Adsorption Properties of Pd$_3$-Modified Double-Vacancy Defect Graphene toward SF$_6$ Decomposition Products

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Abstract: In this study, we investigate Pd$_3$-cluster-modified 555–777 graphene (Pd$_3$-graphene) as a novel resistor-type gas sensor to detect SF$_6$ decomposition products based on density functional theory calculations. We obtained and minutely analyzed the relevant parameters of each most stable adsorption configuration to explore the microscopic mechanism during gas adsorption. Theoretical results reveal that Pd$_3$-graphene shows great adsorption capacity and sensitivity toward those decompositions. High adsorption energies and abundant charge transfer amounts could guarantee a stable adsorption structure of decomposition gases on Pd$_3$-graphene surface. The complex change of density of states verifies a strong chemical reaction between the gases and the surface. Moreover, the conductivity of Pd$_3$-graphene would improve due to the decrease of energy gap, and the sensitivity was calculated as SOF$_2$ > H$_2$S > SO$_2$ > SO$_2$F$_2$. This work provides an effective method to evaluate the operation status of SF$_6$ gas-insulated equipment.

Keywords: Pd$_3$-graphene; SF$_6$ decomposition products; DFT; adsorption

1. Introduction

Owing to its outstanding insulation and arc-extinguishing properties, SF$_6$ has been widely applied in gas-insulated switchgear (GIS) [1,2]. However, in the long-term operation of GIS, several inevitable insulation defects may cause partial discharge and partial overheat, which will lead to the initial decomposition of SF$_6$ [3,4]. Simultaneously, SF$_6$ will ultimately decompose to several characteristic products with the reaction of trace O$_2$ and H$_2$O in SF$_6$-insulated equipment: H$_2$S, SO$_2$, SOF$_2$ and SO$_2$F$_2$ gas [5–7]. These decomposition products can corrode the metal parts inside the equipment, accelerate the aging of the insulation medium—and even result in the sudden failure of GIS [8,9]. Therefore, discovering SF$_6$ decomposition products and dealing with insulation defects in a timely manner have great importance. To date, several methods such as gas chromatography, mass spectrometry and Fourier transform infrared spectroscopy, are suggested to detect SF$_6$ products [10,11]. However, these methods are either inaccurate or complicated, so none of them are used in detecting SF$_6$ decomposition products.

In recent years, the gas sensor method has been used in various fields due to its advantages such as high sensitivity, rapid response and small size. Graphene is a 2D material with a unique 2D monoatomic layer structure and an electronic energy band structure. Its excellent characteristics—including high electron mobility, high thermal conductivity, brilliant mechanical properties and large specific surface area—make it a promising gas sensor material [12–17]. However, in actual production, several intrinsic defects in graphene may be observed, such as single defects, double-vacancy defects and Stone–Wales defects [18]. Lattice defects may cause local charge traps on the graphene surface, which has a
substantial effect on improving the electronic structure and the adsorption capacity of graphene. Liu et al. anchored Sc, Zn, Mo, Ru, Rh, Pd and Ag atoms on defective graphene for N\textsubscript{2} reduction reaction and found that a single Mo embedded on nitrogen-doped 555–777 graphene shows eminent catalytic performance [19]. Arokiyanathan et al. calculated the adsorption properties of small Li clusters on graphene with Stone–Wales defect. The results showed that Li clusters have a strong interaction with the defect region [20]. Ma et al. reported hydrogen adsorption on Co-4-doped defective graphene and discovered that point defects in graphene can effectively improve the hydrogen storage capacity of Co-4 [21]. Despite much research on defective graphene [22–25], few relevant research on SF\textsubscript{6} decomposition product detection have been reported.

555–777 graphene is a double-vacancy defect graphene sheet [18]. The absence of two carbon atoms does not destroy the original SP\textsuperscript{2} hybrid orbital network but forms a stable topological hole. Thus, 555–777 graphene has a more stable electronic structure compared with other defective structures. Previous studies showed that doping transition metal elements on graphene surface can improve its electrical conductivity and enhance its capacity to adsorb gas molecules [26–30]. Liu et al. calculated the adsorption of SF\textsubscript{6} decompositions on Pd (111) surface and found that Pd (111) would have great adsorption capacity on absorbing those products. Thus, doping Pd element on 555–777 graphene may be a potential method to improve its adsorption properties [30]. In this study, Pd\textsubscript{3}-doped 555–777 graphene (Pd\textsubscript{3}-graphene) is carried out to detect SF\textsubscript{6} decomposition products (H\textsubscript{2}S, SO\textsubscript{2}, SOF\textsubscript{2} and SO\textsubscript{2}F\textsubscript{2}). Different adsorption structures of each gas are obtained to find the most stable adsorption structure. Furthermore, adsorption energy, charge transfer, density of states (DOS) and deformation charge density (DCD) of Pd\textsubscript{3}-graphene surface before and after gas adsorption are calculated to reveal the gas response mechanism. Overall, our work aims to provide some theoretical basis for developing a novel graphene sensor.

2. Computational Details and Models

In this work, all calculations are carried out using Dmol\textsuperscript{3} package based on density functional theory (DFT) [31]. Generalized gradient approximation and Perdew–Burke–Ernzerhof function are utilized to deal with the electron exchange-correlation energy and interaction effect of electrons [32,33]. DFT semi-core pseudopots are set to recoup the relativistic effect of Pd atoms. The Brillouin zone is sampled with 6 × 6 × 1 k-points in the Monkhorst–Pack grid [34]. Double numeric plus polarization basis sets are used to obtain a higher calculation precision of hydrogen bond [35]. The smearing is set as 0.001 Ha to ensure the accuracy of the DFT calculation. The SCF tolerance is 1 × 10\textsuperscript{−6} Ha and spin polarization is considered due to the magnetic properties of Pd atoms. Additionally, total energy of convergence tolerance, maximum force and maximum displacement are set as 1 × 10\textsuperscript{−5} Ha, 2 × 10\textsuperscript{−3} Ha/Å and 5 × 10\textsuperscript{−3} Å, respectively.

Intrinsic 555–777 graphene surface consists of a 6 × 6 supercell, and the lattice parameter is 14.760 Å × 14.760 Å. The vacuum area is set as 20 Å to avoid the interaction of neighboring slabs. The Pd\textsubscript{3} cluster is a triangular structure composed of three Pd atoms. Through DFT calculations, various parameters of stable adsorption structures can be acquired, including adsorption energy (E\textsubscript{ad}), charge transfer amount (Q\textsubscript{T}), adsorption distance (D) and energy gap (E\textsubscript{g}). The definition of these parameters are the same as the previous study [36].

3. Results and Discussions

3.1. Geometric Optimization

We apply geometric optimization to minimize their energy and obtain the most stable status of H\textsubscript{2}S, SO\textsubscript{2}, SOF\textsubscript{2}, SO\textsubscript{2}F\textsubscript{2} and Pd\textsubscript{3}-graphene. The optimized structures are shown in Figure 1 (adapted from [36]). Figure 1a shows the stable structure of intrinsic 555–777 graphene with three pentagons and heptagons at the center of the graphene sheet. Considering that the charge trap in the center of the hole has a strong binding ability to electrons and the special D electronic structure of Pd metal,
we dope the Pd$_3$ cluster at the defect center of graphene to form a stable anchored structure. Figure 1b shows that the Pd$_3$ cluster is parallel to the graphene surface, indicating that the force of the crystal plane on the three Pd atoms is almost equal. Bond lengths between the Pd atoms are 2.714, 2.714 and 2.812 Å. Millikan charge analysis shows that 0.16 electrons transfer from the Pd$_3$ cluster to the graphene sheet after geometric optimization, showing an evident orbital hybridization between C and Pd atoms. The electronic structure of the graphene surface will be greatly changed, which may substantially improve gas adsorption capacity.

Figure 1. Optimized structures of intrinsic 555–777 graphene, Pd$_3$-graphene and gas molecules (distance in Å). © 2020 IEEE.

3.2. Adsorption Systems

3.2.1. H$_2$S Adsorption on Pd$_3$-Graphene

The H$_2$S molecule is placed in different distances and angles to approach the Pd$_3$-graphene surface and obtain the most stable adsorption structure of H$_2$S gas. Considering the symmetry of H$_2$S molecule, its two typical stable adsorption structures are acquired through H and S atoms approaching the Pd$_3$-graphene surface, as shown in Figure 2. $E_{\text{ad}}$, $Q_T$ and D are listed in Table 1.

![Figure 2](image-url)

Figure 2. Adsorption structures of H$_2$S on Pd$_3$-graphene surface (distance in Å).

| System | Position | $E_{\text{ad}}$ (eV) | $Q_T$ (e) | D (Å) |
|--------|----------|---------------------|-----------|-------|
| M1     | S–Pd     | $-1.211$            | $0.286$   | $2.338$ |
| M2     | H–Pd     | $-1.185$            | $0.279$   | $1.868$ |

Table 1. Structural parameters of H$_2$S adsorption systems on Pd$_3$-graphene surface. Position represents the approaching way, for instance, S–Pd means the H$_2$S molecule approaches the Pd atom by the S atom.

Figure 2a shows the adsorption configuration of system M1. The H$_2$S molecule approaches the surface by the S atom and forms a stable interaction between the S and Pd atoms. The D of M1 is 2.338 Å, revealing that the reaction is relatively strong. When the adsorption energy is greater than 0.6 eV, the adsorption is generally considered chemical. The corresponding $E_{\text{ad}}$ of M1 is $-1.211$ eV; hence,
the adsorption is chemical, and the process is spontaneous. The positive value of $Q_T$ of M1 (0.286) demonstrates that 0.286 electrons transfer from the H$_2$S molecule to the Pd$_3$-graphene.

In Figure 2b, the H$_2$S molecule approaches the Pd$_3$-graphene by H atom, forming a new ionic bond with the Pd atom. The length of the H–Pd bond is 1.868 Å, indicating a strong chemical interaction between H and Pd atoms. Similar to system M1, 0.279 electrons transfer from the H$_2$S molecule to the sheet during optimization. The $E_{\text{ad}}$ of system M2 (−1.185 eV) is smaller than that of M1 (−1.211 eV), which means that system M1 releases more energy than M2 after H$_2$S adsorption. Above all, according to the greater $E_{\text{ad}}$ and $Q_T$ of configuration M1, M1 is the most stable adsorption structure of H$_2$S on Pd$_3$-graphene surface.

DOS and partial density of states (PDOS) of the most stable adsorption structure (M1) are calculated to analyze the mechanism of H$_2$S adsorption further, as shown in Figure 3. In Figure 3a, the black and red lines represent the DOS before and after H$_2$S adsorption, respectively. Several distinct changes are observed in DOS after H$_2$S adsorption, which mainly reflect in the increase of DOS from −8 eV to −4 eV. The DOS at the Fermi level rises slightly, revealing that electrons can more easily transfer from the valence band to the conduction band, which may have a substantial effect on improving its conductivity. The PDOS in Figure 3b shows that the increased area of DOS from −8 eV to −4 eV mainly consists of the 3p orbit of S atom. The large overlapped area from −7 eV to −3 eV between the 4d orbit of Pd atom and the 3p orbit of S atom manifests that the chemical reaction between these atoms is strong, which is consistent with the above analysis.

![DOS and PDOS](image_url)

**Figure 3.** Density of states (DOS) and partial density of states (PDOS) of system M1. Dashed line represents the Fermi level.

### 3.2.2. SO$_2$ Adsorption on Pd$_3$-Graphene

For the adsorption of SO$_2$ on Pd$_3$-graphene surface, various initial positions of SO$_2$ molecule are set to investigate the most stable adsorption system. After geometric optimization, two typical stable adsorption configurations are obtained. Figure 4 shows the adsorption structures through S and O atoms approaching the sheet. Figure 4a shows that the SO$_2$ molecule forms a stable adsorption structure by building a chemical bond between S and Pd atoms. The length of the S–Pd bond is 2.192 Å, declaring a strong interaction between them. The two O atoms are far from the sheet; thus, no direct interaction may exist between them and the crystal plane. In Figure 4b the SO$_2$ molecule approaches the Pd$_3$ cluster by O atoms, forming two chemical bonds with the Pd atoms. The length of both O–Pd bonds is 2.131 Å, which is shorter than that of the S–Pd bond in system M3. Thus, the chemical reaction in system M4 may be stronger than that in M3.

Table 2 presents the related parameters of configuration M3 and M4. Both their $E_{\text{ad}}$ are negative, manifesting that the adsorption is exothermic and proceeds spontaneously. By contrast, the $E_{\text{ad}}$ of system M4 is greater than that of system M3, implying that the SO$_2$ molecule absorbed on the Pd$_3$-graphene surface through two O atoms is the most stable structure. Given the strong reaction...
between O and Pd atoms in system M4, 0.283 electrons transfer from the sheet to SO$_2$ molecule. For system M3, the small $Q_T$ means that the ionic S–Pd bond is relatively easy to break.

![Figure 4. Adsorption structures of SO$_2$ on Pd$_3$-graphene surface (distance in Å).](image)

**Table 2.** Structural parameters of SO$_2$ adsorption systems on Pd$_3$-graphene surface. Position represents the approaching way, for instance, S–Pd means the SO$_2$ molecule approaches the Pd atom by the S atom.

| System | Position | $E_{ad}$ (eV) | $Q_T$ (e) | D (Å) |
|--------|----------|---------------|-----------|-------|
| M3     | S–Pd     | −1.534        | −0.023    | 2.192 |
| M4     | O–Pd     | −1.591        | −0.283    | 2.131 |

The DOS and PDOS of M4 are intensively calculated to analyze the adsorption mechanism because M4 is the most stable adsorption configuration of SO$_2$ on Pd$_3$-graphene. Figure 5a presents that the DOS of M4 exhibits three new peaks after SO$_2$ adsorption at around −8, −6 and −4 eV. PDOS shows that the new peaks mainly result from the 2p orbit of O atom and the 3p orbit of S atom. The small increase of DOS at fermi level demonstrates an increase of the conductivity of Pd$_3$-graphene. In addition, a large overlapped area between the 2p orbit of O atom and the 4d orbit of Pd atom ranges from −5 eV to −3 eV, reflecting a complex hybridization of those orbits. Therefore, the chemical reaction between O atoms and Pd atom is strong enough to form a stable adsorption configuration.

![Figure 5. Density of states (DOS) and partial density of states (PDOS) of system M4. Dashed line represents the Fermi level.](image)

3.2.3. SOF$_2$ Adsorption on Pd$_3$-Graphene

Subsequently, we place the SOF$_2$ molecule in different directions and distances approaching the sheet to explore the most stable adsorption structure. Figure 6 shows three typical adsorption configurations, in which the SOF$_2$ molecule is absorbed on Pd$_3$-graphene surface by S, F and O atoms. Related parameters are listed in Table 3.

Figure 6a shows that the SOF$_2$ molecule approaches the surface by the S atom and forms a stable adsorption structure ultimately. The S atom is trapped by the Pd atom and builds a new chemical bond with a bond length of 2.170 Å. The $E_{ad}$ of system M5 listed in Table 3 is −1.230 eV, which indicates that the adsorption is chemical, and the structure is stable enough. During adsorption, only 0.038 electrons...
transfer from SOF₂ molecule to the sheet, so their electronic structure may change slightly. For system M6 shown in Figure 6b, SOF₂ molecule absorbs on the Pd₃-graphene surface by forming an ionic bond length of 2.124 Å between F and Pd atoms. The $E_{ad}$ of M6 (−0.284 eV) is smaller than that of M5 (−1.230 eV), revealing that M5 is more stable than M6. In system M7, the SOF₂ molecule absorbs directly above the hollow position of Pd₃ cluster. The length of the O–Pd bond is 2.299 Å, which is longer than that of M5 and M6. However, the specific $E_{ad}$ of M7 (−1.282 eV) is greater than that of M5 (−1.230 eV), implying that system M7 is more stable. Opposite to system M5, 0.132 electrons transfer from the sheet to SOF₂ molecule after absorbing on Pd₃-graphene. Hence, the SOF₂ molecule tends to be absorbed on the Pd₃-graphene surface in the form of M7, establishing an adsorption system with the lowest energy.

![Figure 6. Adsorption structures of SOF₂ on Pd₃-graphene surface (distance in Å).](image)

### Table 3. Structural parameters of SOF₂ adsorption systems on Pd₃-graphene surface. Position represents the approaching way, for instance, S–Pd means the SOF₂ molecule approaches the Pd atom by the S atom.

| System | Position | $E_{ad}$ (eV) | $Q_T$ (e) | D (Å) |
|--------|----------|---------------|-----------|-------|
| M5     | S–Pd     | −1.230        | 0.038     | 2.170 |
| M6     | F–Pd     | −0.284        | −0.255    | 2.124 |
| M7     | O–Pd     | −1.282        | −0.132    | 2.299 |

Figure 7 shows the DOS and PDOS of the most stable adsorption structure of SOF₂ on the Pd₃-graphene surface. The DOS of M7 structure increases distinctly in the range from −9 eV to −7.5 eV and −6 eV to −3 eV after SOF₂ adsorption. These changes are mainly caused by the 2p orbit of O atom and the 2p orbit of F atom. A slight increase of DOS near the fermi level is observed, signifying that SOF₂ adsorption can improve the conductivity of Pd₃-graphene. The PDOS displaces the hybridization of individual atoms during adsorption. The 2p orbit of O atom, the 2p of F atom and the 4d orbit of Pd atom overlap from −6 eV to −1 eV, suggesting that the chemical reaction between them is considered strong, and the electronic structure of the SOF₂ molecule is active.

![Figure 7. Density of states (DOS) and partial density of states (PDOS) of system M7. Dashed line represents the Fermi level.](image)
3.2.4. SO2 F2 Adsorption on Pd3-Graphene

Eventually, the SO2 F2 molecule approaches the Pd3-graphene surface in various directions and distances to find the most stable adsorption structure. After adsorption structure optimization, two typical adsorption systems are obtained, as shown in Figure 8. Correlative parameters of adsorption systems are listed in Table 4.

Table 4. Structural parameters of SO2 F2 adsorption systems on Pd3-graphene surface. Position represents the approaching way, for instance, F–Pd means the SO2 F2 molecule approaches the Pd atom by F atom.

| System | Position | Ead (eV) | QT (e) | D (Å) |
|--------|----------|----------|--------|-------|
| M8     | F–Pd    | −0.920   | −0.705 | 2.014 |
| M9     | O–Pd    | −0.804   | −0.294 | 2.181 |

Figure 8a presents the adsorption configuration of SO2 F2 molecule approaching the Pd3-graphene surface by F atom. The Pd atom builds a chemical connection with the F atom during the approaching process and forms an F–Pd bond with length of 2.014 Å ultimately. The S–F bond is stretched to 2.40 Å due to the radial force of the Pd atom. In system M9, the SO2 F2 molecule approaches the sheet by O atom. Similarly, the O atom forms a chemical bond with the Pd atom, but the length of the O–Pd bond (2.181 Å) is longer than that of the F–Pd bond (2.014 Å), implying a stronger interaction in configuration M8. The Ead of M8 (−0.920 eV) is greater than that of M9 (−0.804 eV), demonstrating that the M8 structure is more stable than the M9 structure. Additionally, 0.705 electrons transfer from the sheet to the SO2 F2 molecule in M8, which is 2.4 times of M9, confirming a stronger oxidation of the F atom. Thus, configuration M8 is supposed to be the most stable adsorption structure of SO2 F2 on the Pd3-graphene surface.

Figure 9a shows that DOS increases substantially in the range of −7 to 0.5 eV. PDOS reveals that the 2p orbit of O atom and the 2p orbit of F atom mainly contribute the increased area, that is, the DOS near the Fermi level rises slightly. Thus, the conductivity of Pd3-graphene is expected to improve after SO2 F2 adsorption. According to the PDOS, a large hybridization is observed between the 2p orbit of F atom and the 4d orbit of Pd atom from −5 eV to −1 eV, implying that these orbits are relatively active, while SO2 F2 approaches the surface.

Figure 9. Density of states (DOS) and partial density of states (PDOS) of system M8. Dashed line represents the Fermi level.
3.2.5. SF₆ Adsorption on Pd₃-Graphene

In order to ensure that the Pd₃-graphene sensor can be utilized in GIS, we further calculated the adsorption of SF₆ gas on Pd₃-graphene surface to eliminate the interference of SF₆ gas. Same as other gases, SF₆ approaches the graphene surface at different angles and distances. After the geometric optimization, we obtained the most stable adsorption structure of SF₆ on Pd₃-graphene surface shown in Figure 10. As presented, SF₆ molecule approaches the Pd₃-graphene surface by F atom and forms a weak interaction with the Pd atom. The adsorption distance of SF₆ is 4.060 Å, which is longer than other gases. Moreover, the $E_{ad}$ of SF₆ is calculated to be $-0.124$ eV, reflecting that the adsorption the adsorption system is not stable enough. During the adsorption, 0.162 electrons transfer from the Pd₃-graphene to SF₆ molecule. In conclusion, the Pd₃-graphene can be a potential sensor applied in the SF₆ gas-insulated equipment.

![Figure 10. The most adsorption structure of SF₆ on Pd₃-graphene surface (distance in Å).](image)

3.3. Electronic Properties

The deformation charge density of pure Pd₃-graphene and the four most stable adsorption systems is calculated to investigate the difference in electronic structure before and after modifying or gas adsorption. As presented in Figure 11, the red region means an increase of charge density after adsorption, whereas the blue region means a decrease. In Figure 11a, the charge density of Pd₃ cluster decreases, revealing that the defect of 555–777 graphene has a strong oxidation during the doping process. Although the absence of carbon atoms do not give rise to dangling bonds, the reconstruction of the graphene structure results in the change of bond lengths. Meanwhile, the defect would cause a rehybridization of the sigma and pi orbitals of carbon atoms, which would enhance the electron activity near the defect. When the transition metal approaches the defect, its special d electrons form a strong chemical interaction with the defect. Figure 11b shows that the charge density of the two Pd atoms decreases, while the S atom receives electrons from the Pd₃ cluster after adsorption. Therefore, the adsorption reaction is concentrated between the S atom and the Pd atom. In Figure 11c, electrons transfer from the Pd atoms to the O atom due to the strong electronegativity of the O atom, indicating that the two O-Pd bonds are stable enough to support the adsorption structure. The O atom also receives electrons from the S atom, such that the electronic structure inside the SO₂ gas changes prominently. As for SOF₂ gas, the charge density neighboring the O atom increases to a certain degree, and the charge density of the Pd atom decreases. In principle, the O atom performs as an electron acceptor during SOF₂ adsorption. In Figure 11e, the DCD of system M8 shows that the F atom receives electrons from the Pd atom and the nearby the S atom, verifying the fairly strong oxidability of the F atom. In conclusion, the Pd₃ cluster behaves as an electron donor during gas adsorption and leads to a violent chemical reaction in the vicinity, certifying that the Pd₃ dopant can substantially enhance the adsorption capacity of intrinsic 555–777 graphene.
13.95% and 9.30%, respectively, manifesting an increase in conductivity of the Pd with the analysis in the DOS part.

Hence, the sensitivity of N\textsubscript{3}S&Ni-graphene to distinguish SF\textsubscript{6} decomposition products. As a result, Pd\textsubscript{3}‐graphene can be a better gas sensor material on detecting SF\textsubscript{6} decomposition product.

According to the evident effect on the electronic structure of Pd\textsubscript{3}‐graphene after SF\textsubscript{6} product adsorption, the sensitivity and selectivity for application of chemical gas sensor must be further investigated. As a resistor-type gas sensor, the change in conductivity is an important factor in detecting SF\textsubscript{6} decomposition products. The conductivity (\(\sigma\)) of Pd\textsubscript{3}‐graphene gas sensor could be evaluated by the following formula [37]:

\[
\sigma \propto e^{-\frac{E_g}{kT}},
\]

where \(k\), \(T\) and \(E_g\) represent the Boltzmann constant, temperature and HOMO–LUMO energy gap, respectively. Therefore, under a certain temperature condition, \(\sigma\) is an exponential function of the \(E_g\) and a smaller energy gap would determine a higher conductivity. We perform frontier molecular orbital theory to calculate the energy of HOMO (\(E_{\text{H}}\)) and LUMO (\(E_{\text{L}}\)) and obtain the specific \(E_g\), which the difference between them.

Figure 12 intuitively presents the \(E_{\text{H}}\), \(E_{\text{L}}\) and \(E_g\) of pristine Pd\textsubscript{3}‐graphene and the four most stable adsorption systems, where the black number represents the \(E_g\). For pristine Pd\textsubscript{3}‐graphene, the \(E_g\) is 0.086 eV, signifying that the basic conductivity is relatively high, which probably results from the Pd\textsubscript{3} dopant. After gas adsorption, the \(E_g\) of different systems decreases without exception. While H\textsubscript{2}S and SO\textsubscript{2} absorbing on the Pd\textsubscript{3}‐graphene surface in the most stable configuration, the \(E_g\) decreases by 13.95% and 9.30%, respectively, manifesting an increase in conductivity of the Pd\textsubscript{3}‐graphene sensor. For the SOF\textsubscript{2} adsorption system, the \(E_g\) of Pd\textsubscript{3}‐graphene decreases by 38.37%, which is the largest among the four adsorption systems, indicating that the electronic structure is more continuous, and the electronic transition is effortless. However, for the SO\textsubscript{2} F\textsubscript{2} adsorption system, \(E_g\) reduces with the smallest degree, only 5.81%, which means the conductivity of the Pd\textsubscript{3}‐graphene sensor has a slight rise. In conclusion, the conductivity of Pd\textsubscript{3}‐graphene sensor increases after gas adsorption, which agrees with the analysis in the DOS part.

As for N\textsubscript{3}&Ni doped 555–777 graphene reported in [36], N\textsubscript{3}&Ni‐graphene has a high sensitivity on absorbing H\textsubscript{2}S and SO\textsubscript{2} gas while the \(E_g\) decreases from 0.426 eV to 0.052 eV and 0.138 eV, respectively. Hence, the sensitivity of N\textsubscript{3}&Ni‐graphene may be higher than Pd\textsubscript{3}‐graphene while absorbing H\textsubscript{2}S and SO\textsubscript{2} gas. However, it is toilsome for N\textsubscript{3}&Ni‐graphene to distinguish SOF\textsubscript{2} molecule and SO\textsubscript{2} F\textsubscript{2} due to their similar \(E_g\). The problem can be solved by using Pd\textsubscript{3}‐graphene gas sensor for its obviously different \(E_g\) of various adsorption systems. As a result, Pd\textsubscript{3}‐graphene can be a better gas sensor material on detecting SF\textsubscript{6} decomposition product.
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The authors declare no conflict of interest.

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