A DFT Calculation of Fluoride-Doped TiO<sub>2</sub> Nanotubes for Detecting SF<sub>6</sub> Decomposition Components

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Abstract: Gas insulated switchgear (GIS) plays an important role in the transmission and distribution of electric energy. Detecting and analyzing the decomposed components of SF<sub>6</sub> is one of the important methods to realize the on-line monitoring of GIS equipment. In this paper, considering the performance limits of intrinsic TiO<sub>2</sub> nanotube gas sensor, the adsorption process of H<sub>2</sub>S, SO<sub>2</sub>, SOF<sub>2</sub> and SO<sub>2</sub>F<sub>2</sub> on fluoride-doped TiO<sub>2</sub> crystal plane was simulated by the first-principle method. The adsorption mechanism of these SF<sub>6</sub> decomposition components on fluoride-doped TiO<sub>2</sub> crystal plane was analyzed from a micro perspective. Calculation results indicate that the order of adsorption effect of four SF<sub>6</sub> decomposition components on fluoride-doped TiO<sub>2</sub> crystal plane is H<sub>2</sub>S > SO<sub>2</sub> > SOF<sub>2</sub> > SO<sub>2</sub>F<sub>2</sub>. Compared with the adsorption results of intrinsic anatase TiO<sub>2</sub> (101) perfect crystal plane, fluorine doping can obviously enhance the adsorption ability of TiO<sub>2</sub> (101) crystal plane. Fluorine-doped TiO<sub>2</sub> can effectively distinguish and detect the SF<sub>6</sub> decomposition components based on theoretical analysis.

Keywords: SF<sub>6</sub> decomposition component; fluorine-doped TiO<sub>2</sub>; first-principle simulation

1. Introduction

Gas insulated switchgear (GIS), with benefits such as small land cover, flexible configuration, high safety, and high reliability, has been widely used in the power system [1]. However, during the long-term operation of GIS equipment, the internal insulation defects may cause partial discharge (PD). SF<sub>6</sub> insulating gas in the GIS will decompose into some types of gases like SO<sub>2</sub>, H<sub>2</sub>S, SOF<sub>2</sub>, SO<sub>2</sub>F<sub>2</sub> [2–5] under the effect of PD. With the decomposition of SF<sub>6</sub>, aging of GIS equipment and corrosion of metal surface will be accelerated, which ultimately may lead to breakdown of GIS equipment, affecting the stable operation of the power system [6]. Therefore, it is of great importance to detect the SF<sub>6</sub> decomposition components in GIS equipment. On one hand, the type of PD can be confirmed by the types of decomposition components; on the other hand, by measuring the contents of decomposition, the level of PD can be determined, even the aging degree of GIS equipment. Therefore, through the monitoring of decomposition components, unnecessary losses can be reduced by timely taking precaution and preventing the breakdown of GIS equipment.

At present, utilizing the gas sensor method to achieve the goal of detecting SF<sub>6</sub> decomposition components has advantages of a small detection unit, easy installation process, fast detection speed, and so on. Therefore, it is of great importance to study gas sensitive response of the gas sensors made of different gas-sensing materials. Our team studied the gas-sensing materials such as carbon nanotubes and graphene [7–12]. However, it is in the early stage of research, and further research...
needs to be conducted. At the same time, with the technology of TiO$_2$ nanotube preparation becoming mature, the TiO$_2$ nanotube gas sensor has advantages of high specific surface area and high symmetry, which makes it a research hotspot in the gas detection field. However, the inherent energy gap of TiO$_2$ is comparatively large (more than 3.0 eV), which hinders its wide development. Research shows that the surface of TiO$_2$ nanotubes can be modified by nonmetallic doping to improve its photosensitive, photocatalytic and other properties. Varghese et al [13,14] sputtered a layer of 10 nm thick of Pd on the surface of TiO$_2$ nanotubes by thermal evaporation, which can improve the sensitivity of TiO$_2$ nanotube gas sensor, and reduce the recovery time. More importantly, the improved sensor can detect H$_2$ at room temperature. At present, the study of nitrogen doping in nonmetallic doping has received the most attention [15-19]. The results show that nitrogen doping can reduce the energy gap of TiO$_2$, which makes the electrons in the valence band transition more easily. In addition, many studies have reported that TiO$_2$ is modified by fluorine doping [20-23]. Fluorine doping does not basically change the size of the TiO$_2$ energy gap, but it can promote the generation of oxygen hole defects, increase the surface acidity and Ti$^{3+}$, which is beneficial to reducing the recombination rate of electron hole pairs, and thereby improving the photocatalytic activity [24].

With the successful doping of fluorine onto the surface of TiO$_2$ [20,25,26], the study of application of fluorine-doped TiO$_2$ nanomaterials in gas sensing detection is deficient. In this paper, the idea of using fluorine-doped TiO$_2$ nanotubes gas sensor to detect SF$_6$ decomposition components was determined. The adsorption process of H$_2$S, SO$_2$, SOF$_2$ and SO$_2$F$_2$ gas molecules onto fluorine-doped anatase TiO$_2$ (101) perfect crystal plane by first-principle calculation. The calculation parameters include adsorption energy, adsorption distance, charge transfer amount and the density of states. The simulation analysis can provide insight for the practical explanation of fluorine-doped TiO$_2$ nanometer array gas sensor detecting SF$_6$ decomposition gases from the microscopic point of view. Finally, the adsorption results of SO$_2$, SOF$_2$ and SO$_2$F$_2$ under different doping conditions were compared in this paper.

2. Calculation Parameters and Methods

The TiO$_2$ model in this paper is an anatase TiO$_2$ (101) perfect facet model derived directly from the database provided by Materials Studio software, and the size is 3.776 $\times$ 3.776 $\times$ 9.486 Å, which is the smallest unit of anatase TiO$_2$. The detailed calculation process is as follows: build the anatase TiO$_2$ (101) perfect crystal plane 2 $\times$ 2 super-cell model, and the gas molecules of SO$_2$, H$_2$S, SOF$_2$ and SO$_2$F$_2$; optimize these models initially in the Dmol$^3$ module, which can make these micro-structure parameters to maximumly close to the idealization, as shown in Figure 1.; replace one of the O atoms on the surface of the anatase TiO$_2$ (101) perfect crystal plane by F atom; After optimized treatment, the fluorine doped anatase TiO$_2$ (101) perfect crystal plane supercell model (F-doped TiO$_2$) is obtained, as shown in Figure 2; finally, the optimized SO$_2$, H$_2$S, SOF$_2$ and SO$_2$F$_2$ gas molecules with different postures approach respectively close to the surface of the perfect crystal plane of the anatase TiO$_2$ (101) to get a different adsorption system. Different adsorption systems were optimized in order to find a more stable adsorption structure for each gas molecule onto F-doped TiO$_2$.

Figure 1. Perfect crystal model of intrinsic anatase TiO$_2$ (101) and SO$_2$, H$_2$S, SOF$_2$ and SO$_2$F$_2$ gas molecular models, Ti atom is gray, O atom is red, S atom is yellow, F atom is blue, H atom is white.
In this paper, parameters are set as follows when optimizing the calculation. Since the number of atoms contained in the perfect crystal plane model of the anatase TiO$_2$ (101) established in this paper is large, the generalized gradient approximate (GGA) with high calculation accuracy was adopted so as to make the calculated physical and chemical characteristics of the different adsorption system more accurate. The exchange and correlation interaction effect between electrons were represented by the Perdew-Burke-Ernzerhof (PBE) function [27]. The energy convergence tolerance and the energy gradient (max. force) are set to 1.0 × 10$^{-5}$ Ha and 0.002 Ha/Å respectively. The atomic displacement (max. displacement) is set to 0.005 Å. The convergence accuracy of the self-consistent field charge density (SCF tolerance) is set to 1.0 × 10$^{-6}$ Ha, Brillouin k-point grid (k-point) is set to 2 × 2 × 1; the double Numeric Basis with Polarization (DNP) was used in the atomic orbits calculation with d, p orbital polarization function at the same time so as to make the results more accurate. Considering the influence of the dispersion force, that is, the van der Waals force, the DFT-D (Grimme) algorithm was utilized; in order to improve the efficiency of computation, the direct inversion of iterative subspace (DIIS) is used to improve the convergence rate of the charge density of the self-consistent field.

3. Simulation Results and Analysis

3.1. Establishment of F-Doped TiO$_2$ Model

The F-doped TiO$_2$ model was established based on the perfect crystal plane model. A fluorine atom replaces one of the O atoms on the surface of the anatase TiO$_2$ (101) perfect crystal plane, and F atom combined with Ti atoms to form Ti-F bonds.

Figure 3 shows the curve of the density of states (DOS) of F-doped TiO$_2$ and intrinsic anatase TiO$_2$ (101) perfect crystal plane. It can be seen from the figure that the peak and shape of the density...
curve almost did not change after the fluorine atom being doped. The doping of the fluorine atoms hardly changes the band gap of TiO$_2$. However, after fluorine element doping, the Ti$^{4+}$ is converted to Ti$^{3+}$, and the presence of a certain amount of Ti$^{3+}$ will reduce the recombination rate of electron hole pairs [28]. Furthermore, fluorine element doping is conducive to the generation of oxygen holes and enhances the mobility of effective electrons [24, 29], which can enhance the conductivity of the adsorbent substrate and improve the gas sensing performance of the fluorine-doped TiO$_2$ nano array gas sensor mentioned above.

3.2. Parameter Calculation of Different Adsorption Systems

Figure 4 shows the adsorption structure of four gas molecules adsorbed on the F atom of the F-doped TiO$_2$ crystal planes in different ways after complete optimization calculation. Due to the structural characteristics of four gas molecules, the way that the gas molecule adsorbed on the crystal plane was considered. Three situations are considered when the SO$_2$ molecule comes close to the crystal plane in the optimization calculations, that is a single S and O atoms close to the crystal plane and two O atoms simultaneously close to the crystal plane. And the adsorption structures after calculation are shown in Figure 4a–c. Three cases were considered for H$_2$S molecules: the single S, H atoms close to the crystal plane and two H atoms simultaneously close to the crystal plane. The calculated adsorption structures are shown in Figure 4d–f. SO$_2$F$_2$ molecules mainly consider four cases: the single S, O, F atoms close to the crystal plane and two F atoms simultaneously close to the crystal plane, the calculated adsorption structure are shown in Figure 4g–j; the SO$_2$F$_2$ molecule is of a tetrahedral structure, and the S atom is inside the structure. So, SO$_2$F$_2$ mainly considers 4 cases: a single O, F atom close to the crystal plane, two O atoms and two F atoms are simultaneously close to the crystal plane, separately. The calculated adsorption structures are shown in Figure 4k–n.
Figure 4. The adsorption structures of four gas molecules adsorbed on the crystal surface in different ways. (a–n) are the adsorption structure of four gas molecules adsorbed on the F-doped TiO$_2$ crystal plane in different ways after complete optimization calculation.

Adsorption energy is the degree of change of total energy before and after the adsorption of gas molecules onto crystal plane, which represents the ability of gas molecules adsorption onto the crystal plane. In this paper, the magnitude of adsorption energy is expressed by $E_a$, and the formula is as follows:

$$E_a = E_{sys} - E_{gas} - E_{sur},$$  \hspace{1cm} (1)

where $E_{sys}$ represents the energy of the whole system after the gas adsorbed on the F-doped TiO$_2$, $E_{gas}$ represents the energy when the gas molecules are present alone, and $E_{sur}$ represents the energy of F-doped TiO$_2$ without the adsorption of gas molecules.

In the adsorption process, besides the change of energy, it may also be accompanied with the electron transfer, which results in the change of the electronic structure of the crystal plane, and shows the changes of electrical properties such as resistance and capacitance at macro level. In practical applications, the gas sensitive response characteristics of gas sensors can be obtained by detecting these electrical characteristics. Therefore, this paper also calculated Mulliken charge distribution of
the gas molecules adsorbed onto the F-doped TiO$_2$, to confirm the amount of charge transfer before and after the adsorption of gas molecules onto the crystal plane. The charge transfer $Q_t$ is defined as the charge change of gas molecules before and after they are adsorbed onto the F-doped TiO$_2$ crystal plane. If $Q_t > 0$, the electron is transferred from the gas molecule to the crystal plane. On the contrary, if $Q_t < 0$, part of the electrons is transferred from the crystal plane to the gas molecule. Table 1 shows the adsorption energies, adsorption distance and charge transfer of four kinds of gas molecules SO$_2$, H$_2$S, SOF$_2$ and SO$_2$F$_2$ adsorbed onto F-doped TiO$_2$ crystal plane in different postures.

| Adsorption System       | Adsorption Structure | Adsorption Energy $E_a$ (eV) | Charge transfer Amount $Q_t$ (e) | Adsorption Distance (Å) |
|------------------------|----------------------|-------------------------------|---------------------------------|-------------------------|
| SO$_2$-S-TiO$_2$       | a                    | −0.173                        | −0.013                          | 2.847                   |
| SO$_2$-O-TiO$_2$       | b                    | −0.132                        | 0                               | 3.229                   |
| SO$_2$-2O-TiO$_2$      | c                    | −0.617                        | −0.12                           | 2.111                   |
| H$_2$S-S-TiO$_2$       | d                    | −0.209                        | 0.008                           | 2.835                   |
| H$_2$S-H-TiO$_2$       | e                    | −0.837                        | 0.267                           | 2.714                   |
| H$_2$S-2H-TiO$_2$      | f                    | −0.836                        | 0.266                           | 2.717                   |
| SOF$_2$-S-TiO$_2$      | g                    | −0.254                        | −0.017                          | 2.749                   |
| SOF$_2$-O-TiO$_2$      | h                    | 0.412                         | 0.098                           | 2.438                   |
| SOF$_2$-F-TiO$_2$      | i                    | −0.534                        | 0.038                           | 2.425                   |
| SOF$_2$-2F-TiO$_2$     | j                    | −0.423                        | 0.098                           | 2.424                   |
| SO$_2$F$_2$-O-TiO$_2$  | k                    | −0.044                        | 0                               | 3.091                   |
| SO$_2$F$_2$-F-TiO$_2$  | l                    | −0.051                        | −0.002                          | 2.863                   |
| SO$_2$F$_2$-2O-TiO$_2$ | m                    | −0.398                        | 0.046                           | 2.652                   |
| SO$_2$F$_2$-2F-TiO$_2$ | n                    | −0.198                        | −0.003                          | 2.833                   |

In Table 1, SO$_2$-S-TiO$_2$ represents an adsorption system in which SO$_2$ molecules are close to the F-doped TiO$_2$ crystal plane with single S atom, and others are similar. $E_a < 0$ indicates that the adsorption of four kinds of molecules onto F-doped TiO$_2$ crystal plane are exothermic. The value of $E_a$ is larger, indicates that the adsorption of gas molecules onto F-doped TiO$_2$ crystal plane is easier, and adsorption structure is more stable.

When H$_2$S gas molecules with a single H atom close to the crystal plane and two H atoms simultaneously close to crystal plane, the adsorption structure after optimization calculation (Figure 4e, f) is almost the same, the calculated adsorption energy ($−0.837$ eV and $−0.836$ eV) and the amount of charge transfer ($0.267$ e and $0.266$ e) is almost exactly the same, which is larger than the adsorption energy and charge transfer ($−0.209$ eV and $0.008$ e) of the adsorption with single S atom close to the crystal plane. At the same time, the adsorption distance ($2.835$ Å) of the adsorption system obtained from H$_2$S gas molecules with single S atom close to the crystal plane should be larger than that of the other two approaching ways ($2.714$ Å and $2.717$ Å). Therefore, the H$_2$S gas molecules are much easier to adsorb onto the crystal plane with a single H atom close to the crystal plane and two H atoms simultaneously close to the F-doped TiO$_2$ crystal plane. When the H$_2$S gas molecules are adsorbed on the crystal plane, the amount of charge transferred to the crystal plane is about $0.266$ e, and the macroscopic gas sensitivity of the gas sensor shows the decrease of the impedance.

Similarly, the adsorption reaction of SOF$_2$ gas molecules more easily occurs in three cases: close to the F-doped TiO$_2$ surface with a single O and F atoms and two F atoms at the same time, and the macroscopic sensitivity of the gas sensor shows the decrease of the impedance. SO$_2$ gas molecule reacts easier with two O atoms at the same time when approaching the crystal surface, and the macroscopic gas sensitivity of the gas sensor shows the increase of the impedance. The comparison shows that the adsorption energy of H$_2$S gas molecules onto F-doped TiO$_2$ crystal plane is the highest, which is about two times of that of SOF$_2$, SO$_2$F$_2$. In addition, when the three types of gas molecules, H$_2$S, SOF$_2$ and SO$_2$F$_2$, adsorb onto F-doped TiO$_2$, the macroscopic gas sensitivity of the gas sensor shows the decrease of the impedance.
sensitivity of the gas sensor shows the increase of the impedance. Therefore, theoretically, F-doped TiO$_2$ nanotube array gas sensor can effectively distinguish and detect the four kinds of gases.

3.3. Analysis of Density of States

When different gas molecules adsorb on the surface of the gas sensor, the resistance of the sensor may change; the fluorine-doped TiO$_2$ nanotube array gas sensor mainly uses this principle to achieve the detection of SF$_6$ decomposition components. So, one of the key parameters in practical applications is the resistance of the sensor and analysis of DOS of the adsorption system can be used to find the reasons from the change in resistance.

![Figure 5](image)

Figure 5. The total density and partial density of SO$_2$ molecules adsorbed on F-doped TiO$_2$, and the green short dashed line is Fermi level. (a1,a2) are the TDOS and PDOS of SO$_2$-S-TiO$_2$, (b1,b2) are the TDOS and PDOS of SO$_2$-O-TiO$_2$, (c1,c2) are the TDOS and PDOS of SO$_2$-2O-TiO$_2$. 
Figure 5 shows the total density of states (TDOS) and the partial density of states (PDOS) curves of SO\textsubscript{2} molecules adsorbed on F-doped TiO\textsubscript{2}. Since the contributes of p-orbit of the gas molecule is greatest to DOS, it is also presented in the figure. It can be seen from Figure 5(a1–b2), when the single S atom and the single O atom are close to the F-doped TiO\textsubscript{2} crystal plane, the SO\textsubscript{2} gas molecules contribute to the DOS of the adsorption system only on the right side of 0 eV. But, it can be seen from Figure 5(c1,c2), when the SO\textsubscript{2} molecule close to the crystal plane with two O atoms at the same time, the SO\textsubscript{2} molecules have a significant contribution to the DOS of the adsorption system on both sides of 0 eV. This corresponds to the charge transfer amount (−0.013 e, 0 e and −0.12 e, respectively) when the SO\textsubscript{2} molecules are adsorbed in three different ways in Table 1. It is shown that SO\textsubscript{2} molecules are more likely to react and adsorb on the crystal plane approaching in the form of with two O atoms. The theoretical analysis shows that SO\textsubscript{2} gas obtain electrons when adsorbed onto the fluorine-doped TiO\textsubscript{2} nano sensors, and the macroscopic gas-sensing properties show an increase in impedance.

![Figure 5: TDOS and PDOS curves of SO\textsubscript{2} molecules adsorbed on F-doped TiO\textsubscript{2}](image)

**Figure 6.** TDOS and PDOS of H\textsubscript{2}S molecules adsorbed onto F-doped TiO\textsubscript{2}, and the green short dashed line is Fermi level. (a1,a2) are the TDOS and PDOS of H\textsubscript{2}S-S-TiO\textsubscript{2}, (b1,b2) are the TDOS and PDOS of H\textsubscript{2}S-H-TiO\textsubscript{2}, (c1,c2) are the TDOS and PDOS of H\textsubscript{2}S-2H-TiO\textsubscript{2}. 
Figure 6 shows TDOS and PDOS curves of H$_2$S molecules adsorbed onto F-doped TiO$_2$. When the H$_2$S gas molecules close to the F-doped TiO$_2$ crystal plane with single S atom, the gas molecules have little contribution to DOS at 0 eV in Figure 6(a1, a2). However, when H$_2$S molecules approach the F-doped TiO$_2$ crystal plane with single H atom and two H atoms at the same time separately, the molecules have a significant contribution to the DOS on the right side of 0 eV in Figure 6(b1–c2). This corresponds to the charge transfer amount (0.008 e, 0.267 e and 0.266 e, respectively) when the H$_2$S molecule close to the crystal plane with single S atom, single H atom and two H atoms at the same time in Table 1. It is shown that H$_2$S molecules are more likely to be adsorbed on the crystal plane approaching in the form of a single H atom and two H atoms at the same time. Similarly, SOF$_2$ gas molecules are more likely to adsorb by single O, single F atom, and two F atoms at the same time when coming close to the crystal plane than by single S atom. The TDOS and PDOS curves of SOF$_2$ adsorption systems are shown in Figure 7. The theoretical analysis shows that H$_2$S and SOF$_2$ gases lose electrons when adsorbed onto the fluorine-doped TiO$_2$ nano sensors, and the macroscopic gas-sensing properties show a decrease in impedance. Furthermore, the changed value of impedance of H$_2$S is bigger than SOF$_2$.

![Figure 6](image1.png)  
![Figure 6](image2.png)  
![Figure 6](image3.png)  

![Figure 7](image4.png)  

Figure 7. Cont.
The theoretical analysis indicates that the charge transfer is very small when $SO_2$ molecules come close to the F-doped TiO$_2$ crystal plane. The theoretical analysis indicates that the changed value of impedance of $SO_2$ is small on the macro level when adsorbed onto the fluorine-doped TiO$_2$ sensor. It can be assumed that the selectivity of fluorine-doped TiO$_2$ nanotubes gas sensor to $SO_2$ is weak.

No matter which way the $SO_2$ gas molecules approaching the crystal surface, the contribution to the DOS is almost 0 on both sides of 0eV, as shown in Figure 8. It can also be seen from Table 1 that the charge transfer is very small when $SO_2$ molecules come close to the F-doped TiO$_2$ crystal plane. The theoretical analysis indicates that the changed value of impedance of $SO_2$ is small on the macro level when adsorbed onto the fluorine-doped TiO$_2$ nano sensors. It can be assumed that the selectivity of fluorine-doped TiO$_2$ nanotubes gas sensor to $SO_2$ gas is weak.
To make the comparison results more meaningful, adsorption parameters of adsorption structure in Figure 4c,h,m were chosen to be compared. It can be seen that SO$_2$ is more likely to adsorb on nitrogen-doped TiO$_2$ crystal plane with O and S atoms. The adsorption of SO$_2$, SOF$_2$, and SO$_2$F$_2$ on the intrinsic anatase TiO$_2$ (101) perfect crystal plane is similar to that of Figure 4c,h,m. Therefore, in order to make the comparison results more meaningful, adsorption parameters of adsorption structure in Figure 4c,h,m were chosen to be compared.

After fluorine doping on the anatase TiO$_2$ (101) perfect crystal plane, the adsorption energy and charge transfer amount of the SO$_2$, SOF$_2$ and SO$_2$F$_2$ gas molecules adsorption system obviously increased, and the adsorption distance also decreased correspondingly. In addition, the adsorption energy of SO$_2$ gas molecules adsorbed on F-doped TiO$_2$ crystal plane is $-0.617$ eV, which indicates that the adsorption of SO$_2$ gas molecules onto the F-doped TiO$_2$ crystal plane was chemical adsorption.

The DOS were also compared and analyzed. In this paper, the corresponding TDOS and PDOS of the adsorption structures of three gas molecules are shown in Figure 5(c1,c2), Figure 7(b1,b2) and Figure 8(c1,c2). It was found that the contribution of SO$_2$ and SOF$_2$ molecules to the PDOS near 0eV significantly increased after fluorine doping, which corresponded to the charge transfer of the adsorption systems in the two cases. Because the crystal shows weak adsorption reaction to SO$_2$F$_2$ gas molecules before and after doping, the contribution of SO$_2$F$_2$ gas molecules to PDOS did not changed much at 0 eV. Through the above analysis, it can be concluded that the adsorption ability of the anatase TiO$_2$ (101) crystal plane to the three gas molecules is enhanced after fluorine doping.

Reference [31] reported modified TiO$_2$ crystal plane by nitrogen doping to detect SF$_6$ decomposition components. It can be seen that SO$_2$ molecules are more likely to adsorb on nitrogen-doped TiO$_2$ crystal plane with S atom. SOF$_2$ is more likely to adsorb on nitrogen-doped TiO$_2$...
crystal plane with O and S atoms, respectively. The adsorption of SO2 and SOF2 on nitrogen-doped TiO2 crystal plane is stronger than that on fluorine-doped TiO2 crystal plane. However, when nitrogen-doped TiO2 crystal plane reacts with SO2 and SOF2, the adsorption energy, charge transfer amount and adsorption distance have little difference, and the macro-gas-sensing characteristics all show the decrease of impedance. Therefore, nitrogen-doped TiO2 cannot effectively distinguish SO2 and SOF2. When fluorine-doped TiO2 crystal plane react with SO2, SO2 molecule obtains electrons, and fluorine-doped TiO2 gas sensor macro-gas-sensing characteristics show the increase of impedance. When fluorine-doped TiO2 crystal plane adsorb SO2, SOF2 molecule loses electrons, and fluorine-doped TiO2 gas sensor macro-gas-sensing characteristics show the decrease of impedance. Although the adsorption of SO2 and SOF2 on fluorine-doped TiO2 crystal plane is weaker than that of nitrogen-doped TiO2 crystal plane, fluorine-doped TiO2 can effectively distinguish SO2 and SOF2.

4. Conclusions

In this paper, one O atom of the anatase TiO2 (101) perfect crystal plane is replaced by one F atom to obtain a fluorine-doped anatase TiO2 (101) perfect crystal plane model. H2S, SO2, SOF2 and SO2F2 of SF6 decomposition components adsorb on the F-doped TiO2 crystal plane in different ways to obtain different adsorption systems, which were then optimized. The adsorption mechanism is obtained by the optimized adsorption parameters. The adsorption results were compared and analyzed with intrinsic and nitrogen doping, with the effects of different doping on adsorption parameters studied. Through the above analysis, the following conclusions are drawn:

(1) Four kinds of gas molecules are close to the crystal plane, which cause gas molecules to be adsorbed on the crystal plane more easily. The adsorption ability of four kinds of gas molecules onto F-doped TiO2 crystal plane is: H2S > SO2 > SOF2 > SO2F2.

(2) The adsorption capacity of TiO2 to SO2, SOF2 and SO2F2 is obviously enhanced after fluorine doping, and the degree of the adsorption to SO2 gas molecules has reached the chemical adsorption.

(3) Based on the change of resistance of fluorine-doped TiO2 sensors on the macro level can effectively distinguish SO2 and SOF2 from theoretical analysis, even though the adsorption of SF6 decomposition components onto nitrogen-doped TiO2 crystal plane is stronger than that on fluorine-doped TiO2 crystal plane.

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