0.08 | −0.26 | −0.74 | −0.16 | −0.75 | −0.12 | −0.13 | −0.23 |
|       | $E_{ad}$+SO$_2$| −4.49 | −3.95 | −2.36 | −1.00 | −13.90 | −1.78 | −2.18 | −1.79 | −3.76 | −10.82 | −1.61 | −3.23 | −0.44 | −3.43 |

**Figure 2.** The configurations of pure Al$_{60}$N$_{60}$ clusters adsorbing hazardous gas molecules at three positions with higher adsorption energy values: (a) NO$_2$, (b) NO, (c) CO$_2$, (d) CO, (e) SO$_2$. Top down in each subbox: the edge, side and top adsorption positions of clusters respectively.

In order to further study the electronic structures of the pure Al$_{60}$N$_{60}$ cluster adsorbing these five gases, we have selected the relatively stable structures when the Al$_{60}$N$_{60}$ cluster adsorbs those gas molecules. After screening, five configurations were obtained: NO$_2$, NO, CO$_2$, CO and SO$_2$ adsorbed at the cluster top.b, edge.a$_p$, edge.a$_h$, edge.a$_p$ and edge.a$_h$ sites, respectively. Compared with other sites of the same gas, these structures are more stable and the adsorption energy values are higher. Based on this, the electronic properties are further studied.

In Figure 3, the differential charge density and charge transfer of the five gas molecules adsorbed at the relatively stable sites are illustrated. The O atoms of NO$_2$, CO$_2$ and SO$_2$ are bonded with the Al atom at the edge of cluster, and the charge density of O atom after bonding is spindle-shaped. When the pure Al$_{60}$N$_{60}$ cluster adsorbs NO$_2$, NO, CO$_2$, CO and SO$_2$, charge is transferred from the nanocluster to the gas molecules. The charge transfer of these five systems is not small. We also calculated the electronic structures of these five systems, as shown in Figure 4. After the pure Al$_{60}$N$_{60}$ cluster adsorbs NO$_2$, the electronic structure changes significantly. From the density of states curve,
it can be seen that after the adsorption of NO$_2$, a new energy level appears between the Fermi level and the conduction band bottom. Before adsorption, the energy gap of pure Al$_{60}$N$_{60}$ cluster is 1.297 eV. After adsorption, the energy gap of the system becomes 0.721 eV and the change rate of gap is 44.40%. The pure Al$_{60}$N$_{60}$ cluster is relatively sensitive to NO$_2$. When the pure Al$_{60}$N$_{60}$ cluster adsorbs CO$_2$, NO and SO$_2$, the energy gap change by 0.035 eV, 0.08 eV and 0.035 eV, respectively. Before and after the adsorption of CO by pure Al$_{60}$N$_{60}$, the energy gap changes by 0.945 eV and the change rate is 27.14%.

![Figure 3](image1.jpg)

**Figure 3.** Differential charge density and charge transfer of (a) NO$_2$ adsorbed at top.b site, (b) NO adsorbed at edge.a$_h$ site, (c) CO$_2$ adsorbed at edge.a$_p$ site, (d) CO adsorbed at edge.a$_p$ site and (e) SO$_2$ adsorbed at edge.a$_h$ site. Yellow and blue represent the charge accumulation and depletion respectively. The isosurface value is 0.0025 e/Å$^3$. The arrow and charge number in the figure indicate the direction and value of the charge transfer between the nanocluster and the gas molecule.

![Figure 4](image2.jpg)

**Figure 4.** The electronic density of states of pure Al$_{60}$N$_{60}$ cluster before and after adsorption of various gas molecules. The Fermi level is set at zero.
Figure 5. Top view and side view of the edge, side and top positions of Al_{60}N_{60} cluster adsorbing single M atom (M atom is Ti, Si and Mn respectively): (a) Edge: From left to right, the M atom is located in front of the four-coordinated N atom, two-coordinated Al atom, three-coordinated N atom and three-coordinated Al atom at the edge position, respectively. (b) Side: From left to right, M atom is located in front of the Al atom recessed and Al-N bond at the side position, respectively. (c) Top: From left to right, M atom is located above the center of the top six-member ring and the top Al-N bond, respectively. The pink, blue and silver-white spheres represent Al, N, and M atoms, respectively.

3.2. Atomic Modification of Al_{60}N_{60} Cluster by Ti, Si and Mn

In order to further improve the adsorption and sensitivity of the cluster to those five gases, in this work we have tried to modify the Al_{60}N_{60} cluster with Ti, Si and Mn heteroatoms and systematically calculated the adsorption energy, adsorption distance, bond length, bond angle and electronic structure of each system. Since the surface of the Al_{60}N_{60} cluster has many different sites, first of all, we have to determine at which site each heteroatom is prone to occupy and which structure is relatively stable. These two aspects are discussed in the following research. When Ti, Si or Mn heteroatoms are adsorbed at the edge, side and top positions of Al_{60}N_{60} cluster surface, there are four, two, and two adsorption sites, respectively, as shown in Figure 5. We have studied these eight adsorption structures and calculated the adsorption energy of each structure as shown in Table 2. It is found that when a Ti, Si or Mn atom is adsorbed at the side a site the respective adsorption energies are \(-14.17\) eV, \(-12.35\) eV and \(-11.38\) eV, which shows that the adsorption energy values of these three adsorption systems are generally higher. When these heteroatoms are adsorbed at some sites of the cluster, the adsorption energy is about 10 eV higher than other sites. To know the reason why the adsorption energy changes...
so much, we have studied the structures after adsorption and selected the geometrically optimized configurations with stable adsorption of the three hetero-atoms at the edge, side and top positions of the cluster as shown in Figure 6. When the cluster adsorbs Ti, Si or Mn atom at the side position, the structures shrink greatly. After the cluster edge site adsorbs a Ti atom, the structure also deforms obviously. The system with obvious deformation of structure after optimization has a relatively high adsorption energy value and unstable structure. Next, we will further study them from the aspect of electronic structures.

Table 2. Adsorption energies of Ti, Si or Mn hetero-atom at different sites of Al60N60 cluster.

| Sites       | Ead (eV)       | Edge | Side | Top |
|-------------|----------------|------|------|-----|
|             | a              | b    | c    | d   |
| Eadj+Ti     | −3.21          | −3.20| −3.36| −14.67|
| Eadj+Si     | −3.64          | −3.63| −2.55| −12.35|
| Eadj+Mn     | −2.58          | −2.59| −1.61| −11.38|

Figure 7 is the differential charge density diagram corresponding to the higher adsorption energy values when Ti, Si or Mn atom is adsorbed on an Al60N60 cluster. When three kinds of atoms are...
adsorbed at the side position of the cluster and Ti atom is adsorbed at the edge, a small amount of charge accumulation will appear at the No.60 and No.57 Al atoms at the far end, and charge depletion will occur at the No.12, No.19 and No.23 N atoms, and the charge distribution will be spindle-like. When a Ti, Si or Mn atom is adsorbed at the top of the cluster, the charge distribution is more uniform. There is a charge aggregation phenomenon between the three kinds of atoms and the Al\textsubscript{60}N\textsubscript{60} cluster, and the Ti, Si and Mn atoms are bonded with the N atom at the top position of the cluster. Thus, when Ti, Si or Mn atom is adsorbed at the top of the Al\textsubscript{60}N\textsubscript{60} cluster, they can have a relatively stable structure and the charge distribution is uniform. In the next section, we will select these configurations of hetero-atom modified at the top position of the Al\textsubscript{60}N\textsubscript{60} cluster to carry out their adsorption properties towards hazardous gas molecules.

3.3. Investigation on the Adsorption of Hazardous Gas Molecules by Ti, Si or Mn-Modified Al\textsubscript{60}N\textsubscript{60} Cluster

NO\textsubscript{2}, NO, CO\textsubscript{2}, CO, and SO\textsubscript{2} gas molecules are adsorbed at the stable sites of Al\textsubscript{60}N\textsubscript{60} clusters modified by Ti, Si or Mn atom. After structural relaxations, the optimized configurations are shown in Figure 8. After relaxations, the heteroatom-modified Al\textsubscript{60}N\textsubscript{60} clusters are not sensitive to CO\textsubscript{2} and do not easily adsorb CO\textsubscript{2}; the Si-Al\textsubscript{60}N\textsubscript{60} cluster does not easily adsorb CO and SO\textsubscript{2}, which can be further proved from Table 3. The M-Al\textsubscript{60}N\textsubscript{60} cluster adsorbs CO\textsubscript{2} with a smaller adsorption energy value, which is physical adsorption. Moreover, CO\textsubscript{2} has a longer adsorption distance from the substrate.
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The optimal configurations of (a) NO2, (b) NO, (c) CO2, (d) CO and (e) SO2 adsorption on Al60N60 cluster modified by Ti, Si and Mn atoms. Top down: Ti, Si and Mn adsorption systems respectively.

Table 3. The adsorption energy (Ead), adsorption distance (d), bond length (d(X-O)), and bond angle (∠(O-X-O)), (X represents N, C or S atom). Adsorption distance is defined as the shortest distance from an atom of gas molecule to an atom in the modified matrix.

| Systems            | Ead (eV) | d (Å) | d(X-O) (Å) | ∠(O-X-O) (°) |
|--------------------|----------|-------|------------|--------------|
| Ti-Al60N60+NO2     | −3.99    | 1.98  | 1.35       | 105.95       |
| Si-Al60N60+NO2     | −2.25    | 1.80  | 1.36       | 101.44       |
| Mn-Al60N60+NO2     | −2.89    | 2.17  | 1.28       | 111.62       |
| Ti-Al60N60+NO      | −3.37    | 1.88  | 1.37       | 180          |
| Si-Al60N60+NO      | −0.93    | 1.72  | 1.27       | 180          |
| Mn-Al60N60+NO      | −2.97    | 1.70  | 1.21       | 180          |
| Ti-Al60N60+CO2     | −0.12    | 2.98  | 1.19       | 172.22       |
| Si-Al60N60+CO2     | −0.15    | 3.35  | 1.18       | 177.44       |
| Mn-Al60N60+CO2     | −0.08    | 3.04  | 1.18       | 178.19       |
| Ti-Al60N60+CO      | −1.74    | 2.04  | 1.18       | 180          |
| Si-Al60N60+CO      | −0.07    | 3.35  | 1.15       | 180          |
| Mn-Al60N60+CO      | −1.44    | 1.90  | 1.17       | 180          |
| Ti-Al60N60+SO2     | −3.59    | 2.02  | 1.62       | 98.31        |
| Si-Al60N60+SO2     | −0.43    | 2.74  | 1.47       | 116.86       |
| Mn-Al60N60+SO2     | −2.06    | 1.93  | 1.54       | 113.89       |

Compared with the structure before adsorption, CO2 is repelled by the substrate. The adsorption energy value of Si-Al60N60 cluster towards CO or SO2 is relatively small, and the adsorption distance is relatively long, which is weak adsorption. When the M-Al60N60 cluster adsorbs these five gas molecules, the bond length of the gas is elongated. Except the linear NO and CO, the bond angles of other molecules shrink. As can be seen from the table, the Ti-modified Al60N60 cluster has higher adsorption energy values when adsorbing NO2, NO, CO and SO2.
In order to further study the mechanism of M-Al\textsubscript{60}N\textsubscript{60} clusters adsorption of those gas molecules, we have analyzed the differential charge density and charge transfer of M-Al\textsubscript{60}N\textsubscript{60} clusters adsorbing NO\textsubscript{2}, NO, CO\textsubscript{2}, CO and SO\textsubscript{2}, respectively. As can be seen from Figure 9, the charge in all systems is transferred from the modified Al\textsubscript{60}N\textsubscript{60} cluster to the gas molecule. The system of M-Al\textsubscript{60}N\textsubscript{60} cluster adsorbing CO\textsubscript{2} and Si-Al\textsubscript{60}N\textsubscript{60} cluster adsorbing CO have smaller charge transfer and weaker interactions between gas and matrix. The system of Si-Al\textsubscript{60}N\textsubscript{60} cluster adsorbing CO\textsubscript{2} and CO hardly shows charge aggregation and loss. The Al\textsubscript{60}N\textsubscript{60} clusters modified with Ti, Si or Mn atom do not easily adsorb CO\textsubscript{2}. When M-Al\textsubscript{60}N\textsubscript{60} clusters adsorb NO\textsubscript{2}, NO and SO\textsubscript{2}, the charge transfers are large and there are strong interactions between gas and matrix. When Ti-Al\textsubscript{60}N\textsubscript{60} and Mn-Al\textsubscript{60}N\textsubscript{60} cluster adsorb those molecules, charge aggregation occurs between the gas and the matrix. When the Si-Al\textsubscript{60}N\textsubscript{60} cluster adsorbs NO\textsubscript{2} and NO, there is charge depletion between gas and matrix. When Ti-Al\textsubscript{60}N\textsubscript{60} and Mn-Al\textsubscript{60}N\textsubscript{60} cluster adsorb those molecules, charge aggregation occurs between the gas and the matrix. When the M-Al\textsubscript{60}N\textsubscript{60} clusters adsorb NO, the N atoms easily form bonds with the heteroatom M. When the M-Al\textsubscript{60}N\textsubscript{60} clusters adsorb NO, the N atoms gain electrons.

To further figure out the electronic structure changes of the Ti, Si or Mn-modified Al\textsubscript{60}N\textsubscript{60} clusters adsorbing those five hazardous gas molecules, we have calculated their corresponding density of states as shown in Figure 10. It can be seen from the figure that for the M-Al\textsubscript{60}N\textsubscript{60} clusters adsorbing NO\textsubscript{2}, NO, CO\textsubscript{2}, CO and SO\textsubscript{2}, the energy gap of the system varies and the effects of three modifying atoms on the electronic structures are also different. In the figure, $\Delta E_g$ represents the energy gap change of the system before and after hetero-atom modification and the formula is as follows:

$$\Delta E_g = E_g(\text{M-Al}_{60}\text{N}_{60} \text{+gas}) - E_g(\text{Al}_{60}\text{N}_{60} \text{+gas})$$

\text{(2)}
where $E_g(M-Al_{60}N_{60}+\text{gas})$ represents the energy gap of the gas adsorption system by modified $Al_{60}N_{60}$ cluster with M heteroatoms, $E_g(Al_{60}N_{60}+\text{gas})$ represents the gap of the system by pure $Al_{60}N_{60}$ cluster. It is found that for the Ti-$Al_{60}N_{60}$ cluster adsorbing $CO_2$, $CO$, and $SO_2$ and the Mn-$Al_{60}N_{60}$ cluster adsorbing $CO_2$, the energy gap of these four systems are sharply reduced and the energy gap change rate are 75%, 62%, 50% and 57% respectively. The change rate of energy gap of Ti-$Al_{60}N_{60}$ cluster adsorbing $NO_2$ was 25%. While, the energy gap of Si-modified $Al_{60}N_{60}$ cluster after adsorbing NO is unchanged. The energy gaps of the Ti-$Al_{60}N_{60}$ cluster adsorbing $CO_2$, $CO$ and $SO_2$ and the Mn-$Al_{60}N_{60}$ cluster adsorbing $CO_2$ are decreased, but the $Al_{60}N_{60}$ clusters modified by Ti or Mn atom do not easily adsorb $CO_2$. Therefore, it is regarded that the Ti-atom modification can improve the sensitivity and sensing of $Al_{60}N_{60}$ cluster towards $CO$ and $SO_2$ and have potential to be used as a choice of related gas-sensing materials design.

![Density of states of various M-$Al_{60}N_{60}$ clusters adsorbing five gas molecules respectively: (a) NO$_2$; (b) NO; (c) CO$_2$; (d) CO; (e) SO$_2$. The Fermi level is set at zero. $\Delta E_g$ represents the energy gap change of the system before and after hetero-atom (M) modification.](image)

**Figure 10.** Density of states of various M-$Al_{60}N_{60}$ clusters adsorbing five gas molecules respectively: (a) NO$_2$; (b) NO; (c) CO$_2$; (d) CO; (e) SO$_2$. The Fermi level is set at zero. $\Delta E_g$ represents the energy gap change of the system before and after hetero-atom (M) modification.

### 4. Summary and Outlook

We have systematically investigated the atomic scale configurations and electronic structures of various hazardous gas molecules adsorbed by pure and heteroatom-modified $Al_{60}N_{60}$ clusters with Ti, Si and Mn using Density Functional Theory. It is found that for the pure $Al_{60}N_{60}$ cluster adsorbing those gas molecules, when NO$_2$, NO, CO$_2$, CO and SO$_2$ are adsorbed on the top.b, edge.a$_p$, edge.a$_h$, edge.a$_p$ and edge.a$_h$ sites of the nanocluster, respectively, the corresponding structures are relatively stable and the charge transfer is relatively large. The chemisorption between $Al_{60}N_{60}$ cluster and gas molecule in
these five systems is strong. The energy gap of pure Al\(_{60}\)N\(_{60}\) cluster is reduced by 44\% when adsorbing NO\(_2\) at its stable site, which is expected to be a candidate gas sensing material for NO\(_2\). When Ti, Si and Mn atoms are respectively adsorbed on the top sites of Al\(_{60}\)N\(_{60}\) cluster, the corresponding structures are relatively stable and the charge distribution is uniform. When Ti-modified Al\(_{60}\)N\(_{60}\) cluster adsorbs CO and SO\(_2\) gas molecules, the energy gap decreases sharply. Compared with the pure cluster adsorption system, the energy gap changes by 62\% and 50\% respectively, which greatly improves the sensitivity of Al\(_{60}\)N\(_{60}\) nanocluster to CO and SO\(_2\). This theoretical work is proposed to supply fundamental clues and guide for experimentalists to develop appropriate nanoclusters for environmental and health applications.

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