Research Article

Application of Flower-Like ZnO Nanorods Gas Sensor Detecting SF₆ Decomposition Products

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Gas insulated switchgear (GIS) is an important electric power equipment in a substation, and its running state has a significant relationship with stability, security, and reliability of the whole electric power system. Detecting and analyzing the decomposition byproducts of sulfur hexafluoride gas (SF₆) is an effective method for GIS state assessment and fault diagnosis. This paper proposes a novel gas sensor based on flower-like ZnO nanorods to detect typical SF₆ decompositions. Flower-like ZnO nanoparticles were synthesized via a simple hydrothermal method and characterized by X-ray powder diffraction and field-emission scanning electron microscopy, respectively. The gas sensor was fabricated with a planar-type structure and applied to detect SF₆ decomposition products. It shows excellent sensing properties to SO₂, SOF₂, and SO₂F₂ with rapid response and recovery time and long-term stability and repeatability. Moreover, the sensor shows a remarkable discrimination among SO₂, SOF₂, and SO₂F₂ with high linearity, which makes the prepared sensor a good candidate and a wide application prospect detecting SF₆ decomposition products in the future.

1. Introduction

Gas insulated switchgear (GIS) filled with pressurized sulfur hexafluoride gas (SF₆) is widely used in electric power system in recent decades with the advantages of small floor space, high stability and reliability, high-strength insulation, none smearable oil, lower maintenance cost, and so on [1–6]. Sulphur hexafluoride gas has excellent insulating performance and arc extinction function, and it can dramatically improve the insulation intensity when used as an insulating medium. So it is widely applied to GIS and other gas insulation equipments [1, 3]. However, there exist some unavoidable insulating defects in the process of GIS design, manufacture, installation, and operation [4].

As an inert gas, pure SF₆ is colorless, tasteless, nontoxic, and nonflammable, and its decomposition temperature is as high as 500°C [7]. Although SF₆ is of great chemical inertness and the reliability of GIS is very high, inevitable insulating faults based on arc discharge, spark discharge, or partial discharge may occur due to the internal insulating defects. Researches both at home and abroad demonstrate that such internal insulation faults would cause SF₆ gas to decompose, and generate several kinds of low-fluorine sulfides, such as SF₄, SF₃, and SF₂ [2, 4, 5, 8, 9]. If the SF₆ in GIS is pure, the decomposed low-fluorine sulfides will reduce to SF₆ fast with the decrease of operating temperature. Actually, it always contains a certain amount of impurities, such as air and water. Some low-fluorine sulfides are very active to react with trace moisture and oxygen and generate the compounds of SOF₄, SOF₂, SO₂F₂, SO₂, HF, and so on. As the GIS insulating defects vary, the decomposed gas mixtures will be different. And the composition contents and decomposition rates are also various. Therefore, detecting and analyzing the decomposed chemical byproducts accurately can efficiently identity and diagnose fault type occurred in GIS.

At present, many methods [10–13] are used to detect the SF₆ decomposition components in GIS, for instance, gas chromatography, gas detection tube, infrared absorption spectrometry, and semiconductor gas sensor. Gas chromatography [10] is mainly used for offline testing and it takes a quite long time. Gas detection tube [11] has no response to some decomposition components and its stability depends on environment condition. Infrared absorption spectrometry [12, 13] has cross-response on SF₆ and cannot quantitatively...
detect the decomposition components. In recent years, metal oxide semiconductor gas sensor based on ZnO [14], SnO₂ [15], TiO₂ [16], Fe₂O₃ [17], WO₃ [18], or In₂O₃ [19] has been widely used for detecting and online monitoring target gas, owing to advantages of simple fabrication process, rapid response and recovery time, low maintenance cost, long service life, long-term stability and repeatability, and so on. With the development of nanotechnology, various gas sensors have been fabricated with small particle size and high surface-to-volume ratio [20]. However, most of these gas sensors mainly focus on toxic gas [21, 22], organic gas [23, 24], carbon dioxide [25], hydrogen [26], and rare studies concerning the SF₆ decompositions. Meanwhile, the cross-sensitivity among the decomposition components is tough, so investigating sensing properties especially selectivity is the most crucial issue for online monitoring SF₆ decompositions.

In this work, we proposed a simple and effective hydrothermal synthesis route to prepare flower-like ZnO nanorods. X-ray powder diffraction (XRD) and field-emission scanning electron microscopy (FESEM) were used to characterize the microstructures and morphologies of the prepared samples. Then a gas sensor based on the flower-like ZnO nanorods was fabricated, and its gas sensing properties against SF₆ decompositions were investigated. Particularly, the study mainly focused on the sensing behaviors of the prepared sensor against SOF₂, SO₂F₂, and SO₂, and its cross-sensitivity was also demonstrated. The prepared sensor exhibited excellent gas response to different SF₆ decompositions at different working temperature with high linearity, rapid response-recovery, and long-time stability and repeatability.

2. Experimental

2.1. Preparation and Characterization of ZnO Nanorods. Flower-like zinc oxide nanorods samples were successfully synthesized through a hydrothermal method using ammonium hydroxide (NH₄OH, 28 wt% NH₃ in H₂O) as the base source and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) as the source of Zn²⁺ ions. All chemicals were of analytical reagent grade and purchased from Beijing Chemicals Co., Ltd. In a typical synthesis process, an adequate amount of Zn(NO₃)₂·6H₂O was dissolved in deionized water (DI water) with a large beaker, and NH₄OH was added slowly to the solution under intense magnetic stirring. The mixed solution was stirred for 30 min and then transferred into a sealed Teflon autoclave with 100 mL of inner volume and 80% of fill ratio. After 24 h reaction at 180 °C, the reactor was cooled to room temperature naturally. Subsequently, the prepared white products were centrifuged, washed two or three times with DI water and ethanol alternately, and dried at 80 °C in air for further use.

XRD analysis was conducted on a Rigaku D/max-2500 X-ray diffractometer with the 2θ range of 20–80 °C at room temperature, and Cu Kα as the source of X-ray at 40 kV, 40 mA, and λ = 1.5418 Å. FESEM images were performed on a JEOL JEM-6700F microscope operating at 3 and 5 kV, respectively.

2.2. Fabrication and Measurement of ZnO Sensor. ZnO nanorods gas sensor was fabricated based on a planar construction with a simple and convenient fabrication procedure. The scheme of the planar ZnO gas sensor structure was shown in Figure 1, where prepared planar ZnO nanorods gas sensor is constituted of planar ceramic substrate, Ag-Pd interdigitated electrodes, and sensing material. The length, width, and height of the planar ceramic substrate are suggested to be about 6, 3, and 0.5 mm, respectively. There are five pairs of Ag-Pd interdigitated electrodes on planar ceramic substrate with both width and distance about 0.15 mm. As-prepared samples were further ground into fine powder and mixed with diethanolamine and ethanol to form a paste with a weight ratio of 100:10:10. It was subsequently screen printed onto the planar ceramic substrate to form a sensing film and the thickness was about 10 um and then dried in air at 60 °C for 5 h. Finally, the sensor was further aged at an aging test chamber for 240 h.

Gas sensing properties of the prepared planar ZnO gas sensor to SF₆ decomposition byproducts were investigated using an intelligent gas detecting system. Targeted gases were...
mixed with N\textsubscript{2} by a dynamic gas distributing system which worked with high accuracy mass flow controllers and then injected into the gas sensing chamber. The concentration of detecting gas was controlled and detected by gas mass flow meter. The operating temperature of the gas sensor was controlled by varying current flow of the heater. And the surface temperature of the planar sensor was measured by a thermocouple in real time. When the testing sensor was preheated at 300°C for some time in air and the baseline of resistance was smooth and stable, we could start our gas sensing properties test.

Gas response was defined as the relative variation of the electrical resistance of the gas sensor: $S\% = (R - R_0)/R_0 \times 100\%$. $R$ is the resistance of flower-like ZnO nanorods gas sensor in target gas environment and $R_0$ being in pure air. The response time was defined as the time taken by the sensor to achieve 90% of the total resistance change in the case of gas in or the recovery time in the case of gas out. All experiments were repeated several times to ensure the reproducibility and stability of the sensor.

### 3. Results and Discussion

#### 3.1. Structure and Morphology

Figure 2 shows the XRD patterns of the as-prepared ZnO nanorods. All the diffraction peaks are consistent with the values in the standard card (JCPDS 36-1451) and can be indexed as typical wurtzite hexagonal ZnO crystal structure with lattice constants $a = 3.249$ Å and $c = 5.206$ Å. No other diffraction peaks from any impurities are detected.
sensing experiments are performed with an intelligent gas detecting system at different operating temperatures to find out the optimum working temperature. Figure 4 shows the gas responses of the prepared flower-like ZnO nanorods gas sensor against 50 µL/L of SF₆ compositions as a function of operating temperature, which ranges from 120 °C to 420 °C. As seen in Figure 4, the measured gas response curves have a common change trend, in which gas response increases firstly with rising operating temperature and reaches the maximum, and then decreases with an continuous increase of the operating temperature.

This behavior can be understood by a dynamic equilibrium mechanism between gas adsorption and desorption process of gas molecule on the surface of ZnO or other similar semiconducting metal oxides. In the beginning, the rate of gas adsorption is much higher than that of desorption, and the amount of net adsorbed gas increases as the operating temperature rises. It would reach a saturated adsorption state and maintain a dynamic balance at the constant operating temperature. With a sequential increase of the operating temperature, the balance will be broken and it changes to a net desorption process, which ultimately results in a decreasing gas response. As shown in Figure 4, the optimal operating temperatures of the sensor to 50 µL/L of SO₂, SOF₂, and SO₂F₂ are 250, 300, and 300 °C with gas response of −33.44, −12.47, and −18.06, respectively, which are applied in all the following investigations in this paper.

At their optimal operating temperatures, we performed the gas responses of the prepared plane flower-like ZnO gas sensor against different concentrations of SO₂, SOF₂, and SO₂F₂. Figure 5 shows the relationship between gas responses and 10, 20, 30, 40, 50, and 100 µL/L of SO₂, SOF₂, and SO₂F₂, respectively. The gas response measured is manifested to persistently increase with a rising gas concentration. At the same level of gas concentration, the gas response values of the sensor to the three targeted gases decrease in the order of SO₂, SO₂F₂, and SOF₂.

If the gas response curve is linear or quasilinear, the sensor can be applied to engineering application in practice. Therefore, based on the linear fitting tool in Origin software, linear characteristics of the prepared sensor to SO₂, SOF₂, and SO₂F₂ were discussed. Figure 6 shows the linear calibration curves of the sensor to SO₂, SO₂F₂, and SOF₂ with gas concentrations in the range of 10–100 µL/L. As seen in Figure 6, all the three gas response curves meet highly linear with gas concentration, and the linear correlation coefficient $R^2$ for SO₂, SO₂F₂, and SOF₂ is suggested to be about 0.982, 0.979, and 0.963, respectively. Such a higher linear dependence indicates that our prepared flower-like ZnO gas sensor can be used as promising materials for detecting SF₆ decompositions such as SO₂, SO₂F₂, and SOF₂.

Response time and recovery time are other two key indicators to evaluate gas sensor performances. Figure 7 shows the response and recovery characteristic of the prepared sensor to 10 µL/L of SO₂, SO₂F₂, and SOF₂ with the sensor working at its optimum operating temperature. As shown in Figure 7, the response times for 10 µL/L of SO₂, SO₂F₂, and SOF₂ are about 21, 13, and 10 s, and correspondingly the recovery times are about 45, 32, and 17 s, respectively.
the gas response amplitude increases apparently, nevertheless
the response and recovery property changes slightly which
indicates a very good and satisfying reproducibility of pre-
pared sensor against the decompositions. Figure 9 shows the
long-term stability and repeatability of the sensor against
50 μL/L of SO₂, SO₂F₂, and SOF₂. One can clearly see in
Figure 9 that the gas response changes slightly and keeps
at a nearly constant value during the long experimental
cycles, which confirms the excellent longtime stability and
repeatability of the prepared flower-like ZnO nanorods gas
sensor for detecting SO₂, SO₂F₂, and SOF₂.

For most metal oxide semiconductor gas sensors such as
zinc oxide, tin oxide, titanium oxide, ferric oxide, and indium
oxide, the sensing properties are dominantly controlled by the
change of electrical resistance [27], which is fundamentally
attributed to the chemical adsorption and desorption process
of gas molecules on sensing surface of the sensor.

It is well known to all that zinc oxide is a typical n-
type semiconducting material and there exist many oxygen
vacancies in the crystal lattices [28–30], where various kinds
of oxygen could be adsorbed. The species of adsorbed oxygen
are closely related to the ambient temperature [31]. At room
temperature, oxygen is likely to be adsorbed on ZnO surface
or grain boundaries with a typical physical adsorption mode.
And it would turn into chemical adsorption by thermal
excitation or electric excitation with certain energy.

As shown in Figure 10(a), oxygen would capture electrons
and form a depletion region on the surface area, which results
in a decrease in the concentration of charge carrier and elec-
tron mobility, thus gas sensor shows a higher electrical resis-
tance. Figure 10(b) illustrates the gas sensing process of SO₂
as an example exploring the gas sensing mechanism of the
prepared sensor detecting SF₆ decompositions. When flower-
like ZnO nanorods are reducing gas ambient at moderate
temperature (such as in certain concentration of SO₂, SO₂F₂,
and SOF₂), the reducing gas reacts with chemical adsorbed
oxygen, and then trapped electrons would be released back
into ZnO surface. Electrons released from chemical adsorbed
oxygen would reduce the height of barriers in the depletion
region and increase the number of charge carriers [32, 33],
which promotes the movements of charge carriers between
conduction band and valence band and eventually increases
the electrical conductivity of the sensor [34, 35].

With temperature rising, chemical adsorbed oxygen
exists in various forms, namely, O₂ads⁻, Oads⁻, and O_ads ²⁻, as
shown in the following reaction equations:

\[
\begin{align*}
O_{2\text{gas}} & \rightarrow O_{2\text{ads}} & O_{2\text{ads}} + e^- & \rightarrow O_{2\text{ads}}^- \\
O_{2\text{ads}}^- + e^- & \rightarrow 2O_{\text{ads}}^- & O_{\text{ads}}^- + e^- & \rightarrow O_{\text{ads}}^{2-}
\end{align*}
\]

(1)

As mentioned above the state of adsorbed oxygen is
mainly determined by the ambient temperature. At lower
experimental temperatures, oxygen dominantly exists in
the form of a “molecular ion” O₂ads⁻ and transfers into
“atomic ion” Oads⁻ and O_ads ²⁻ with a further rising operating
temperature. Experimental results indicate that the transition
temperature for oxygen from “molecular ion” to “atomic ion”
is about 450–500 K. As performed in Figure 4, the optimum

![Figure 8: The response and recovery behaviors of the sensor to SO₂.](image)

![Figure 9: The stability and repeatability of the sensor against 50 μL/L of SO₂, SO₂F₂, and SOF₂.](image)

Such rapid response and recovery characteristic could be
ascribed to the structure of the prepared flower-like sensor,
which has a much bigger specific surface area than other
conventional sensing structures, provides a larger adsorption
area, and increases the amount of gas molecules adsorbed
on the surface. Those advantages increase the rate of charge
carriers and facilitate the movement of carriers through the
barriers, consequently fast response and response property
are observed.

The response and recovery behaviors versus SO₂ with
concentration at 10, 20, 30, 40, 50, and 100 μL/L are shown in
Figure 8. With the concentration of detected gas increasing,
working temperatures for SO2, SO2F2, and SOF2 are about 250, 300, and 300°C, respectively. Thus, we draw a conclusion that the sensing behavior of the prepared sensor to SO2 gas may belong to the “molecular ion” reaction pattern, while it is an “atomic ion” gas response mode for SO2F2 and SOF2.

4. Conclusions

In summary, Flower-like ZnO nanorods have been successfully synthesized and characterized by XRD and FESEM. The optimum operating temperatures of the prepared sensor to SO2, SO2F2, and SOF2 are about 250, 300, and 300°C. The response (recovery) time of the sensor to 10 μL/L of SO2, SO2F2, and SOF2 is 21 (45), 13 (32), and 10 (17) s, respectively. Especially, the flower-like ZnO nanorods gas sensor shows high linearity to SO2, SO2F2, and SOF2 at the range of 10–100 μL/L with excellent linear correlation coefficient R² at 0.982, 0.979, and 0.963, separately. These findings demonstrate that our prepared flower-like ZnO nanorods have some excellent potential advantages for using as gas sensors to detect and online monitor the SF6 decompositions such as SO2, SO2F2, and SO2F2 in practice, although further studies are still needed.

References


