Platinum-Doped Anatase (101) Surface as Promising Gas-Sensor Materials for HF, CS₂, and COF₂: A Density Functional Theory Study
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ABSTRACT: In order to find promising sensor materials for HF, CS₂, and COF₂ detection to realize the online internal insulation defect diagnosis of a SF₆ gas electrical device, the gas sensing property, binding energy, adsorption distance, charge transfer, and density of states distribution, of Pt-doped anatase TiO₂ (101) surfaces on HF, CS₂, and COF₂ gas molecules was calculated and analyzed in this paper based on the density functional theory. The work suggested that the Pt−TiO₂ surface has a nice gas sensing upon CS₂ and COF₂ because of the increase of the conductivity of the Pt−TiO₂ surface and the suitable adsorption parameter after CS₂ and COF₂ adsorbing on it. However, this material is not suitable as a gas sensor for HF gas. All of the works provide theoretical adsorption information of Pt−TiO₂ as a gas sensor material for HF, CS₂, and COF₂ detection.

1. INTRODUCTION
SF₆ gas has been widely used as insulation media in the electrical industry with excellent insulation and arc extinction properties. However, it could decompose and react with trace moisture, O₂, and epoxy resin material in the SF₆ gas electrical device to generate CO₂, CF₄, SOF₂, SO₂F₂, CS₂, HF, COF₂, etc. under partial discharge. To guarantee the safe operation of the gas electrical device, the analysis of chemical gas sensors is performed for on-line detection of SF₆ characteristic decomposition gases to diagnose the insulation-mode SF₆ gas electrical device by SF₆ decomposition product analysis.

Considering the remarkably high catalytic property, the exploration of noble metal-doped anatase titania (101) for the detection of some SF₆ decomposition components of online internal insulation defect diagnosis of a gas electrical device via decomposition products analysis has been studied, and Pt-doped TiO₂ has a nice gas-sensitivity performance on SOF₂, SO₂F₂, SO₂, NO, CO, and N₂O₄. However, there are a few of studies about the gas-sensing property of some key SF₆ characteristic decomposition components on noble metal-doped TiO₂ nanotube materials, that is, HF, CS₂, and COF₂, which could better indicate the internal insulation defects of the gas electrical device. The contents of CS₂ could be 12 μL/L and those of COF₂ could be 80 μL/L during the operation of the gas electrical device. In this paper, in order to study the gas-sensing characteristics of Pt-doped anatase TiO₂ (Pt-TiO₂) for HF, CS₂, and COF₂, we calculated and analyzed the adsorption property, including binding energy, charge transfer, and density of states.

2. COMPUTATIONAL METHODS
All the simulations were implemented by the Dmol3 package based on the density functional theory (DFT). Perdew−Burke−Ernzerhof (PBE) function with general gradient approximate (GGA) was used to deal with the electron exchange and correlations. Double numerical plus polarization (DNP) was utilized as the atomic orbital basis set. The Tkatchenko and Scheffler (TS) DFT-D was used to deal with the dispersion forces. For the convergence criteria, the energy tolerance accuracy was selected at 1.0 × 10⁻⁵ Ha. The maximum force was chosen at 0.002 Ha/Å. Also, the maximum atom displacement was chosen at 5 × 10⁻³ Å. The smearing is 0.005 Ha. The self-consistent field (SCF) tolerance of 1.0 × 10⁻⁶ Ha and global orbital cut-off radius of 5.0 Å were utilized to guarantee the accurate calculation of total energy.

In addition, the k-point sample of the Monkhorst−Pack grid was sampled to 2 × 2 × 1 at the Brillouin zone for geometric optimization. The binding energy \( E_d \) for the adsorption system after gas molecules adsorbing on Pt-TiO₂ is shown in eq 1.

\[
E_d = E_{gas + sur} - E_{gas} - E_{sur}
\]
In the formula, $E_{\text{sur}}$ is the energy of the isolated Pt−TiO$_2$ surface. $E_{\text{gas}}$ is the energy of gas molecule before adsorption. Also, $E_{\text{gas}+\text{sur}}$ is the energy of the adsorption system after gas molecules adsorbed on the Pt−TiO$_2$ surface.

3. RESULTS AND DISCUSSION

The doping position of the Pt atom is based on the previous study,$^{19}$ namely, one platinum atom form two Pt-O bonds with the oxygen atom of the outer surface of Pt−TiO$_2$. The geometric structures of Pt−TiO$_2$ are shown in Figure 1. The supersize of the Pt−TiO$_2$ surface is 10.88 × 11.33 × 19.35 Å with a 12 Å vacuum layer. The concentration of the Pt dopant is 1/120. In addition, comparing with the Ti$_{5c}$ site and O$_{2c}$ site, the Pt site of Pt−TiO$_2$ are more favorable for the adsorption of gas molecules.

3.1. Adsorption Property of HF on Pt−TiO$_2$

For HF gas molecules, there are two adsorption modes; that is, the H atom and F atom approached the Pt site of the Pt−TiO$_2$ surface, as shown in Figure 2. For the F atom adsorption mode, the binding energy and adsorption distance are $-0.241$ eV and 2.754 Å, respectively, with the electrons of 0.006 e transferring from the HF molecule to the Pt−TiO$_2$ surface. However, the Pt−TiO$_2$ donates 0.004 e electrons to HF in the H adsorption mode with a binding energy of $-0.170$ eV and an adsorption distance of 2.256 Å.

3.2. Adsorption Property of CS$_2$ on Pt−TiO$_2$

Figure 4 shows that the CS$_2$ adsorbs on the Pt−TiO$_2$ surface, where two adsorption modes are considered. As for the C adsorption mode, CS$_2$ donated 0.005 e electrons to the Pt−TiO$_2$ surface in the adsorption process with a binding energy of $-1.594$ eV and an adsorption distance of 2.120 Å. At the same time, the bond angle $S$−$C$−$S$ of the CS$_2$ molecule changes from 180 to 150.508°. As for the S adsorption mode, the calculation adsorption distance is 2.463 Å and the binding energy is $-1.596$ eV. There are 0.003 e electrons transferred from the CS$_2$ gas molecule to the Pt−TiO$_2$ surface by the Mulliken population analysis.

The DOS configurations of CS$_2$ adsorbed on Pt-TiO$_2$ (101) surface are shown in Figure 5. Both the TDOS of C and S adsorption modes shifted 1−2 eV to the right as a whole markedly after adsorption. In addition, there are three novel peaks appearing in the TDOS configurations of both adsorption modes around $-15$, $-13$, and $-7$ eV. The pseudogaps of 1.068 eV in S adsorption mode and 1.063 eV in the C adsorption mode are quite larger than those of the isolated Pt−TiO$_2$ surface with 0.557 eV. It could be hypothesized that the covalence of the material would increase after CS$_2$ gas molecules adsorb on the material surface, and the material probably has a fairly nice gas sensitivity to CS$_2$.

3.3. Adsorption Property of COF$_2$ on Pt−TiO$_2$

Figure 6 shows the optimized adsorption structure of COF$_2$ on the Pt−TiO$_2$ surface. In the O adsorption mode, the binding energy is $-0.308$ eV, the adsorption distance is $-2.611$ Å, and the COF$_2$...
gas molecule transferred 0.002 e electrons to Pt−TiO₂. As for the F adsorption mode, the binding energy and adsorption distance are −0.866 eV and −5.360 Å, respectively, with the COF₂ gas molecule donating electrons of 0.002 e. In addition,
for the C adsorption mode, the binding energy and adsorption distance are $-0.506$ eV and $-2.164$ Å, respectively. The charge transfer is the same as that in the F atom oriented system.

The DOS distributions of the COF$_2$ molecule absorbed on the Pt-doped TiO$_2$ (101) surface under three kinds of adsorption modes is shown in Figure 7. One can observe that the TDOS distributions of O and F adsorption modes resemble the TDOS of the isolated Pt–TiO$_2$ surface, except that three novel peaks appeared near $-12.5$, $-11$, and $-9$ eV. Comparing with PDOS distributions, the 2p orbital of the F atom is the main
contributor of three novel peaks. However, the TDOS distribution of C adsorption mode is shifted to right in contrast to that of isolated Pt–TiO₂. In addition, the overlapping areas between the 2p orbital of the C atom and the 5d orbital of Pt in the C adsorption mode is significantly larger than those in the O and F adsorption modes. Both pseudogaps of the O adsorption mode with 0.546 eV and F adsorption mode with 0.635 eV are a little different from that of the isolated Pt–TiO₂ surface with 0.557 eV. However, the pseudogap of the C adsorption mode with 1.021 eV is quite larger than that of the isolated Pt–TiO₂ surface. Consequently, COF₂ gas molecules are most easily adsorbed by the Pt–TiO₂ surface by the C adsorption mode in three kinds of adsorption modes. Moreover, it could be hypothesized that the covalency of Pt–TiO₂ may increase with the adsorption of the COF₂ gas molecule.

In a word, due to the increased conductivity, the Pt-doped TiO₂ surface could be used as the gas sensor material to detect COF₂ and CS₂. However, considering the results of calculation, this material should not be applicable to detect HF gas accurately.

4. CONCLUSIONS

In this paper, several parameters of HF, CS₂, and COF₂ adsorbing on a Pt-doped anatase TiO₂ (101) surface were simulated to evaluate the feasibility of this material for the detection of HF, CS₂, and COF₂ based on DFT. Considering the adsorption mode and DOS distributions, it could be concluded that the Pt–TiO₂ surface has a nice gas-sensitivity performance on CS₂ and COF₂. However, this material is not suitable to be used as a gas sensor for HF.

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Notes
The authors declare no competing financial interest.

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