SF₆ decomposed products based on AlN nanocage

R. A. Taha, A. S. Shalabi, M. M. Assem, K. A. Soliman

Abstract

SF₆ decomposition products: SO₂, SOF₂, and SO₂F₂ were investigated using Al₂₃N₃₄ nanocage based on density functional theory (DFT). The adsorption properties were studied by analyzing adsorption energy, charge transfer, frontier molecular orbitals, and density of states (DOS). Our calculation suggests that the adsorption ability of Al₂₃N₃₄ to SO₂ and SOF₂ are stronger than adsorption of SO₂F₂ gas due to chemical adsorption. The results show that Al₂₃N₃₄ nanocage plays crucial role for detecting SF₆ decomposition gas with high sensitivity and selectivity.

Keywords: DFT – SF₆ decomposition products - Al₂₃N₃₄ nanocage -Adsorption properties

1. The introduction

SF₆ is an excellent gas used in gas insulated switchgear (GIS) and electrical and power system [1, 2, 3] s. Because it has high stability and difficult to decompose. The defects produced during the insulating process leads to partial discharge and caused decomposition of SF₆ gas [4, 5, 6, 7, 8, 9]. The gases that are produced from decomposition such as SO₂, SO₂F₂, SOF₂, H₂S and SOF₆ cause many problems in power system and are harmful to human health [10, 11, 12, 13, 14, 15, 16]. Thus are very important to detect these gases to reduce their damages. Many methods and materials developed to detect these gases [17, 18, 19, 20, 21, 22, 23, 24, 25, 26]. Li et al. used intrinsic MoS₂ and Sc-MoS₂ to detect and adsorbed SF₆ decomposition gases such as H₂S, SO₂F₂, SOF₂ and SO₂ by using DFT calculations and their study show that adsorption of these gases increase by adding Sc as active center atom. The adsorption of SO₂F₂, SOF₂ and SO₂ on Sc-MoS₂ is very strong but H₂S has weak adsorption, so MoS₂ and doped MoS₂ can used as gas sensor to detect SF₆ decomposition gases [27]. Xia et al. used two-dimensional (2D) nanomaterials such as Rh-doped h-BN (Rh/BN) monolayer as a gas sensor to adsorb SF₆ decomposition gases by using DFT calculation and the results of their calculations show that Rh-BN monolayer is an excellent gas sensor to adsorb and detect SF₆ decomposition gases [28]. Zhang et al. used metal oxide (TiO₂, Fe₂O₃, NiO) cluster-modified single-layer graphene as a gas sensor to adsorb and detect SF₆ decomposition gases by using DFT calculation. Their work show that TiO₂ modification has an excellent adsorption effect for these gases as a gas sensor [29]. Liao et al. used planar 2D material indium triphosphate (InP₃) as a gas sensor to detect SF₆ decomposed gases such as SO₂, SOF₂, SO₂F₂ and H₂S by using DFT calculation [30]. Qian et al. used Ga-doped single-walled boron nitride nanotube (Ga-BNNT) as a gas sensor to detect SF₆ decomposition gases such as SO₂, SOF₂, SO₂F₂ by using DFT calculation. Their results show that by doping the adsorption of these gases increase on Ga-BNNT more than BNNT and the conductivity of SO₂F₂ is better than SOF₂ after the adsorption [31]. Cao et al. used Pt cluster-modified gallium nitride nanotubes (Pt₂-GaNNTs) as a gas sensor to detect SF₆ decomposition gases such as H₂S, SO₂, SO₂F₂, and SO₂F₆ by using DFT calculations. Their study show that the adsorption increases by doping [32]. Liu et al. used Sc-doped WSe₂ monolayers as gas sensors to detect the adsorption and decomposition of gases such as SO₂, SOF₂, and SO₂F₂ by using DFT calculations. Their work show that the adsorption on Sc-WSe₂ is more than WSe₂ [33]. Cui et al. used Pd-doped PtSe₂ (Pd-PtSe₂) monolayer as a gas sensor to detect and adsorb H₂S and SOF₂ by using DFT calculations and their work show that doped form reduces band gap and increases the adsorption properties more than PtSe₂ and the adsorption of SO₂F₂ on Pd-PtSe₂ is better than H₂S gas [34]. Li et al. used Pd-doped MoS₂ (Pd-MoS₂) monolayer as a gas sensor to detect gases such as SO₂F₂ and SO₂F₆ by using DFT calculations and the results of this work show that Pd-MoS₂ has a good chemical properties to form chemisorption with these gases and it can be used as gas sensor to these gases [35]. Gui et al. used Rh doped MoS₂ to adsorb and detect gases such as SO₂, SOF₂, SO₂F₂ gases by using DFT calculation and their work show that Rh-MoS₂ has adsorption properties more than pristine MoS₂ and the adsorption of SO₂F₂ is less than other gases [36]. In the present study investigate the Al₂₃N₃₄ nanocage as a sensing material for SF₆ decomposed products (SO₂, SOF₂, and SO₂F₂) using the density functional theory (DFT). The structural parameters of these gases on the nanocage were determined such as adsorption energy, frontier orbitals, charge transfer using NBO, and density of states.

2. Computational details

DFT calculations were performed for the investigation of adsorption properties of SO₂, SOF₂, and SO₂F₂ gases on the Al₂₃N₃₄ nanocage. The optimization of the pristine Al₂₃N₃₄ nanocage and adsorption of SO₂, SOF₂, and SO₂F₂ gases on Al₂₃N₃₄ nanocage were carried out using the B3LYP level of theory and 6-31g(d) basis set. All calculations utilized Gaussian 09 code [37]. The adsorption energy, charge transfer, NBO analysis and the energy gap parameters were determined.
The adsorption energy (Eads), the charge transfer quantity (Q), and the energy gap (Eg) were calculated from the following equations:

\[
\text{Eads} = \frac{\text{Egas/Al}_{24}\text{N}_{24} - \text{Egas} - \text{EAl}_{24}\text{N}_{24}}{\text{Q}} = \text{Qads} - \text{Qiso}
\]

Where Egas/Al24N24, Egas, and EAl24N24 are the total energy of gas adsorbed on the nanocage, total energy of gas molecule (SO2, SOF2, and SO2F2), and the total energy of the Al24N24 nanocage respectively. Qads and Qiso are the total charges of the adsorbed gas molecule and isolated gas respectively.

3. Results and discussion

The optimized structures of SO2, SOF2, and SO2F2 gas molecules are seen in Fig 1 and the structure parameters are listed in Table 1. Geometries of SO2, SOF2, and SO2F2 gas molecules

**Table 1** structure parameters of SO2, SOF2, and SO2F2 gas molecules

<table>
<thead>
<tr>
<th>Gas molecule</th>
<th>Bond length (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO2</td>
<td>S-O 1.46</td>
<td>O-S-O 119.11</td>
</tr>
<tr>
<td>SOF2</td>
<td>S-F 1.62</td>
<td>O-S-F 107.10</td>
</tr>
<tr>
<td>SO2F2</td>
<td>S-F 1.58</td>
<td>O-S-F 108.11</td>
</tr>
<tr>
<td></td>
<td>S-O 1.43</td>
<td>F-S-F 94.73</td>
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The adsorptions of SF6 decomposed products (SO2, SOF2, and SO2F2 gas molecules) on the Al24N24 nanocage were calculated to analyze the sensitivity of nanocage towards these gas molecules. The optimized configurations of gas molecules on Al24N24 nanocage are seen in Fig 1. Based on the structural parameters as presented in Table 1, the charge of the adsorbed SO2 molecule is -0.3 e. This means that the electron was transferred from Al24N24 nanocage to SO2 gas molecule. The distribution of the HOMO and LUMO is displayed in Fig 3, and the parameters are determined as listed in Table 2.

**Table 2** The HOMO distributed mainly on the six membered ring near SO2 adsorbed gas and the LUMO distributed on the Al24N24 nanocage. For SOF2 system, the SO2 gas molecule dissociates over the Al24N24 nanocage which F atom bind with Al atom of nanocage with bond distance 1.96 Å. S atom interact with N atom of nanocage by a distance 1.63 Å and O atom with Al of nanocage by a distance 1.90 Å. The adsorption energy of SOF2 molecules on Al24N24 nanocage is -5.07 eV. The amount of charge transferred from the Al24N24 nanocage to the SOF2 molecule is -0.32 e. As shown in Fig 3,
Fig 2) The optimized structure and DOS of the AL24N24 nanocage.

Table (2) The structural parameters of SO2, SOF2, and SO2F2 on the pristine AL24N24 nanocage

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<th>Compounds</th>
<th>d (Å)</th>
<th>Eads(eV)</th>
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<td>AL24N24</td>
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<td>-6.48</td>
<td>-2.39</td>
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<td>-</td>
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<tr>
<td>SO2/AL24N24</td>
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<td>-6.15</td>
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<td>SO2F2/AL24N24</td>
<td>2.15</td>
<td>-0.42</td>
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the HOMO distributed on the F atom of SOF2 and N atom of nanocage and the LUMO distributed on the Al24N24 nanocage. For SO2F2 system, the adsorption of SO2F2 on the Al24N24 nanocage exhibits a weak interaction. The distance between O atom of SO2F2 molecule and the nearest Al atom of nanocage is 2.15 Å and the adsorption energy is -0.42 eV. By analyzing NBO as presented in Table (2), we found that the charge on SO2F2 after adsorption on nanocage is 0.1 e which indicates the charge transfer from the SO2F2 molecule to the nanocage. As seen in Fig(3) adsorption configuration and frontier orbitals of SO2, SOF2, and SO2F2 on the Al24N24 nanocage, the HOMO is distributed around on the Al24N24 nanocage while the LUMO distributed on the whole system. The comparison between the three SF6 decomposed products shows that the adsorption energy value for SO2F2 system is smaller than SO2 and SOF2 systems, and the electron transfer manifests the occurrence of strong chemisorption in SO2 and SOF2 adsorption system. Fig(4) shows the DOS plots after the adsorption of SO2, SOF2, and SO2F2 on the Al24N24 nanocage. As shown in Fig 5 and Table 2 the Al24N24 nanocage has a minimum LUMO of -2.39 eV and a maximum HOMO of -6.48 eV. Upon adsorption of SO2, SOF2, and SO2F2 on the Al24N24 nanocage, it can be inferred that a significant effect on the electronic properties of the Al24N24 nanocage occurs. As presented in Table (2), the Al24N24 nanocage has a LUMO of -2.39 eV while for SO2, SOF2, and SO2F2 on the Al24N24 nanocage are -2.40 eV, -2.45 eV, and -2.27 eV respectively. The band gap decreases significantly for SO2, and SOF2 on the Al24N24 nanocage implying the chemisorption of these gases on the nanocage.
Fig (3) adsorption configuration and frontier orbitals of SO2, SOF2, and SO2F2 on the Al24N24 nanocage.

Fig (4) DOS plots of SO2, SOF2, and SO2F2 on the Al24N24 nanocage.
The desorption time represents an important factor for gas sensing material. The desorption time can be calculated by the following equation

\[ \tau = A^{-1} e^{\frac{K_g}{k_B T}} \]

Where A is the apparent frequency factor (10^{15} \text{ s}^{-1}), K_g is the Boltzmann’s constant, and T is the tested temperature respectively. The E_d represent the potential barrier of the desorption process and the value equal to Eads. The desorption property of the three gases (SO_2, SOF_2, and SO_2F_2) on the Al_{2}O_{3}N_{24} nanocage were extra-long desorption time for the SO_2, and SOF_2 gas molecules but short desorption time for SO_2F_2 gas molecule. Therefore, Al_{2}O_{3}N_{24} nanocage can be selected as adsorbents to SO_2 and SOF_2 gas molecules because of long desorption time at room temperature.

4. Conclusion

In the present study investigate the Al_{2}O_{3}N_{24} nanocage as a sensing material for SF_6 decomposed products (SO_2, SOF_2, and SO_2F_2) using the density functional theory (DFT). The structural parameters of these gases on the nanocage were determined such as adsorption energy, frontier orbitals, charge transfer using NBO, and density of states. The results reveals that the adsorption of SO2 and SOF2 gases are chemisorption on the Al_{2}O_{3}N_{24} nanocage, while SOF2 gas is physisorbed on the nanocage which can be desorbed easily.

References


