Ni-CNT Chemical Sensor for SF₆ Decomposition Components Detection: A Combined Experimental and Theoretical Study

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Abstract: SF₆ decomposition components detection is a key technology to evaluate and diagnose the insulation status of SF₆-insulated equipment online, especially when insulation defects-induced discharge occurs in equipment. In order to detect the type and concentration of SF₆ decomposition components, a Ni-modified carbon nanotube (Ni-CNT) gas sensor has been prepared to analyze its gas sensitivity and selectivity to SF₆ decomposition components based on an experimental and density functional theory (DFT) theoretical study. Experimental results show that a Ni-CNT gas sensor presents an outstanding gas sensing property according to the significant change of conductivity during the gas molecule adsorption. The conductivity increases in the following order: H₂S > SOF₂ > SO₂ > SO₂F₂. The limit of detection of the Ni-CNT gas sensor reaches 1 ppm. In addition, the excellent recovery property of the Ni-CNT gas sensor makes it easy to be widely used. A DFT theoretical study was applied to analyze the influence mechanism of Ni modification on SF₆ decomposition components detection. In summary, the Ni-CNT gas sensor prepared in this study can be an effective way to evaluate and diagnose the insulation status of SF₆-insulated equipment online.

Keywords: SF₆ decomposition components; carbon nanotube sensor; Ni modification; adsorption; DFT calculations

1. Introduction

Due to the strong insulation strength and electronegativity of SF₆ gas, it has been widely used as filling gas in insulated equipment, such as SF₆-insulated high-voltage switchgear (GIS), SF₆-insulated transmission lines (GIL), and SF₆-insulated circuit breakers (GCB) [1–3]. However, insulation defects inevitably occur in SF₆-insulated equipment, which induces SF₆ to decompose into various decomposition components: SO₂, H₂S, SO₂F₂, and SO₂F₂ under electric discharge [4–7]. In addition, the existence of insulation defects and SF₆ decomposition dramatically reduce the insulation strength of SF₆-insulated equipment [8]. A lot of methods have been studied to detect the insulation defects, including the ultra-high frequency method (UHF) [9,10], the transient earth voltage method (TEV) [11], the ultrasonic method [12], the gas chromatographic method [13], and the gas sensor detection method [14]. However, UHF, TEV, and the ultrasonic method are easily affected by interference signals, and the gas chromatographic method is an offline detection method. Because of the non-contact, high accuracy, and low detection limit features of gas sensors, the gas sensor detection
method has been an effective way to realize the online detection of SF$_6$-insulated equipment based on SF$_6$ decomposition components detection [15,16].

One dimensional carbon nanotube (CNT) material has attracted extensive study due to its outstanding characteristics [17,18], such as large specific surface area and good electrical properties. It is demonstrated that CNTs shows excellent gas sensing performance to gases [19,20], making it an effective detection method used in environmental, industrial, and military fields [21,22]. Li et al. fabricated single-wall carbon nanotube (SWNT) based gas sensors on interdigitated gold electrodes; its detection limit reaches 44 ppb for NO$_2$ and 262 ppb for nitrotoluene at room temperature [19]. Chopra et al. reported that multi-wall carbon nanotube (MWCNT) and polymer composites exhibited excellent sensitivity and selectivity to NH$_3$ and NO$_2$ at room temperature [23]. Surface modification based on metal particles can greatly improve the gas sensitivity and selectivity of CNTs. Penza et al. verified that the functionalization of Pt and Pd nanoclusters on the MWCNT surface significantly improved its detection limit to sub-ppm level upon NO$_2$, H$_2$S, NH$_3$, and CO detection [24]. Although the development of CNT gas sensors has made a remarkable improvement in common gas detection, there are few reports about its application in the field of SF$_6$ decomposition components detection.

Here, Nickel functionalized CNTs (Ni-CNTs) are adopted as the gas sensing material to detect the characteristic SF$_6$ decomposition components: SO$_2$, H$_2$S, SOF$_2$ and SO$_2$F$_2$. Experimentally, the Ni-CNT gas sensor is prepared by the drop-casting method, which significantly reduces the preparation cost and benefits for industrial-scale production. In addition, the gas sensing mechanism of Ni-CNTs to the characteristic SF$_6$ decomposition components is studied by density functional theory (DFT) calculation. We conclude that the Ni-CNT gas sensor can be an effective way to detect the insulation defects and diagnose the running status of SF$_6$-insulated equipment online.

2. Material and Methods

2.1. Synthesis of Ni-CNT Gas Sensor

Ni-CNTs (inner diameter: 5–10 nm, external diameter: 10–20 nm, and length: 10–30 μm) were bought from Aladdin Reagent Corporation (Shanghai, China). Figure 1a shows the interdigitated Cu electrodes; Cu electrodes (thickness: 30 μm, gap: 0.2 mm) were fabricated on epoxy resin as a substrate of the Ni-CNT gas sensor. Ni-CNTs were dispersed in dimethylformamide (DMF) to form a solution of 0.025 mg/mL by the following steps: soak 6 h, then ultrasonic treat 2 h. The solution was sprayed onto the surface of the Cu electrodes at 80 °C to accelerate the evaporation of DMF. As shown in Figure 1b, Ni-CNTs evenly distribute on the surface of the Cu electrodes, which benefits the gas molecule adsorption and desorption process.

![Figure 1. (a) Interdigitated Cu electrodes, (b) the prepared Ni-modified carbon nanotube (Ni-CNT) gas sensor.](image)

2.2. Material Characterization and Gas Sensing Measurement

Transmission electron microscopy (TEM) was tested by FEI Tecnai G2 F20 S-TWIN at 200 kV. The gas-sensing detection system was composed of standard gases (SO$_2$, H$_2$S, SOF$_2$, and SO$_2$F$_2$), the gas distribution system, the gas sensing chamber, and an electrochemical workstation. The concentration
of standard gases was 400 ppm with N\textsubscript{2} as the background gas. The standard gases were diluted to different concentrations: 1, 10, 50, 100, 200, 300, and 400 ppm by the gas distribution system. Then, the diluted gases were led to the closed gas chamber. The resistance of the Ni-CNT gas sensor was measured by the electrochemical workstation at room temperature and ambient pressure. The gas response (GR) was defined by Equation (1). In which, \( R_i \) is the initial electric resistance of the Ni-CNT gas sensor in dry synthesis air and \( R_f \) is the resistance of the sensor in SF\textsubscript{6} decomposition components’ atmosphere. In addition, the sensitivity (S) of the Ni-CNT gas sensor was defined by Equation (2), where \( C_T \) was the concentration of tested gas.

\[
GR = \frac{R_f - R_i}{R_i} \times 100\% \quad (1)
\]

\[
S = \frac{G \times R}{C_T} \times 100\% \quad (2)
\]

2.3. DFT Calculation

The DFT calculations were performed using Dmol\textsuperscript{3} package of materials studio. The structure of (8, 0) Ni-CNTs was built by substituting a carbon atom by one Ni atom. In addition, a 20 \( \times \) 20 \( \times \) 8.5 Å periodic-boundary supercell was built to avoid the interference of adjacent cells. Then, the optimized adsorption structures of SO\textsubscript{2}, H\textsubscript{2}S, SOF\textsubscript{2}, and SO\textsubscript{2}F\textsubscript{2} on the surface of Ni-CNTs were calculated with different initial gas positions. The Perdew–Burke–Ernzerhof (PBE) function generalized gradient approximation was adopted to treat the exchange-correlation potential. The convergence criterion for energy and force was set at \( 10^{-5} \) Ha and \( 2 \times 10^{-3} \) Ha/Å, respectively. The Brillouin zone was sampled with \( 1 \times 1 \times 2 \) Monkhorst–Pack mesh. The adsorption energy (\( E_{ads} \)) of the molecules adsorbed on Ni-CNTs was defined by the following Equation (3):

\[
E_{ads} = E_{gas/surf} - E_{gas} - E_{surf} \quad (3)
\]

where \( E_{gas/surf} \) was the energy of gas adsorbed CNTs, \( E_{surf} \) and \( E_{gas} \) were the energy of isolated Ni-CNTs and molecules of SF\textsubscript{6} decomposition components.

The electron density distribution was obtained by Mulliken population analysis. The charge transfer (\( Q_t \)) in the adsorption process was defined by Equation (4), where \( Q_{iso} \) and \( Q_{ads} \) were the respective total charge of gas molecules before and after adsorption.

\[
Q_t = Q_{ads} - Q_{iso} \quad (4)
\]

3. Results and Discussion

3.1. Preparation and Gas Sensing Property of Ni-CNT Gas Sensor

As per the formation mechanism of Ni-CNTs shown in Figure 2a, it is important to make sure that Ni particles evenly decorate onto the outside wall of intrinsic CNTs, which plays a key role to the gas-sensing properties of the prepared Ni-CNT gas sensor. As per the typical TEM images shown in Figure 2b–d with different magnifications, Ni-CNTs evenly disperse on the surface of the prepared gas sensor. Hence, there will be large, hollow structures for gas diffusion among the Ni-CNTs, which not only increase the adsorption capacity, but reduce the adsorption and desorption time. Ni nanoparticles mainly distribute on the outside wall of CNTs due to the long length and closed structure of CNTs (about 30 \( \mu \)m). The small diameter of Ni-CNTs (about 20 nm) signifies large curvature and high surface activity. Besides, the surface defects that existed on the surface of CNTs provide the adsorption sites for gas molecules. As a result, Ni nanoparticles evenly decorate on the surface of CNTs with their size distinctly smaller than the diameter of CNTs. Ni nanoparticles act as the active sites for gas molecule adsorption, which effectively enhances the gas-sensing properties of CNT-based sensors.
Figure 2. (a) The formation mechanism of Ni-CNTs, (b–d) structure characterization of Ni-CNTs.

Considering the concentration range of SF₆ decomposition components generated in SF₆-insulated equipment reported in previous studies [4,25], a series of SF₆ decomposition components concentrations, 1, 10, 50, 100, 200, 300, and 400 ppm, were prepared to analyze the gas-sensing performance of the Ni-CNT gas sensor. As shown in Figure 3, the resistance of the gas sensor significantly reduces when it contacts SF₆ decomposition components [26–29]. The Ni-CNT gas sensor presents a large gas response to SF₆ decomposition components at room temperature and ambient pressure due to the catalytic property of evenly distributed Ni nanoparticles. Furthermore, the CNT sensor presents a fast gas response because of the large gas diffusion channel among Ni-CNTs, which also implies a fast gas-sensing recovery speed. The resistance rapidly reduces when the sensor just contacts the SF₆ decomposition components, because the gas molecules quickly interact with the gas-sensing material on the surface of the Ni-CNT gas sensor. Meanwhile, the reduction speed gradually decreased as the gas diffusion rate sharply reduced with diffusion depth in the sensor film.

Figure 3. Gas response of the Ni-CNT gas sensor to different concentrations of SF₆ decomposition components: (a) H₂S, (b) SOF₂, (c) SO₂, and (d) SO₂F₂ at room temperature and ambient temperature.

As shown in Figure 3, it takes about 10 min for the gas response to reach a steady state. The variation of gas response is greatly influenced by the concentration of SF₆ decomposition
components. For instance, the difference of gas response as the gas concentration increases from 300 to 400 ppm is smaller than that of 200 to 300 ppm. Comparing the value of gas responses shown in Figure 3a–d under the same gas concentration, the variation of gas responses is placed in the following order: H$_2$S > SOF$_2$ > SO$_2$ > SO$_2$F$_2$. The largest value of gas response to H$_2$S is $-30.54\%$ at the concentration of 400 ppm, and the value of the gas response still reached $-9.50\%$ at the lowest concentration (1 ppm) as shown in Figure 3a. The high gas response mainly comes from the strong interaction between Ni-CNTs and H$_2$S molecules at the Ni atom functionalized sites, which contributes to the detection of the H$_2$S component up to sub-ppm level. According to Figure 3b, the gas response of the Ni-CNT gas sensor to SOF$_2$ changes a little under different gas concentrations. The gas responses at 400 ppm and 1 ppm are $-8.04\%$ and $-5.91\%$, respectively. On the contrary, different concentrations of SO$_2$ leads to a significant change of gas response, as shown in Figure 3c. The value of gas response increases from $-1.62\%$ (1 ppm) to $-6.37\%$ (400 ppm). Although Ni atom functionalization on the Ni-CNT surface enhances its adsorption to SO$_2$F$_2$, the Ni-CNT gas sensor was still not sensitive to SO$_2$F$_2$. As shown in Figure 3d, the gas responses to SO$_2$F$_2$ are $-2.65\%$ and $-0.7\%$ at 400 ppm and 1 ppm, respectively. In summary, the Ni-CNT gas sensor shows a high gas response to SF$_6$ decomposition components, and its high gas-sensing selectivity can be used to identify the gas types of SF$_6$ decomposition components produced in SF$_6$-insulated equipment, making it suitable to detect the insulation defects and diagnose the running status of SF$_6$ insulated equipment online.

Table 1 shows the comparison of the limit of detection (LOD) for different sensors to SF$_6$ decomposition components reported in recent studies, including the most studied gas-sensing material: CNTs, graphene, and TiO$_2$ nanotubes. In this study, the highest gas response of the Ni-CNT sensor studied in this work reaches $-9.5\%$ upon 1 ppm H$_2$S measurement, which was slightly higher than that of reported CNT-based gas sensors. Meanwhile, a TiO$_2$-based gas sensor usually needs a high working temperature to receive a high gas response to SF$_6$ decomposition components. It was reported that the LOD of Au-Graphene was only 50 ppm with a gas response of 18.75% to H$_2$S [28]. Therefore, the Ni-CNT sensor obviously presents advantages in high gas response and low working temperature.

Table 1. The limit of detection (LOD) of different gas sensors to SF$_6$ decomposition components. RT represents room temperature. CNTs: carbon nanotubes.

| Sensor          | LOD (ppm) | T (°C) | Gas   | Reference       |
|-----------------|-----------|--------|-------|-----------------|
| Ni-CNTs         | 1         | RT     | H$_2$S| This work       |
| Sieve/CNTs      | 10        | RT     | H$_2$S| Zhang et al. [30]|
| Pd-CNTs         | 50        | RT     | H$_2$S| Star et al. [31]|
| Pt-TiO$_2$NTs   | 25        | 160    | SO$_2$| Jing et al. [32]|
| Au-Graphene     | 50        | RT     | H$_2$S| Yu et al. [28]  |

To demonstrate the reusability of the prepared Ni-CNT gas sensor, we have done multiple measurements to obtain its response and recovery properties to different types of SF$_6$ decomposition components at the same concentration (400 ppm). As shown in Figure 4, the flow rate of SF$_6$ decomposition components is 100 sccm during the gas-sensing process, and the N$_2$ flow is used in the recovery process with a flow rate of 200 sccm. In addition, the illumination of UV light is applied to enhance the recovery process as it greatly increases the molecular vibration of SF$_6$ decomposition components. Gas-in and N$_2$ + UV represent the flow of SF$_6$ decomposition components (SO$_2$, H$_2$S, SOF$_2$, and SO$_2$F$_2$) and the flow of pure N$_2$ flow with UV illumination, respectively. Simultaneously, N$_2$ flow transfers the desorbed gas from the surface of Ni-CNTs and avoids re-adsorption. The Ni-CNT gas sensor still keeps a good gas response to SO$_2$, H$_2$S, SOF$_2$, and SO$_2$F$_2$ after multiple gas adsorption and desorption detections, as the gas response changes little with measurement times. The value of gas response reduces from initially $-30.54\%$ to $-28.13\%$ upon H$_2$S detection. In addition, the change of gas response to SOF$_2$, SO$_2$, and SO$_2$F$_2$ was 0.55% (from $-8.04\%$ to $-7.49\%$), 0.69% (from $-6.37\%$ to...
5.68%), and 0.31% (from −2.65% to −2.34%) after three lots of measurements, which is much less than the change of gas response to H$_2$S.

![Figure 4](image)

**Figure 4.** The gas response and recovery properties of the Ni-CNT gas sensor to SF$_6$ decomposition components.

Figure 5a shows the change of gas response with the increase of concentration of SF$_6$ decomposition components. Upon H$_2$S and SOF$_2$ detection, the gas response sharply enhances when gas concentration increases from 1 to 50 ppm, and then tends to linearly increase under high gas concentration of detected gases, from 50 to 400 ppm. This also demonstrates that the Ni-CNT sensor is sensitive to H$_2$S and SOF$_2$. Upon SO$_2$ and SO$_2$F$_2$ detection, the increase of the gas response shows an exponential growth trend. Figure 5b shows the change of sensitivity to SF$_6$ decomposition components; the sensitivity presents an exponential attenuation from 1 to 400 ppm, because it tends to be saturated at a high gas concentration. The attenuation speed is listed in the following order: H$_2$S > SOF$_2$ > SO$_2$ > SO$_2$F$_2$ at the same gas concentration.

![Figure 5](image)

**Figure 5.** (a) The change of gas response, and (b) the change of sensitivity with the increase of concentration of SF$_6$ decomposition components.

### 3.2. DFT Study of the Ni-CNT Gas Sensor

DFT study is used to analyze the adsorption properties of Ni-CNTs to SF$_6$ decomposition components: SO$_2$, H$_2$S, SOF$_2$, and SO$_2$F$_2$. As Ni nanoparticles modified on the CNT surface always exist as clusters, single and double Ni atom-doped CNT structures are built to reflect the influence of Ni nanoparticles, represented by 1Ni-CNTs and 2Ni-CNTs. Figure 6 and Table 2 show the most stable adsorption structures and corresponding data for one gas molecule adsorption on Ni-CNTs. It is found that all the gas molecules tend to adsorb around Ni atoms due to its high adsorption activity. SO$_2$, H$_2$S, and SOF$_2$ interact with Ni-CNTs with physisorption. Due to the polyvalent properties of the...
sulfur atom, the chemisorption between SO₂F₂ and the Ni-CNT surface leads to the structure break of SO₂F₂ in the adsorption process, reducing the reusability of the CNT gas sensor as it impedes the gas molecule desorption. The H₂S molecule interacts with Ni-CNTs by sulfur atoms. The nearest adsorption distance for H₂S reduces from 2.33 Å to 2.15 Å when the doped Ni atoms increase from single to double. SO₂ and SOF₂ molecules interact with Ni-CNTs by oxygen atoms rather than sulfur atoms because the sulfur atom has already built a strong covalent bond with two oxygen atoms or two fluorine atoms. The nearest adsorption distance for SO₂ and SOF₂ on 2Ni-CNTs are 1.88 Å and 1.94 Å, respectively. The nearest distance from the SO₂F₂ adsorption on 2Ni-CNTs is 1.86 Å on 2Ni-CNTs. Except for H₂S adsorption, electrons transfer from Ni-CNTs to gas molecules in the adsorption process as Ni atoms act as the electron donor. The large adsorption energy for all of the gas molecules shows that Ni-doped CNTs are an effective gas-sensing material to detect the SF₆ decomposition components.

![Figure 6. Optimized geometries of SF₆ decomposition components adsorbed Ni-doped CNTs, distances in Å.](image)

**Table 2.** Interaction distance (d), adsorption energy $E_{ads}$, charge transfer $Q_t$ of SF₆ decomposition components adsorbed Ni-doped CNTs.

| System                   | d (Å) | $Q_t$ (e) | $E_{ads}$ (eV) |
|--------------------------|-------|-----------|----------------|
| 1Ni-CNTs/H₂S            | 2.33  | 0.25      | -0.81          |
| 1Ni-CNTs/SO₂            | 2.00  | -0.35     | -1.13          |
| 1Ni-CNTs/SOF₂           | 2.06  | -0.06     | -0.49          |
| 1Ni-CNTs/SOF₂₂          | 2.07  | -0.94     | -1.93          |
| 2Ni-CNTs/H₂S            | 2.15  | 0.19      | -3.05          |
| 2Ni-CNTs/SO₂            | 1.88  | -0.30     | -2.26          |
| 2Ni-CNTs/SOF₂           | 1.94  | -0.26     | -2.83          |
| 2Ni-CNTs/SOF₂₂          | 1.86  | -0.98     | 0.97           |

Generally, gas sensors detect the concentration of contacted gas by measuring the change of conductivity during the adsorption process. Density of states (DOS) is one of the effective ways to analyze the change of conductivity upon SO₂, H₂S, SOF₂, and SO₂F₂ adsorption. As shown in Figure 7, the DOS around Fermi level for H₂S, H₂S, and SOF₂ adsorptions obviously increase in different...
degrees, which leads to the corresponding change of conductivity. The change of conductivity has just verified that the Ni-CNT sensor shows a high gas response to H$_2$S, H$_2$S, and SOF$_2$. Meanwhile, the inconspicuous change of DOS upon SO$_2$F$_2$ adsorption slightly increases the conductivity of the adsorption system, which is consistent with the experimental study.

Figure 7. Density of states (DOS) of Ni-CNTs, 2Ni-CNTs, and gas adsorbed Ni-CNTs: (a1–d1) represent gas adsorption on Ni-CNTs, (a2–d2) represent gas adsorption on 2Ni-CNTs.
In DOS analysis, the change of conductivity upon H₂S adsorption is less than SO₂, SOF₂, and SO₂F₂ adsorption, based on the calculation condition that the default temperature is 0 K. However, the detection temperature has increased to ambient temperature, which distinctly enhances the reaction activity of the S atom. In addition, S in H₂S is much more active than that in SO₂, SOF₂, and SO₂F₂ because it only builds two monovalences with H atoms. As a result, the change of conductivity for a single H₂S molecule is the largest among four gas molecule adsorptions in the experiment.

4. Conclusions

This study introduces Ni modification on the CNT surface for the sensitive and selective detection of SF₆ decomposition components: SO₂, H₂S, SOF₂, and SO₂F₂. The TEM results show that Ni particles evenly distribute on the surface of CNTs. The prepared Ni-CNT gas sensor shows high gas sensitivity as its LOD reaches 1 ppm to SF₆ decomposition components. The sensitivity of the Ni-CNT gas sensor is placed in the following order: H₂S > SOF₂ > SO₂ > SO₂F₂. In addition, the Ni-CNT gas sensor shows good gas-sensing recovery property, which makes it easy to be widely used. DFT theoretical study results verify that conductivity of the adsorption system significantly changes when SF₆ decomposition components interact with Ni-CNTs. Thus, our finding is certainly beneficial to broaden the perspective of Ni-CNT gas sensor applications in evaluating and diagnosing the insulation status of SF₆-insulated equipment online.

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