

First-principles Study of SF₆ Decomposed Gas Adsorption and Sensing on Pt and N Co-doped Graphene

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The detection of SF₆ insulation gas decomposition components in gas-insulated switchgear (GIS) is essential for assessing the GIS operating status and ensuring equipment safety. In this study, we explored the adsorption of SF₆ major decomposition products (SO₂, SOF₂, and SO₂F₂) on Pt and N co-doped graphene (PtN₃-GN) using density functional theory (DFT) calculations. The adsorption structure, energy, and charge transfer of the three adsorbed gases on the PtN₃-GN surface were investigated. Gas adsorption results showed that PtN₃-GN has a high adsorption capacity for these gas molecules, and adsorption energies are -2.55 , -2.54 , and -3.54 eV, respectively. To explore the interaction mechanism between gas molecules and the PtN₃-GN structure, the total and partial densities of states of the system before and after gas adsorption were compared and analyzed. PtN₃-GN strongly interacts with gas molecules, leading to high orbital hybridization between the Pt dopant and gas molecules. PtN₃-GN has good adsorption performance for gas molecules and has good application prospects in GIS decomposition component detection and fault diagnosis.

1. Introduction

SF₆ has high electronegativity, excellent insulating performance, arc quenching capability, and good chemical stability, so it is widely used in gas-insulated switchgear (GIS) power systems.⁽¹⁾ When electrical equipment is operated for a long time, unavoidable insulation defects, such as partial, arc, spark, and corona discharges can occur.⁽²⁾ Under the action of the discharge, SF₆ reacts with the moisture and oxygen in the equipment to generate specific components for the decomposition of gases, such as SO₂, SOF₂, and SO₂F₂.⁽³⁾ The presence of these compounds can significantly negatively impact the insulation performance of SF₆, leading to accidents.⁽⁴⁾ In other words, detecting or removing these hazardous gases is the primary focus for the safe operation of SF₆ insulating devices.

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Graphene's good thermal conductivity, high hardness, high flexibility, low electronic noise, high specific surface area, and excellent optical and charge transfer properties have attracted researchers' attention.⁽⁵⁾ Many studies have shown that graphene can adsorb and desorb various molecules and atoms. The adsorption of these molecules or atoms as electron donors or acceptors will lead to changes in the conductivity of graphene molecules, which offers the potential for graphene to be applied in gas sensing.⁽⁶⁾ This is because when graphene interacts with molecules or atoms, charge transfer will cause a change in graphene's conductivity, and this modification can serve as a signal for the detection of gas molecules.⁽⁷⁾ However, graphene as a gas sensor has some limitations, including sensitivity and selectivity.⁽⁸⁾ Researchers have conducted modification studies on graphene to broaden the range of applications of graphene materials. They found that heteroatom doping or defect introduction can significantly enhance the adsorption of gas molecules on graphene and improve the sensitivity and selectivity of graphene for gas molecule adsorption.^(9,10) Nasehnia and Seifi investigated the adsorption effect of graphene doped with transition metals (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt) on oxygen. They found that graphene doped with transition metals exhibited high oxygen sensitivity.⁽¹¹⁾ Ao *et al.* investigated the adsorption characteristics of the Al-doped graphene system and found that the CO adsorption energy in the doped graphene system was significantly increased.⁽¹²⁾

Pt is a transition metal element. Its nanoparticles have excellent sensing performance, catalytic activity, and high specific surface, and Pt has been widely used in various fields. Many studies have shown that Pt-doped graphene has good gas sensing properties.^(13,14) Research showed that doping non metallic N atoms into graphene monolayer material can lead to chemical activity and carrier mobility much higher than those of pure graphene. N doping graphene has structural stability similar to graphene. These outstanding properties make it the most promising graphene functional material.^(15,16) On the basis of the DFT method, we analyze and study the adsorption behavior of SF₆ decomposition components (including SO₂, SOF₂, and SO₂F₂) on Pt and N co-doped graphene, and provide a theoretical basis for PtN₃-GN monolayer materials as chemical sensors used in the field of electrical and gas engineering.

2. Calculation Method

Density functional theory (DFT) was adopted for simulation calculations, which were analyzed in the modules Dmol³ and CASTEP. The electron density difference (EDD) is calculated in CASTEP. Other simulation calculations are analyzed in Dmol³. This study used generalized gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) functions to handle exchange crosslinking between electrons. PBE and Grimme dispersion correction is the most suitable theoretical method for studying the interaction between molecules and graphene. Grimme dispersion correction was adopted. DFT semi-core pseudopotential (DSSP) was selected to replace the single effective nuclear electron potential. Dual numerical plus polarization (DNP) was chosen as the atomic orbital basis group.

A $5 \times 5 \times 1$ single-layer graphene supercell model, consisting of 50 carbon atoms, was constructed; its boundary conditions are periodic *x*- and *y*-axes to simulate infinite graphene sheets. We set a vacuum layer of 20 Å (1 Å = 10⁻¹⁰ m) to avoid interaction between cycles. The

optimized C–C bond length of graphene is 2.47 Å, which is close to the theoretical and experimental values, ensuring the correctness of the model.

The energy convergence accuracy, maximum stress, and maximum displacement were set to 1×10^{-5} Ha (1 Ha = 27.212 eV), 2×10^{-3} Ha/Å, and 5×10^{-3} Å, respectively. During structural optimization and electronic property calculations, the corresponding k-points were set to $5 \times 5 \times 1$ and $9 \times 9 \times 1$, respectively. The self-consistent field convergence precision was set to 1×10^{-6} Ha, and the direct inversion DIIS of the iterative subspace was set to 6, which improves the convergence speed of the self-consistent field charge density, thus improving efficiency.

The adsorption energy E_{ads} of gas molecules on the surface of doped graphene is

$$E_{ads} = E_{\text{PtN}_3\text{-GN-gas}} - E_{\text{PtN}_3\text{-GN}} - E_{\text{gas}}, \quad (1)$$

where $E_{\text{PtN}_3\text{-GN-gas}}$ is the total energy of PtN₃-GN adsorbed gas, $E_{\text{PtN}_3\text{-GN}}$ is the energy of PtN₃-GN, and E_{gas} is the energy of the gas. If the calculated adsorption energy is negative, then the adsorption is exothermic, can occur spontaneously, and is stable. The greater the absolute value of the adsorption energy, the more significant the change in total energy in the adsorption process and the stronger the interaction between the sensing material and the adsorbed gas.

The Hirshfeld charge analysis method is used to calculate and analyze the charge transfer (Q_t) between gas molecules and the PtN₃-GN structure,

$$Q_t = Q_a - Q_b, \quad (2)$$

where Q_a and Q_b represent the total charges of the gas molecules after and before adsorption, respectively.

3. Results and Analysis

3.1 Pt and N co-doped on graphene

A graphene system loaded with Pt and N atoms is built to study the adsorption performance of its sensing on SF₆ decomposition gas. A single Pt atom replaces a carbon atom in graphene; N atoms replace the three carbon atoms connected with Pt. The structure is optimized, as shown in Fig. 1.

The Pt atom is larger than the C atom. Owing to steric hindrance and tension, the Pt atom maintains a certain distance from the graphene plane when the Pt atom is embedded in graphene.

The total density of states (TDOS) of the PtN₃-GN system and intrinsic graphene is shown in Fig. 2. It is found that after doping Pt and N, the electron distribution of TDOS near the Fermi level significantly increases compared with that of the intrinsic graphene. This shows that the doping of Pt and N enhances the conductivity of the graphene structure.

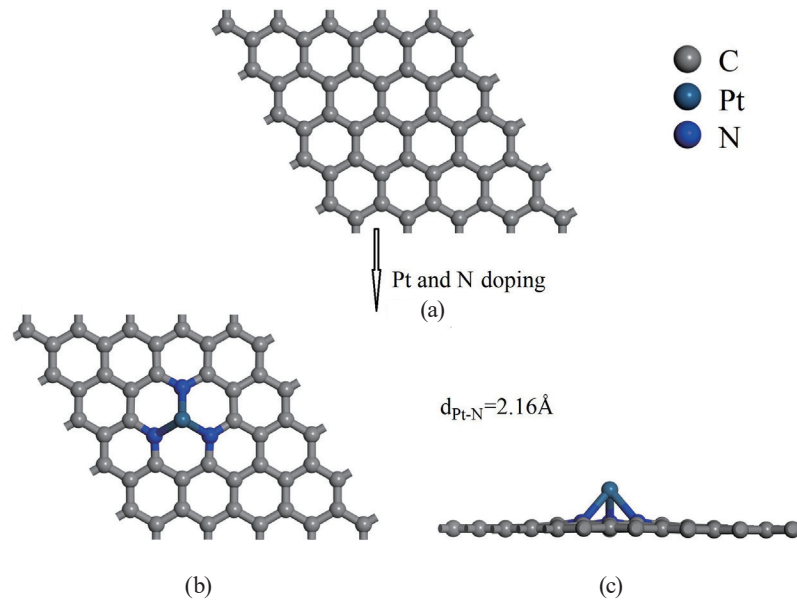


Fig. 1. (Color online) Structure of Pt and N co-doped graphite: (a) top view of graphene before doping, (b) top view of PtN₃-GN after doping, and (c) side view of PtN₃-GN.

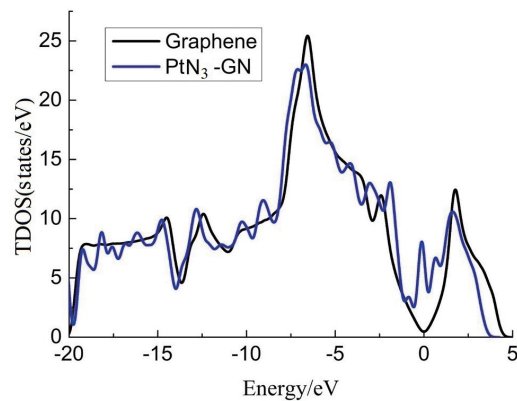


Fig. 2. (Color online) TDOS of PtN₃-GN.

3.2 Adsorption of SF₆ decomposition gas molecules on PtN₃-GN

To obtain the optimal adsorption configuration, we consider the gas molecules' approach to the PtN₃-GN system at different angles and positions. After complete optimization, the most stable structures for gas adsorption with the lowest energy and EDD are shown in Fig. 3. Relevant structural parameters such as adsorption distances (d), adsorption energy, and charge transfer are shown in Table 1.

Fig. 3(a) shows the adsorption structure of SO₂ on PtN₃-GN. SO₂ molecules are preferentially captured by the parallel position of the molecules, where Pt adsorbs one S atom and one O atom, and the lengths of Pt–S and Pt–O bonds are 2.33 and 2.09 Å, respectively. The length of the S–O

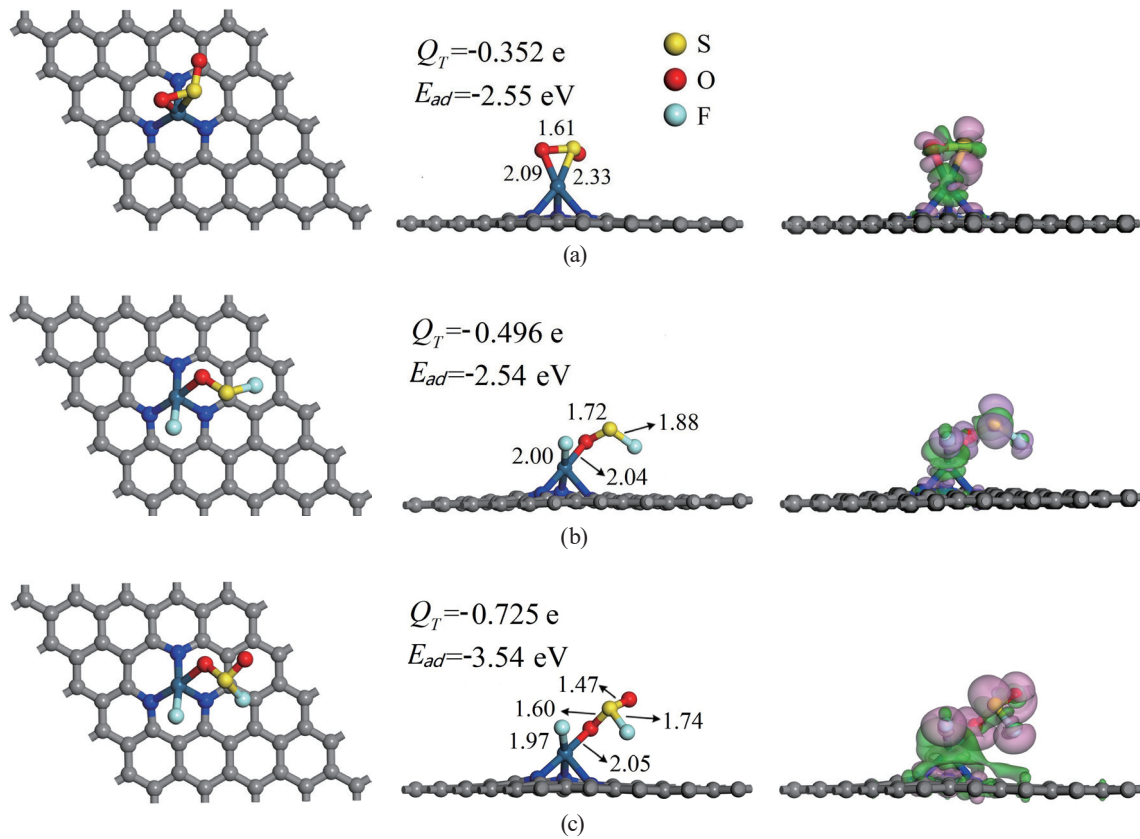


Fig. 3. (Color online) Adsorption structures and EDDs of the three gases on PtN₃-GN monolayer. (a) SO₂, (b) SOF₂, and (c) SO₂F₂ systems. The black values are the bond lengths. In EDDs, the green and violet areas represent electron accumulation and depletion, respectively. The isosurface is set to 0.02 e/Å³.

Table 1
Adsorption parameters of SO₂, SOF₂ and SO₂F₂ on PtN₃-GN.

Gas molecules	d (Å)	E_{ads}/eV	Q_T/e	Bond length of gas (Å)
SO ₂	2.09	−2.55	−0.352	S–O: 1.61
				1.48
SOF ₂	2.04	−2.54	−0.496	S–O: 1.72
				S–F: 1.88
SO ₂ F ₂	2.05	−3.54	−0.725	S–O: 1.61
				1.48
				S–F: 1.74

bond formed by the O atom adsorbed by the Pt atom in the SO₂ molecule significantly increases to 1.61 Å, which means that the SO₂ molecule is strongly activated during its interaction with PtN₃-GN. The adsorption energy of the system for SO₂ molecules is −2.55 eV, and the adsorption effect is strong.

Figure 3(b) shows the adsorption structure of SOF₂ on PtN₃-GN. It can be seen from the figure that there is an apparent deformation adsorption, one S–F bond of SOF₂ breaks, and Pt

atoms capture F atoms to form a Pt–F bond with a length of 2.00 Å. In addition, the remaining SOF group is captured by the Pt dopant through the Pt–O bond (bond length is 2.04 Å). The adsorption energy reaches -2.54 eV, resulting in the severe deformation of the SOF₂ molecule.

Figure 3(c) shows the adsorption structure of SO₂F₂ on PtN₃-GN. It can be seen from the figure that there is an apparent deformation adsorption, one S–F bond of SO₂F₂ breaks, and Pt atoms capture F atoms to form a Pt–F bond with a length of 1.97 Å. In addition, the remaining SO₂F group is captured by the Pt dopant through the Pt–O bond (the bond length is 2.05 Å). The adsorption energy reaches -3.54 eV, resulting in the severe deformation of the SO₂F₂ molecule. In addition, some studies have shown that S–F bond fracture usually occurs when metal-doped 2D materials are used to detect SO₂F₂ molecules.⁽¹⁷⁾ This phenomenon is attributed to the S–F bond being longer and weaker than the S–O bond, and the F atom has strong nonmetallic characteristics.⁽¹⁸⁾ The adsorption of SO₂, SOF₂, and SO₂F₂ on PtN₃-GN can be considered chemical adsorption because their adsorption energies are higher than 0.8 eV.⁽¹⁹⁾ SO₂, SOF₂, and SO₂F₂ are electron acceptors. Electrons are transferred from Pt atoms to the adsorbed gas, and adsorption charges are 0.352, 0.496, and 0.725 e, respectively. Pt loss electrons may be due to the large electronegativity of gas atoms and doped Pt. From the EDD, the Pt atom is in the green region, indicating that Pt loses electrons, and the adsorbed gas is mainly purple, which is close to the calculated results.

3.3 Analysis of electronic properties of gas adsorption on PtN₃-GN

To further study the electronic characteristics of gas adsorption, TDOS before and after gas adsorption and PDOS (partial DOS, PDOS) of central interacting atoms were calculated, and the results are shown in Fig. 4. The central interacting atoms in the SO₂ adsorption system are Pt, S, and O atoms, whereas those in the SOF₂ adsorption system are Pt, F, and O atoms.

From the TDOS of the three gases shown in Fig. 4, it can be seen that the curve moves slightly to the right and changes significantly near the Fermi level, indicating that the electron behavior of PtN₃-GN has changed, which is due to the strong electron hybridization between the adsorbed gas and the Pt dopant. In the SO₂ system, it can be seen that owing to the charge transfer between the adsorbent surface and adsorbate molecules, some peaks disappear relative to the system before adsorption, especially peaks near the Fermi level. In PDOS, the 2p orbital of the O atom overlaps with the 5d orbital of the Pt atom in a large area, and the 2p orbital of the O atom shows a prominent Fermi energy level peak, indicating its vital role in electron conduction, and the strong hybridization of electrons between O and Pt. In the SOF₂ system, it can also be found that the peak near the Fermi level has a notable change, which may be the sharp redistribution of electrons. The 5d orbital of Pt atoms overlaps significantly with the 2p orbital of O and F atoms. The 2p orbital of O and F atoms shows prominent Fermi energy level peaks, indicating that the orbital of O and Pt atoms and that of F and Pt atoms are highly hybridized during adsorption. In the SO₂F₂ system, the DOS curve changes most before and after adsorption, and peak disappearance near the Fermi level can also be observed, which may be caused by the sharp redistribution of electrons. The significant overlap area between the 5d

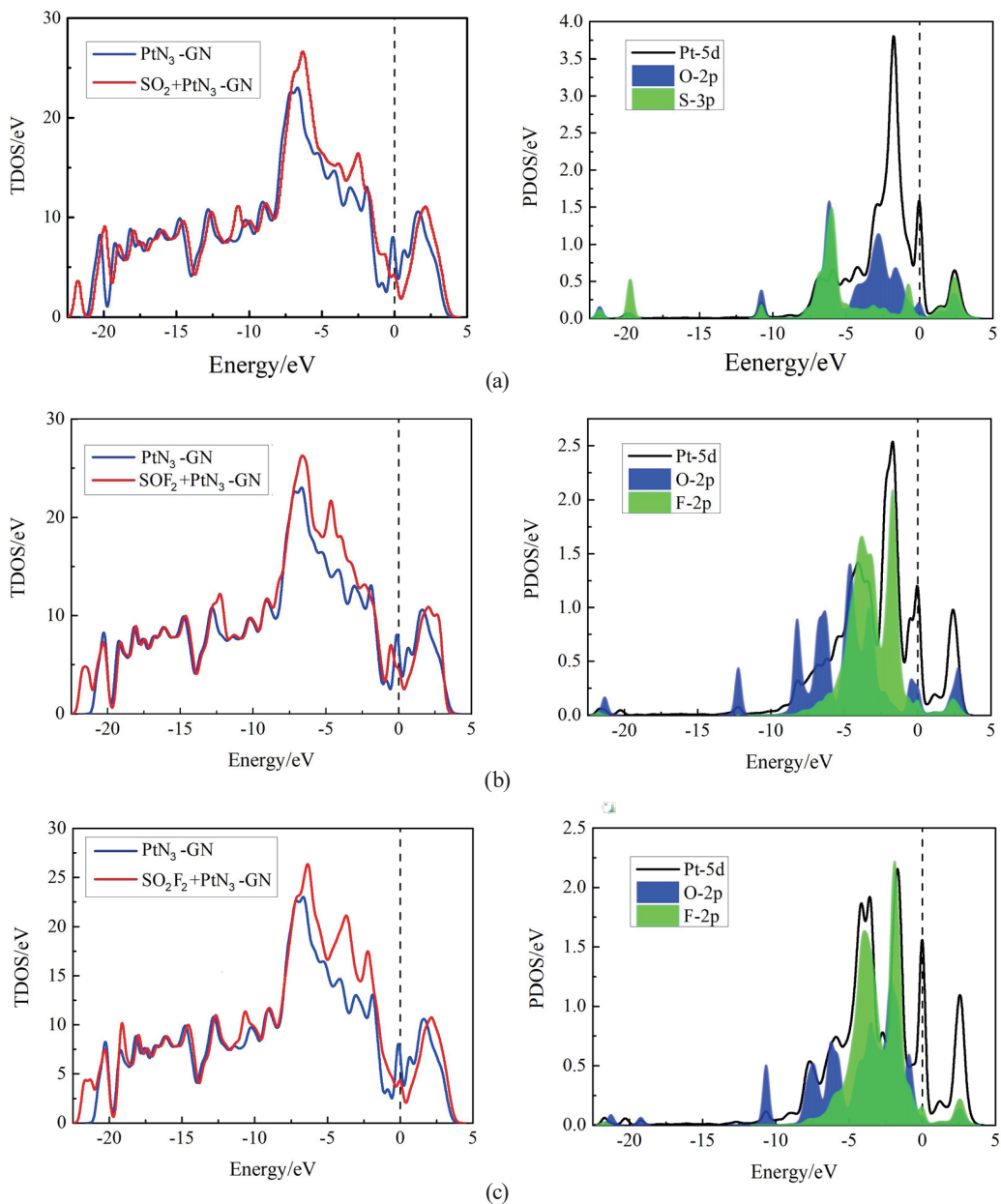


Fig. 4. (Color online) TDOS before and after SO₂, SO₂F, and SO₂F₂ adsorption and PDOS of the main interacting atoms in PtN₃-GN system. (a) SO₂ system, (b) SOF₂ system, and (c) SO₂F₂ system.

orbital of the Pt atom and the 2p orbital of the O and F atoms shows prominent Fermi energy level peaks, indicating that their orbitals are highly hybrid during adsorption. A strong hybridization between the 5d orbital of the Pt atom, the 2p orbital of the F atom, and the 2p orbital of the O atom can also be observed, confirming the connection between these atoms.

4. Conclusions

In this paper, the adsorption characteristics of graphene sensor materials for SF₆ decomposition gases SO₂, SOF₂, and SO₂F₂ were theoretically studied using first-principles calculations. The Pt and N co-doped graphene substrate was constructed. The adsorption structure, related structural parameters, adsorption energy, and electronic properties of SO₂, SOF₂, and SO₂F₂ on PtN₃-GN were studied. The results showed that PtN₃-GN has significant adsorption on the three gases. The adsorption energies of the three gases are −2.55, −2.54, and −3.54 eV, respectively. PDOS analysis revealed that atoms show colossal overlap. This result reflects that gas molecules are adsorbed on PtN₃-GN. The results of this study provide a new idea for developing Pt/N co-doped modified graphene gas sensors and realizing the fault detection of SF₆ insulation equipment online.

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