Research Article

Hydrothermal Synthesis and Responsive Characteristics of Hierarchical Zinc Oxide Nanoflowers to Sulfur Dioxide

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Sulfur dioxide, SO_2 , is one of the most important decomposition byproducts of sulfur hexafluoride, SF_6 , under partial discharge in GIS apparatus. The sensing performances of semiconductor gas sensors can be improved by morphology tailoring. This paper reported the synthesis method, structural characterization, and SO_2 responsive characteristics of hierarchical flower-shaped ZnO nanostructures. Hierarchical ZnO nanoflowers were successfully prepared via a facile and simple hydrothermal method and characterized by X-ray powder diffraction, scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy, respectively. Planar chemical gas sensor was fabricated and its responsive characteristics towards SO_2 were systematically performed. The optimum operating temperature of the fabricated sensor was measured to be about 260°C , and the corresponding maximum responses were 16.72 and 26.14 to 30 and 60 ppm of SO_2 . Its saturated gas concentration was 2000 ppm with a response value of 67.41. Moreover, a quick response and recovery feature (7 s and 8 s versus 80 ppm of SO_2) and good stability were also observed. All results indicate that the proposed sensor is a promising candidate for detecting SF_6 decomposition byproduct SO_2 .

1. Introduction

Sulfur hexafluoride, SF_6 , is a typical kind of colorless, tasteless, nontoxic, and nonflammable inert gas under general conditions with an extreme high thermal decomposition temperature [1, 2]. With the prominent advantages of small floor space, high reliability and stability, excellent insulation strength, non-smeary oil, and lower maintenance cost, gas insulated switchgear (GIS) apparatus filled with pressurized SF_6 gas are widely used in electrical power system in recent decades. Inevitable defects existed during the design, manufacture, transportation, installation, and operation processes of a GIS system [3]. These internal insulation defects, like metal burrs or suspended particles, may cause insulation degradation and even partial discharge in the long-term service cycle. If partial discharge occurs in GIS, SF_6 gas molecules firstly decompose into some low-fluorine sulfides and then react with trace oxygen and water vapor to generate various kinds of decomposition byproducts, for instance,

SO_2 , SOF_2 , SO_2F_2 , SOF_4 , H_2S , and HF [4, 5]. These decomposition byproducts would speed up the aging of insulation material and the corrosion of metal, eventually resulting in faults that happened in GIS.

Recent researches at home and abroad demonstrated that the composition and concentration of SF_6 decomposition byproducts are closely related to the insulation status of GIS. Monitoring and analyzing the component contents of these characteristic decomposition products and their generation rates are one of the most effective and convenient methods for GIS condition assessment and fault diagnosis [3, 5]. Till now, the main sensing approaches employed for recognizing SF_6 decomposition byproducts are gas chromatography [1, 2], infrared absorption spectrometry [6, 7], and metal oxide semiconductor [8, 9]. Gas chromatography is mainly used for offline testing in laboratory and cross sensitivity between SF_6 and its decomposition byproducts exists for infrared absorption spectrometry [10, 11]. With the advantages of simple fabrication, low cost, high response, rapid response

and recovery time, and facile integration, metal oxide semiconductor like n-type ZnO [12–14] or n-type SnO₂ [15–18] may represent the most promising sensing technology for sensing SF₆ decomposition byproducts. However, due to the deficiencies of low gas response and high working temperature, the application of using metal oxide semiconductor based sensors detecting SF₆ decomposition byproducts is greatly limited [8, 10].

Hence, in this study, we prepare hierarchical ZnO nanoflowers through a simple hydrothermal process and report systematically their responsive characteristics to SO₂, one of the most important decomposition byproducts of SF₆ under partial discharge in GIS apparatus.

2. Experimental Details

All chemicals were analytical grade reagents purchased from Chongqing Chuandong Chemical Reagent Co. Ltd. and used as received without any further purification. Hierarchical flower-shaped ZnO nanostructures were synthesized with a simple, facile, and environment-friendly hydrothermal method. The detailed synthesis processes were represented as follows.

Typically, 2.0 mmol zinc nitrate hexahydrate, Zn(NO₃)₂·6H₂O, 4.0 mmol NH₄OH, 28 wt% NH₃ in H₂O, 0.83 g CTAB, 30 mL absolute ethanol, and 30 mL distilled water were mixed together with intense magnetic stirring, which were subsequently transferred into a Teflon autoclave, sealed, and heated at 160°C for 24 h in an electric furnace. After reaction, the autoclave was cooled to room temperature naturally, harvested by centrifugation, washed with distilled water and absolute ethanol several times to remove the ions possibly remaining in the final product, and finally dried at 80°C in air for further use.

The crystalline structures of the as-prepared ZnO samples were performed by X-ray powder diffraction (XRD, Rigaku D/Max-1200X, Japan) with Cu K α radiation operated at 40 kV and 200 mA and a scanning rate of 0.02° s⁻¹ from 20° to 80° [12]. Surface morphologies and microstructures of the as-prepared nanostructures were observed with a Nova 400 Nano field emission scanning electron microscope (FESEM, FEI, Hillsboro, OR, USA) equipped with an energy dispersive X-ray spectroscopy (EDS) [15]. X-ray photoelectron spectroscopy (XPS) was performed on an ESCLAB MKII using monochromatic Al K α as the X-ray exciting source to investigate the chemical state of elements existing in the samples.

Planar chemical gas sensors based on the as-prepared powders were fabricated with screen-printing technique, and the planar ceramic substrates were purchased from Beijing Elite Tech Co., Ltd., China [12]. Firstly, the as-prepared nanostructures were mixed with deionized water and absolute ethanol in a weight ratio of 10:2:1 to form a suspension. Then it was subsequently screen-printed onto the planar ceramic substrate to form a sensing film with a thickness of about 50 μ m. Finally, the fabricated sensor was dried in air at 100°C to volatilize the organic solvent and further aged in an aging test chamber for 36 h. Responsive characteristics of the fabricated sensors to SO₂ were measured

FIGURE 1: Schematic diagram of the CGS-ITP gas sensing analysis system.

FIGURE 2: Typical XRD patterns of the synthesized hierarchical ZnO nanoflowers.

and automatically recorded by a CGS-ITP intelligent gas sensing analysis system, purchased from Beijing Elite Tech Co., Ltd., China. Figure 1 shows the schematic diagram of the CGS-ITP gas sensing analysis system [15].

In this study, gas response of the sensor to SF₆ partial discharge decomposition byproduct SO₂ was defined as $S = R_a/R_g$ [19, 20], where R_a denotes the resistance value of the sensor in pure N₂ and R_g in certain concentration of target gas mixed with pure N₂. The response and recovery time were defined as the time required by the sensor to achieve 90% of the total resistance change in the case of gas adsorption or gas desorption [21, 22]. All measurements were repeated several times to ensure the repeatability of the sensor.

3. Results and Discussion

The crystalline phases and structures of the as-prepared hierarchical ZnO nanostructures after annealing at 600°C for 5 h were characterized by the X-ray powder diffraction measurement and shown in Figure 2. One can clearly see from this figure that all the peaks are corresponding to wurtzite hexagonal ZnO structure given in the standard data file of JCPDS. 36-1451 [23]. The prominent peaks at 31.7°,

FIGURE 3: EDS spectrum of the synthesized hierarchical ZnO nanoflowers.

FIGURE 4: XPS survey spectra of the synthesized hierarchical ZnO nanoflowers.

34.4° , and 36.2° can be well indexed as the (100), (002), and (101) planes of wurtzite hexagonal ZnO, respectively [24, 25]. No other diffraction peaks from any impurities are detected, indicating a high purity of the as-prepared samples.

Energy dispersive X-ray spectroscopy measurement was further performed to investigate the element components of the as-synthesized samples. Figure 3 demonstrates the EDS spectrum of the synthesized ZnO nanostructures. As shown in Figure 3, only Zn and O element peaks were observed, which confirms the availability of Zn and O in the synthesized samples [25–27].

To further investigate the composition and the chemical state of the elements existing in the synthesized ZnO nanostructures, X-ray photoelectron spectroscopy XPS measurement was performed and collected. Adventitious hydrocarbon C 1s binding energy at 285 eV was used as a reference to correct the energy shift of O 1s. The XPS wide survey spectrum of the synthesized hierarchical samples as shown in Figure 4 confirms the existence of Zn, O, and C. The binding energies at 1022.3 eV and 1044.9 eV could be well identified as Zn 2p_{3/2} and Zn 2p_{1/2}, which could be attributed to Zn²⁺ ions [25–27]. Thus, based on these XRD, EDS, and XPS results, we can draw a conclusion that pure ZnO nanostructures have been successfully synthesized with the current route [23].

The surface structures and morphologies of the as-synthesized ZnO nanostructures were performed by FESEM. As illustrated in Figure 5 the panoramic image of the as-prepared hierarchical ZnO nanostructures is in flower shape,

FIGURE 5: FESEM image of the synthesized hierarchical ZnO nanoflowers.

FIGURE 6: Resistance of the hierarchical ZnO nanoflowers sensor versus operating temperature.

which consisted of a large number of nanorods. These nanorods are rectangular with high uniformity in shape and size. No other morphologies have been detected, suggesting a high yield of the flower-like ZnO nanostructures.

Figure 6 shows the electrical resistance curve of the sensor fabricated from the as-prepared hierarchical ZnO nanoflowers versus various operating temperatures from 160 to 440°C in pure N₂. As shown in Figure 6, the resistance value of the sensor decreases with increasing temperature in the whole temperature range, which is an intrinsic characteristic of an n-type semiconductor gas sensor.

Figure 7 illustrates the gas responses of the fabricated sensors to 30 ppm and 60 ppm of SO₂ at various working temperatures. As shown in Figure 7, each response curve of the sensor increases rapidly and achieves the maximum value and then decreases quickly with further increasing temperature. The optimum operating temperature of the fabricated hierarchical ZnO nanoflowers sensor to SO₂ gas was measured at 260°C, where the sensor exhibits the maximum gas response. And the corresponding maximum response value is 16.72 and 26.14, respectively.

FIGURE 7: Gas response of the hierarchical ZnO nanoflowers sensor to 30 and 60 ppm of SO_2 at various working temperatures.

FIGURE 8: Gas response of the hierarchical ZnO nanoflowers sensor to various concentrations of SO_2 at 260°C .

Figure 8 shows the gas response of the sensor as a function of SO_2 gas concentration in the range of 5–2000 ppm, where the sensor worked at its own optimum operating temperature mentioned above. As represented, the sensing responses of the sensor versus SO_2 gas increase greatly with increasing gas concentration in the range of 5–100 ppm and achieve saturation when exposed to more than 2000 ppm. The saturated gas sensing response value of the sensor to SO_2 gas was measured to be about 67.41.

Figure 9 gives the dynamic response and recovery curve of the sensor versus 80 ppm SO_2 to investigate its response-recovery feature. As seen in Figure 9, when certain concentration of SO_2 gas was injected into the test chamber, gas response of the sensor increases rapidly and dramatically decreases when the sensor was exposed for recovering, which is an intrinsic characteristic for n-type semiconductor material. Meanwhile, the sensor response returns to its initial value after testing, implying a satisfying stability of the prepared sensor. According to the definition above, the response and

FIGURE 9: Dynamic sensing transient of the hierarchical ZnO nanoflowers sensor to 80 ppm of SO_2 at 260°C .

FIGURE 10: Stability of the hierarchical ZnO nanoflowers sensor to 30, 60, and 80 ppm of SO_2 at 260°C .

recovery times of the sensor are calculated to be about 7 s and 8 s, respectively.

Finally, the long-term stability of the fabricated hierarchical ZnO nanoflowers sensor to 30, 60, and 80 ppm of SO_2 at 260°C was measured and displayed in Figure 10. As seen from the stability plot, the gas response of sensor changes slightly and keeps at a nearly constant value during the long experimental cycles, confirming an excellent longtime stability and repeatability of the sensor for SO_2 detection.

4. Conclusions

In summary, hierarchical ZnO nanoflowers were synthesized via hydrothermal method and characterized by XRD, SEM, EDS, and XPS, respectively. Planar chemical gas sensors based on the as-prepared powders were fabricated with screen-printing technique, and their responsive characteristics towards SO_2 , a most important SF_6 decomposition

byproduct under partial discharge, were systematically investigated with the CGS-ITP intelligent gas sensing analysis system. Lower operating temperature, higher sensing response, good linearity, quick response-recovery characteristic, and good stability were measured with the fabricated planar chemical sensor. All results demonstrate that the sensor fabricated with hierarchical ZnO nanoflowers is a promising candidate for detecting SO_2 .

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

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